2012

Ozone Treatment of Municipal Wastewater Effluent for Oxidation of Emerging Contaminants and Disinfection

Saileshkumar Singh
University of Windsor

Ozone Treatment of Municipal Wastewater Effluent for Oxidation of Emerging Contaminants and Disinfection

by

Saileshkumar Singh

A Thesis
Submitted to the Faculty of Graduate Studies
through Environmental Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science at the
University of Windsor

Windsor, Ontario, Canada

2012

Ozone Treatment of Municipal Wastewater Effluent for Oxidation of Emerging Contaminants and Disinfection

by

Saileshkumar Singh

APPROVED BY:

_____

Dr. Keith Taylor
Department of Chemistry and Biochemistry

_____

Dr. Nihar Biswas
Department of Civil and Environmental Engineering

_____

Dr. Rajesh Seth, Advisor
Department of Civil and Environmental Engineering

_____

Dr. Shahram Tabe, Co-Advisor
Ontario Ministry of Environment

_____

Dr. Hanna Maoh, Chair of Defence
Department of Civil and Environmental Engineering

June 15, 2012

DECLARATION OF CO-AUTHORSHIP

This thesis incorporates the outcome of research undertaken in collaboration with the Applied Chromatography Section, Laboratory Service Branch, Ontario Ministry of the Environment (MOE), as part of research project under the supervision of Dr. Rajesh Seth and Dr. Shahram Tabe. The collaboration related to research included analysis of PPCPs/EDCs in the wastewater samples, which were performed by the Applied Chromatography Section as detailed in Chapter 3 of this thesis.

I certify that, with the above qualification, this thesis, and the research to which it refers, are the products of my own work, and that any ideas or quotations from the work of other people, published or otherwise, are fully acknowledged in accordance with the standard referencing practices of the discipline.

I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University or Institution.

ABSTRACT

Municipal wastewater effluent (MWWE) is a major source of contaminants of emerging concern (CECs) in the aquatic environment. Studies have shown ozonation of MWWE to be effective in disinfection as well as transformation of the CECs. However, the characteristics of the MWWE matrix influence the oxidation efficacy with ozone. In the current study, a pilot unit was set up to examine efficiency of ozonation of MWWE in disinfection and transformation of target CECs. A transferred ozone dose (TOD) of 0.72 mg O_3/mg DOC was sufficient to consistently achieve the Ontario MOE disinfection target of < 200 MPN *E. coli*/100 mL. A similar TOD transformed the majority of the detected CECs by over 80%. Out of the 31 CECs for which transformation efficiencies could be calculated, transformations of 21 CECs were > 80%. Transformations of 4 CECs of antibiotics group were less than 30%.

DEDICATION

To my parents and teachers.

ACKNOWLEDGEMENTS

I am greatly thankful and indebted to Dr. Rajesh Seth and Dr. Shahram Tabe for their advice, guidance, and encouragement throughout the research and completion of this thesis. I consider myself very fortunate to have worked with my supervisors on this project.

Special thanks to my committee members, Dr. Keith Taylor and Dr. Nihar Biswas, for their advice and input that has resulted in improvement of this work.

Thanks to Dr. Paul Yang at Laboratory Services Branch, Ontario Ministry of the Environment, for his support to this project and help with sample analysis. Assistance of Dr. Elizabeth Fidalgo da Silva, University of Windsor, is also thankfully acknowledged.

I am thankful to our lab technicians, Mr. Bill Middleton and Mr. Matt St. Louis, for their help in laboratory, and with design and construction of the pilot unit. Many thanks to my colleagues in the laboratory and department. I am grateful to the faculty and staff of Department of Civil and Environmental Engineering for their support.

City of Windsor and Little River Pollution Control Plant (LRPCP) are thankfully acknowledged for their support to this project. Special thanks to the staff of LRPCP and Plant Manager, Mr. Chris Manzon.

Ontario Ministry of the Environment is thankfully acknowledged for financial support. In-kind contribution to the project by Calgon Carbon Corporation and Orthos Liquid Systems is acknowledged. Thanks to the Faculty of Graduate Studies and Research, University of Windsor, for providing me scholarship.

Finally, I am thankful to my wife, Renu, and my kids, Rishabh and Yash, for their support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AOD	Applied ozone dose
AOP	Advanced oxidation process
BOD	Biological oxygen demand
BPA	Bisphenol-A
CECs	Contaminants of concern
CFU	Colony-forming units
COD	Chemical oxygen demand
DBP	Disinfection by-product
DC	Dissolution chamber
DL	Detection limit
DO	Dissolved oxygen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
E1	Estrone
E2	17-β-estradiol
E3	Estriol
EE2	17-α-ethinylestradiol
E. coli	*Escherichia coli*
EDCs	Endocrine disruptive chemicals
EfOM	Effluent organic matter
GAC	Granular activated carbon

HRT	Hydraulic retention time
ImOD	Immediate ozone demand
IOD	Initial ozone demand
LRPCP	Little River Pollution Control Plant
MDL	Method detection limit
mgd	Million gallons per day
MOE	Ministry of the Environment
MPN	Most probable number
MWWE	Municipal wastewater effluent
MWWTP	Municipal wastewater treatment plant
ng/L	Nanograms per liter
NOM	Natural organic matter
NSAID	Non-steroidal anti-inflammatory drug
O_3	Ozone
OH•	Hydroxyl radical
OMOE	Ontario Ministry of the Environment
ORP	Oxidation reduction potential
PAC	Powdered activated carbon
PCPs	Personal care products
PhACs	Pharmaceutically active compounds
PPCPs	Pharmaceutical and personal care products
RC	Reaction chamber
SCF	Short-circuiting factor

SUVA	Specific UV absorbance
TE	Transfer efficiency
TOC	Total organic carbon
TOD	Transferred ozone dose
USEPA	United States Environmental Protection Agency
UV	Ultra violet
UVA	UV absorption at 254 nm
WWTP	Wastewater treatment plant
Z	Ozone consumption
Z_{spec}	Specific ozone consumption

CHAPTER I

INTRODUCTION

1.1 BACKGROUND

Many municipal wastewater treatment plants (MWWTPs) discharge the effluent in water bodies such as rivers and lakes that are important sources of drinking water. The MWWTPs are typically designed for and are efficient in removing suspended solids, organics, and nutrients. Municipalities in North America have increasingly targeted treated municipal wastewater effluent (MWWE) since the 1970s to protect public health. They are typically required to achieve some level of disinfection before discharging the MWWE to receiving water bodies. The regulatory limit varies with jurisdiction as well as sensitivity of the receiving bodies. A disinfection limit of around 200 most probable number (MPN) of fecal coliform or *Escherichia coli* (*E. coli*) per 100 mL is common both in the USA and in Canada (Minnow Environmental and CCME, 2005; Black & Veatch, 2010).

Historically, chlorine was used for disinfection of MWWE because of its effectiveness, residual properties, and low cost. However, studies in the early 1970s showed that free chlorine reacts with the organics to form disinfection by-products (DBPs) such as trihalomethanes and haloacetic acids. These DBPs could adversely affect public health and aquatic life because of their carcinogenic properties (Morris and McKay, 1975; Rice et al., 1981). Fish kills were also experienced in water bodies receiving municipal wastewater disinfected with chlorine (Rice, 1999). The concerns with adverse effects of chlorinated effluent led United States Environmental Protection

Agency (USEPA) to promote research in alternate disinfection technologies such as ozonation and UV disinfection (Rice et al., 1981; Whitby and Scheible, 2004). At that time, both these technologies were already in use for disinfection of drinking water. The researchers quickly realized the advantages of using ozone for disinfection (Rice, 1999). However, the technology to produce ozone was not mature and reliable. This resulted in ozone treatment systems having high manufacturing cost, high operating and maintenance cost, and low reliability.

The first full scale UV system was installed in a MWWTP in 1978 and in a MWWTP with gravity fed open channel in 1982 (Whitby and Scheible, 2004). The UV radiation technology continuously and rapidly improved, making it more reliable and cost effective. Hence, UV treatment became the preferred method for wastewater disinfection (Rice, 1999; Whitby and Scheible, 2004).

Studies in the 1990s discovered an additional threat with MWWE due to the finding of trace amounts of estrogenic compounds and the possible link to the feminization of male fish (Folmar et al., 1996; Harries et al., 1997). Daughton and Ternes (1999) revealed that the active compounds in pharmaceutical and personal care products (PPCPs) released with municipal effluents could induce estrogenic effects. These discoveries have led to a significant increase in the research of occurrence, fate, transport, and removal of potential estrogenic compounds from water and wastewater (Snyder et al., 2003; Ternes et al., 2004; Shon et al., 2006). Researchers have discovered many more chemicals and compounds in water and wastewater in concentrations that can be a cause of various other ecological concerns. These more recently discovered pollutants of concern are commonly being grouped as contaminants of emerging concern (CECs). As

per Bhandari et al. (2009), the CECs are usually unregulated and consist of pharmaceutically active compounds (PhACs), personal care products (PCPs), antibiotics, hormones, endocrine disruptive chemicals (EDCs), plasticizers, surfactants, fire retardants, pesticides, herbicides, insecticides, industrial and household chemicals, and nanomaterials. The current knowledge base on many of these CECs in low concentrations does not give any indication if they pose risks to human health. However, researchers have shown that these micropollutants can cause reproductive abnormalities and feminization of fish as well as of other vertebrates such as reptiles, mammals, and birds (Bloetscher and Plummer, 2011). Hence, to protect the aquatic ecosystem and public health from probable adverse effects, it is advisable to take precautionary steps by limiting the release of the estrogenic compounds in the environment.

Studies conducted in various parts of the world show the presence of CECs in potable water sources (Daughton and Ternes, 1999; Huber et al., 2003; Auriol et al., 2006; Benotti et al., 2009; Tabe et al., 2009). Municipal wastewater treatment plants are an important point source of the CECs released in the environment and water bodies (Daughton and Ternes, 1999; Petrović et al., 2003). It makes logical sense to treat and remove the CECs from the MWWE when their concentration is higher, rather than from a water supply for potable water in which they have been diluted several orders of magnitude (Oneby et al., 2010). The conventional technologies to treat MWWE are efficient in removing suspended solids, organics, and nutrients. However, they are not effective in removing the CECs that are present in trace quantities (Ternes, 1998). Hence, new treatment technologies or additional treatment processes are required to remove these CECs, which are normally low molecular weight compounds in the size range of

about 150 to 500 Dalton (Snyder et al., 2003). These new treatment technologies or treatment processes should meet the following requirements:

- Remove CECs to acceptable levels
- Remove biologically active compounds
- Provide effective disinfection
- The disinfection by-products should have lower toxicity than the parent compounds
- Use minimum possible resources such as energy and water
- Require low maintenance (specially human labor)
- Economically viable
- Environmentally friendly

The scientific community has been aware of the disinfection property of ozone since the start of the 19th century. Higher costs and operational problems related to it have led to the choice of UV as the preferred technology for wastewater disinfection in North America since the 1990s. Since then, studies have shown ozone and ozone based advanced oxidation processes (AOPs) to be effective in the oxidation of CECs both in water and wastewater matrices (Snyder et al., 2003; Ternes et al., 2003). The ozonation of MWWE has several other advantages such as an increase in dissolved oxygen, decrease in chemical oxygen demand, and improvement in aesthetic characteristics due to reduction in turbidity and color. Chlorination and UV radiation do not provide these additional benefits. In addition, due to the significant advances in the ozone manufacturing technology in the last couple of decades and the experience gained by ozone treatment of water and wastewater, ozonation is now a mature technology (Leong et al., 2008). The cost of ozonation is now almost at par or lower than that of UV

disinfection technology (Drury et al., 2006; Oneby et al., 2010). These developments have led to a huge surge in research related to ozone treatment of secondary and tertiary treated municipal wastewater the world over in recent years. While studies have demonstrated the potential for ozonation to transform effectively many CECs present in MWWE, such studies are still limited both in number and list of CECs examined. Studies have further shown that the effectiveness of such transformations by ozone is strongly dependent on the properties of the CEC and the matrix, particularly the nature and concentration of dissolved organic carbon. In addition, the list of CECs in the water environment continues to grow. Hence, there is a continued need to study the ozone and ozone-based advanced oxidation processes (AOPs) for different wastewater matrices and CEC groups to better understand and apply them for wastewater treatment. Ozone treatment of municipal wastewater in Canada for disinfection has been studied and is being considered as a special circumstance for the primary treated wastewater effluent in the City of Montreal. However, to the best knowledge of the author, study on disinfection and oxidation of CECs using ozone for treatment of the more common secondary treated municipal wastewater effluent has not been conducted in Canada.

1.2 OBJECTIVES

The main objective of this study was:

- To investigate the effect of ozone treatment of secondary treated wastewater effluent on disinfection and the transformation of selected contaminants of emerging concern.

Other objectives of the study were:

- Examine the effect of different ozone doses on the characteristics of the treated wastewater.
- Check for the correlation of the transformation of the CECs and inactivation of the disinfection indicator microorganisms with easy to monitor surrogate parameters such as UV absorption at 254 nm (UVA) and color.

1.3 SCOPE

The scope of this project was to:

- design and build a pilot unit keeping in view process parameters such as dissolution time, air-to-water flow ratio, hydraulic retention time, and length to diameter ratio of the contactors;
- determine the effect of different air-to-water flow ratios on ozone transfer efficiency and residual ozone in water;
- examine the effect of different transferred ozone dose, residual ozone, and hydraulic retention time on the level of disinfection;
- study the reduction in the concentration of the monitored CECs at typical disinfection ozone dose; and
- monitor the changes in the characteristics of the MWWE such as total organic carbon concentration, UV absorption at 254 nm, and color due to ozone treatment.

1.4 ORGANIZATION OF THE THESIS

This thesis is organized into five chapters. Chapter I consists of the introduction and objective of this study. Chapter II consists of literature review related to the history of wastewater ozonation, factors effecting ozonation, disinfection by ozone and oxidation of the CECs. The topics included in Chapter III are details of the experimental setup and experiment methodology. The results and discussion are included in Chapter IV. Chapter V includes the conclusions of this study as well as recommendation for future study.

CHAPTER II

REVIEW OF THE LITERATURE

2.1 HISTORY OF OZONATION OF MWWE

Historically, chlorine was the choice of disinfectant for MWWE. In 1892, the disinfection of sewage with chlorine first occurred in Hamburg, Germany and Brewster, New York (Gascoigne, 1931). By 1906, disinfection of sewage by chlorination was established as a practical and economical process, and its application for sewage disinfection increased (Gascoigne, 1931). In 1911, eight sewage treatment plants in New York treated sewage effluent with chlorinated lime (Black & Veatch, 2010). Phelps (1912) has documented the use of chlorine for disinfection of sewage by several full-scale sewage treatment plants, and its benefit for public health as well as shellfisheries. For comparison, in the USA the first successful commercial application of chlorine for water disinfection started in 1908 (Baker, 1925) and by 1912 the drinking water was regularly disinfected in several hundred American cities (Phelps, 1912). By 1911, Canadian cities - Montreal, Ottawa, and Toronto, chlorinated the drinking water (Race, 1918). As per Baldwin (1927), laboratory scale to full scale experiments were being conducted in 1927 in USA, Canada, and Germany to determine all the possible and proper use of chlorine for sewage disinfection and disposal. Gascoigne (1931) has noted the use of chlorine in Toronto for improvement in performance of activated sludge process. The use of chlorine for disinfection of MWWE in United Sates became more common from 1945 (Black & Veatch, 2010).

Studies in the 1970s found that disinfection of MWWE with chlorine lead to the formation of carcinogenic disinfection by-products (Morris and McKay, 1975). This concern led to research in alternate disinfection technologies. Research revealed that ozone treatment and UV radiation were viable alternate modes for disinfection of MWWE (Rice, 1999; Whitby and Scheible, 2004).

The use of ozone for MWWE disinfection started in the United States in the early 1970s (Rice et al., 1981) and there was a gradual increase in the number of MWWTPs using this process. However, the change in the USEPA disinfection policy in 1976, higher capital cost, and operational problems lead to the gradual decline of the use of ozone for disinfection of MWWE (Rice, 1999). At the same time, its application in water treatment has continued to grow. The number of municipal wastewater plants using ozone peaked at around 45 in the early 1980s (Rice, 1999). Only nine MWWTPs were using ozone for disinfection in 2008 - 2009 (Black & Veatch, 2010; Oneby et al., 2010). For comparison, there were nearly 201 water treatment plants (WTPs) using ozone in the USA in 1997 (Rice, 1999). However, since 1990s, the concerns related to the toxic and mutagenic effect of CECs present in MWWE on aquatic species has renewed the interest in ozone treatment of MWWE for disinfection as well as transformation of CECs. Various full scale and pilot scale studies have been conducted (Snyder et al., 2006; Wert et al., 2007; Dickenson et al., 2009; Wert et al., 2009a; Gerrity et al., 2011; Lee et al., 2012).

As per Larocque (1999), two Canadian MWWTPs were using ozone primarily for disinfection and six were using it probably for odor control. The paper does not provide any detail or name of these plants. Literature research did not reveal any full

scale MWWTP currently operating in Canada that uses ozone for final disinfection of MWWE. The Montreal Urban Community WWTP having capacity of 700 mgd is considering ozone treatment for effluent disinfection (Black & Veatch, 2010). Absi et al. (1993), Gehr and Nicell (1996), and Gehr et al. (2003) have conducted pilot-scale ozone disinfection study at this MWWTP.

In general, the regulations in Europe do not require disinfection of MWWE (Rice et al., 1981; Black & Veatch, 2010). However, concerns related to CECs in MWWE have resulted in a surge in research and use of ozonation for the transformation of CECs in recent years around the globe. In Europe, full-scale MWWTPs that apply ozone mainly for micropollutant removal are now operational in Switzerland (Hollender et al., 2009), and France (Ruel et al., 2011). In Germany, three municipal wastewater treatment plants have full scale ozonation plants for micropollutant removal, one of which is in operation since 2009 (Grünebaum, 2011; Launer et al., 2012). A full-scale ozonation unit exists in Italy that treats effluent of a wastewater plant that receives municipal and industrial wastewater (Bertanza et al., 2012). Pilot scale ozonation studies are being conducted in Austria (Schaar et al., 2010), Germany (Bahr et al., 2005; Ried et al., 2009), and Great Britain (Ried et al., 2009). The results from these studies would be helpful to the MWWTPs exploring the possibility of upgrading to or selecting ozonation for disinfection of MWWE as well as micropollutant removal.

In Japan, 65 sewage treatment plants had an ozonation process in the year 2004. Ten of them were constructed between 2002 and 2004 (Takahara et al., 2006). A full-scale water reclamation plant in Australia uses ozone for disinfection of the effluent. It receives tertiary treated effluent from a WWTP that serves 40,000 people (van Leeuwen

et al., 2003; Reungoat et al., 2010). A water reclamation plant existed in South Africa in 1978 that disinfected the effluent with ozone (van Leeuwen and Prinsloo, 1980). The ozone dosages used and the results obtained have varied considerably depending on the wastewater characteristics and the treatment objective.

2.2 OZONE CHEMISTRY

2.2.1 Properties of Ozone

Ozone (O_3) is a pale blue gas and has a pungent odor. It is generated from oxygen molecules. The electric discharge method is the most common method for generating ozone on industrial scale. The electrical discharge ionizes the oxygen molecules. The ionized oxygen atom then combines with molecular oxygen to form ozone. The feed gas to produce ozone can be air or oxygen. The concentration of ozone produced is 3 to 4% by weight with air as feed gas and 10 to 13.5% by weight when oxygen is the feed gas (Gottschalk et al., 2000).

Ozone is one of the most powerful disinfectants having high oxidation potential of 2.07 eV (Alvares et al., 2001). It is highly unstable and hence produced on site prior to use. Ozone is more than 10 times as soluble as oxygen, however only a few mg/L ozone dissolves in water in actual operating conditions due to its low partial pressure (Sawyer, 1976). The solubility of ozone in water or wastewater is an important property as the disinfection and oxidation of the micropollutants depend on the amount of ozone transferred. The solubility of ozone in water or wastewater can be calculated using Henry's law (USEPA, 1986b; Metcalf & Eddy et al., 2002):

$$H_u = \frac{C_g}{C_s} \qquad (2.1)$$

H_u Henry's law constant, unitless (H_u for ozone = 3.97 at 20 ^oC)

C_g concentration of ozone in gas phase, mg/L

C_s saturation concentration of ozone in liquid, mg/L

Equation 2.1 shows that the solubility of ozone in water increases with an increase in the concentration of ozone in the gas that is bubbled through the water.

2.2.2 Oxidation pathways

As per Hoigné and Bader (1976), ozone can oxidize and transform a substrate (S) by the direct or indirect pathway. Figure 2.1 shows the two pathways. The ozone molecule reacts directly with the substrate to form product in the direct pathway. In the indirect pathway, ozone reacts with hydroxide ions (OH^-) or radicals (R•) and decomposes to form oxidants such as hydroxyl radical (OH•) which then reacts with the substrate (S). While the oxidation potential of molecular ozone is 2.07 eV, that of OH• formed is 2.8 eV (Alvares et al., 2001). The oxidation pathway that will dictate the transformation will depend on the reaction rate of ozone and the substrate, and the reaction products that may promote or inhibit ozone decomposition (S').

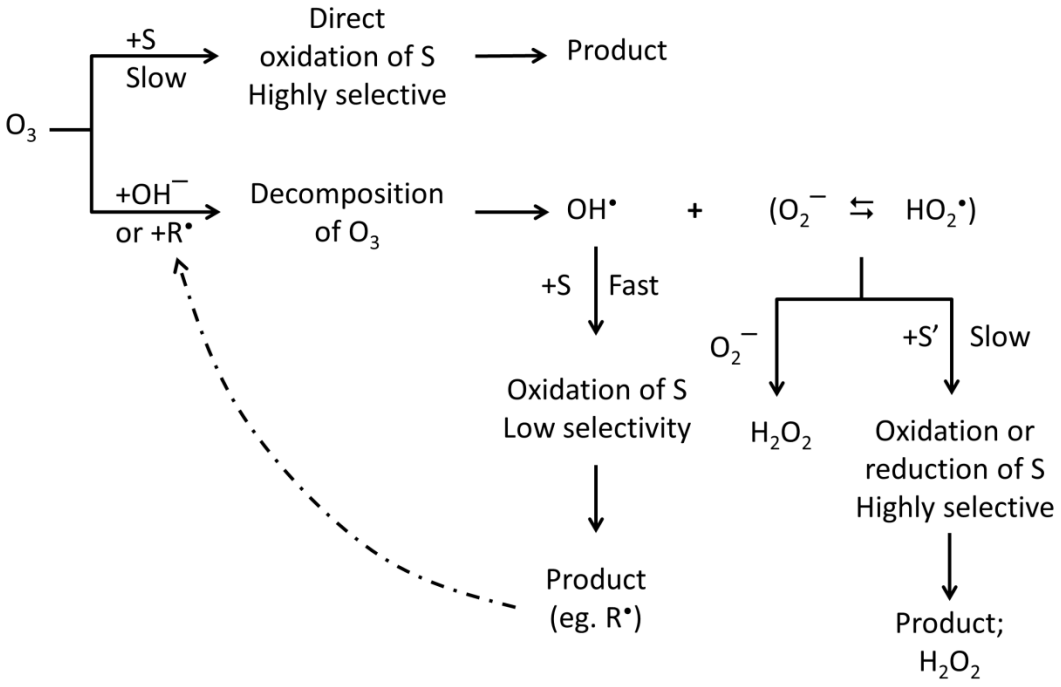


Figure 2.1 **Oxidation of substrate during ozonation of water and wastewater (Adapted from Hoigné and Bader, 1976)**

The direct reaction of ozone is highly selective and slow. The second-order reaction rate constant of ozone with organics and inorganics in water is in the range of <1 to 10^9 M^{-1} s^{-1}, but most of the rate constants are in the order of 1 to 10^3 M^{-1} s^{-1} (Hoigné and Bader, 1983a; b; Hoigné et al., 1985). Compounds that have reaction rate with ozone << 10^3 M^{-1} s^{-1} can be considered as "ozone refractory" and react slowly with ozone (Nöthe et al., 2009). The second-order reaction rate constant of *E. coli* with ozone is 130 l/(mg.s), i.e. 6.24 x 10^6 M^{-1} s^{-1} (Hunt and Mariñas, 1997).

In comparison with molecular ozone, hydroxyl radical is less selective and its diffusion rate controls its reaction rate with solutes such as aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols, and formic acid (Hoigné and Bader, 1976).

The second-order reaction rate constants of hydroxyl radical with these solutes are in the range of 10^7 to 10^{10} M^{-1} s^{-1} (Hoigné and Bader, 1976; Glaze and Kang, 1989; von Gunten and Ramseier, 2010). With carbonates and bicarbonates, their reaction rate constant is 2 - 3.9 x 10^8 M^{-1} s^{-1} and 0.85 - 1.5 x 10^7 M^{-1} s^{-1} (Hoigné and Bader, 1976; Buxton et al., 1988). Due to such high rate constants, they are scavenged quickly (Hoigné and Bader, 1976) and their lifetime is in the range of 10^{-3} to 10^{-7} seconds (Dhar, 1934; Hoigné and Bader, 1983a; b; Buxton et al., 1988). In addition, the concentration of hydroxyl radicals in water is less than 10^{-12} M (Elovitz and von Gunten, 1999; von Gunten, 2003a).

2.2.3 Factors affecting oxidation efficacy with ozone

The main factors affecting the stability of ozone are the water or wastewater characteristics such as pH, alkalinity, and the organic matter content (von Gunten, 2003a). The effects of each of these parameters are discussed in the following sections.

2.2.3.1 Alkalinity

Carbonate and bicarbonate ions act as hydroxyl radical scavengers (Hoigné and Bader, 1976). The hydroxyl radicals are a part of the chain reaction that results in decomposition of ozone (Figure 2.1). Hence, the decomposition rate of ozone molecules decreases with an increase in the carbonates and bicarbonates. In addition, they compete with organics and other micropollutants for hydroxyl radicals and hence protect them from oxidation (Hoigné, 1994). The reaction rate of hydroxyl radicals with bicarbonates $\left(HCO_3^-\right)$ is 0.85 - 1.5 x 10^7 M^{-1} s^{-1} (Buxton and Elliot, 1986; Glaze and Kang, 1989), and with carbonates $\left(CO_3^{2-}\right)$ is 2 - 4.2 x 10^8 M^{-1} s^{-1} (Hoigné and Bader, 1976; Glaze and

Kang, 1989). Even with this high reaction rate, Nöthe et al. (2009) found the hydroxyl radical scavenging capacity of the bicarbonates in MWWE to be only around 10% of that of the DOC.

2.2.3.2 Dissolved Organic Matter

The dissolved organic matter (DOM) reacts directly with ozone and decreases its stability or it reacts with the hydroxyl radicals, which in turn affect the ozone stability. Ozone reacts directly mostly with aromatic compounds, amines, and sulfides. If DOM reacts with hydroxyl radicals, it can scavenge it and increase the ozone stability, or it can form superoxide radicals that react with ozone to form hydroxyl radicals. This chain reaction can decrease the ozone stability (von Gunten, 2003a). The DOM scavenges ozone and hydroxyl radicals and shields the micropollutants (Hoigné, 1994) and microorganisms from oxidation. Hence, it reduces the oxidation efficacy. The reaction rate of organic matter with hydroxyl radicals is in the order of 10^4 $(mg\ C/L)^{-1}\ s^{-1}$ (Elovitz and von Gunten, 1999; Reisz et al., 2003; Nöthe et al., 2009) to 10^8 $(mg\ C/L)^{-1}\ s^{-1}$ (Westerhoff et al., 1999). Rosario-Ortiz et al. (2008) have reported this rate constant to be in the range of 0.27 to 1.21 x 10^9 $M_c^{-1}\ s^{-1}$ (where M_c is the molarity of NOM present and is calculated assuming 12 g C per mole C). Dong et al. (2010) have shown that the effluent organic matter with smaller apparent molecular weight have higher reactivity with hydroxyl radicals. The reactivity of <1 kDa fraction organic matter with hydroxyl radical was approximately 2.31 times higher than that of corresponding bulk organic matter.

2.2.3.3 Temperature

The reaction rate of ozone with organic as well as inorganic compound increases with increase in temperature (Hoigné and Bader, 1983a). The reaction rate constant as per the Arrhenius equation is as follows (Gottschalk et al., 2000):

$$k = A\, e^{-\frac{E_a}{RT}} \qquad (2.2)$$

k reaction rate constant

A frequency factor or pre-exponential factor

e mathematical quantity, 2.71828

E_a activation energy, J mol^{-1}

R ideal gas law constant, 8.314 J mol^{-1} K^{-1}

T temperature, K

Activation energy required for reaction of most of the compounds with ozone is 35 to 50 kJ mol^{-1} (Hoigné and Bader, 1983a). The frequency factor can be considered constant across a small temperature range. Considering the above and from Equation 2.2, an increase in temperature by 10 ^{o}C will increase the reaction rate by a factor close to two.

The temperature also affects the ozone exposure. Ozone exposure is commonly known as CT value, i.e. product of residual ozone concentration and the time of exposure of a compound or microorganism to ozone. The ozone depletion rate increases with increase in temperature. Hence, the ozone exposure decreases substantially but the hydroxyl radical exposure remains unchanged (Elovitz et al., 2000).

The temperature affects the solubility of ozone in water. The solubility of ozone in water decreases with increase in water temperature (Sotelo et al., 1989). The empirical formula of solubility of ozone in water as given by Morris (1988) is:

$$\text{Log}_{10}S = -0.25 - 0.013\,T \qquad (2.3)$$

S aqueous solubility of ozone (mg per liter in water/mg per liter in gas)

T temperature of water, ^{o}C

2.2.3.4 pH

Ozone reacts with substrates directly or indirectly by decomposing to hydroxyl radicals that then react with the substrate. However, the indirect mode of reaction is predominant above a critical pH value (Hoigné and Bader, 1976). Studies have shown that hydroxide ions initiate the decomposition of ozone (Tomiyasu et al., 1985; von Gunten, 2003a). The following are the initiation reaction as per von Gunten (2003a):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad k = 70\,M^{-1}s^{-1} \qquad (2.4)$$

$$O_3 + HO_2^- \rightarrow OH\bullet + O_2^{\bullet -} + O_2 \qquad k = 2.8 \times 10^6\ M^{-1}s^{-1} \qquad (2.5)$$

Since, at lower pH the hydroxide ions are less in water solution, decreasing the pH of the solution will result in a lower rate of decomposition of ozone (Hoigné and Bader, 1983a). The dissolved ozone concentration decreases with increase in pH (Sotelo et al., 1989).

2.2.3.5 Other factors

The turbidity of water and the concentration of the following compounds in water can also affect the oxidation efficiency with ozone: nitrites, iron, manganese, chloride ion, bromide ion, and ammonia (Hoigné, 1994).

2.3 DISINFECTION OF MWWE BY OZONE

2.3.1 MWWE disinfection standards

Disinfection of MWWE is not required unless the receiving water body is used for (a) a drinking water intake source (b) cultivation of shell fish or aquaculture, or (c) recreation use resulting is human contact (Rice, 1999). For the protection of public health, disinfection of MWWE before discharge to receiving bodies is important (Chambers et al., 1997). Municipalities in North America are typically required to achieve some level of disinfection, but the regulatory limit varies with jurisdiction or sensitivity of the receiving bodies. In the Ontario province of Canada, as per the Ontario Water Resources Act (Section 17 and 24 – R.S.O. 1980), unless specifically exempted by the Guidelines, all municipal, institutional, and private communal sewage works that discharge their effluent to surface water are required to disinfect the effluent (Ontario MOE, 2001). A disinfection limit of around 200 MPN/100 mL or less of fecal coliform or *E. coli* is common both in the USA and in Canada (Minnow Environmental and CCME, 2005; Black & Veatch, 2010). In Ontario, as per the regulations the monthly geometric mean density of *E. coli* should not exceed 200 MPN per 100 mL (Ontario MOE, 2008).

Total coliform, fecal coliform and *E. coli* are the most common microorganisms monitored to determine the effectiveness of disinfection treatment. The method for

enumeration of fecal coliform may overestimate the true fecal level in water due to the interference from non-fecal coliforms (Elmund et al., 1999). The fecal coliform has been the preferred disinfection indicator in North America only because of the simple method required for its enumeration (Dufour, 1977). The *E. coli* accounts for more than 90% of coliform species in human feces (Dufour, 1977; Rice et al., 1990), and is a better indicator of disinfection than fecal coliform (USEPA, 1986a; Rice et al., 1990; Elmund et al., 1999).

2.3.2 Pathways of inactivation of microorganism with ozone

Theoretically, the inactivation of microorganisms by ozone can occur through the direct as well as the indirect pathway. The microorganisms are inactivated by attack of molecular ozone in the direct pathway and by the hydroxyl radicals formed on decomposition of molecular ozone in the indirect pathway. There is no clear agreement among the researchers on the predominant mode responsible for the inactivation of disinfection indicator microorganism *E. coli*. As per Hoigné and Bader (1976), the inactivation is mainly due to the direct attack of ozone. They hypothesize that the dissolved species in water react quickly with hydroxyl radicals and scavenge them before the radicals can react with dispersed particles such as microorganisms. Hunt and Mariñas (1997) studied the inactivation of *E. coli* with ozone. They conducted ozonation experiments with and without radical scavengers in water. They concluded that dissolved ozone, i.e. direct attack by ozone, was primarily responsible for *E. coli* inactivation. von Gunten (2003b) estimated the reaction rate constant of hydroxyl radicals for inactivation of microorganisms from the kinetic data. They found that for hydroxyl radicals to be the

main mode of disinfection, the rate constant has to be a minimum of 10 times their typical rate constant. In addition, they observed that the cell wall of the microorganism would probably scavenge the hydroxyl radical before it can attack the DNA and cause inactivation of the microorganism. They concluded that hydroxyl radicals do not have a major effect on disinfection. However, as per Dahi (1976), the free radicals formed on decomposition of ozone are mainly responsible for disinfection. He hypothesized establishment of free radical activity at the end of initial ozone demand phase that causes rapid inactivation of the microorganisms. The results and hypothesis by Bancroft et al. (1984) also support the hydroxyl radical mediated mechanism as the primary mode of disinfection.

The experimental results in recent literature show that direct attack by ozone is mainly responsible for inactivation of microorganisms. Wolfe et al. (1989), and Can and Çakir (2010) have conducted ozone based advanced oxidation process (AOP) experiments by adding hydrogen peroxide (H_2O_2) to ozone. They observed a decrease in disinfection efficiency with an increase in hydrogen peroxide to ozone ratio. The residual ozone concentration decreases with an increase in hydrogen peroxide to ozone ratio. Hence, the decrease in disinfection efficiency in the AOP can be due to the decrease in the residual ozone concentration, and this can indicate that the direct attack by ozone is the predominant mode of disinfection. Finch et al. (1992) have also reported results of a study on disinfection of *E. coli* with ozone and peroxone. They observed that the rapid decomposition of ozone to form hydroxyl radicals did not increase the disinfection effectiveness. The presence of residual ozone improved inactivation of *E. coli*. Their results also indicate that *E. coli* inactivation is primarily through direct pathway.

Researchers have attempted to study the change in the *E. coli* structure after their inactivation by ozone. As per Finch and Smith (1987), ozone acts on the cell membrane and changes the permeability of the cell that results in the transfer of the contents of the cell into surrounding aqueous environment and inactivation. Cho et al. (2010) have shown that ozone inactivates the *E. coli* by causing damage to its cell surface. Ozone reacts with the cell wall, changes the permeability, and reacts with the cell wall components to destroy them. However, Hunt and Mariñas (1999) did not notice any notable change in the structure of *E. coli* at the ozone dose that resulted in approximately 99.999% inactivation. They did observe change in structure of *E. coli* and subsequent lysis of the cells with an increase in the ozone dose.

2.3.3 Kinetics of disinfection with ozone

Conventionally, the Chick-Watson equation used to calculate the disinfection kinetics is (Haas and Karra, 1984; Metcalf & Eddy et al., 2002):

$$\ln\left(\frac{N}{N_O}\right) = -k\,c^n\,t \qquad (2.6)$$

N_o Number of microorganisms at time 0

N Number of microorganisms at time t

k Die-off constant, empirical constant

c Concentration of the disinfectant

n Coefficient of dilution, empirical constant

t Contact time

In the above equation, the term c^n t relates to the exposure of disinfectant. Replacing this exposure term with ozone and hydroxyl radical exposure, the modified equation becomes:

$$\ln\left(\frac{N}{N_O}\right) = -k_{O3}\int[O_3]\,dt \; - k_{OH}\int[OH]\,dt \qquad (2.7)$$

k_{O3} Second-order reaction rate constant for inactivation of microorganism with ozone

k_{OH} Second-order reaction rate constant for inactivation of microorganism with hydroxyl radical

$[O_3]$ Concentration of ozone

$[OH]$ Concentration of hydroxyl radical

It is difficult to measure directly the concentration of hydroxyl radical. Elovitz and von Gunten (1999) measured their concentration indirectly by calculating the ratio of hydroxyl radical exposure and ozone exposure. They have termed this ratio as R_{CT} value, i.e. $R_{CT} = \int[OH]dt \,/\, \int[O_3]dt$. The R_{CT} value is calculated from the measured transformation of a compound having low reactivity with ozone (< 1 M^{-1} s^{-1}) and high reactivity with hydroxyl radicals (> 10^9 M^{-1} s^{-1}). Substituting this value in Equation 2.7, it transforms to:

$$\ln\left(\frac{N}{N_O}\right) = -(k_{O3} + k_{OH}\,R_{CT})\int[O_3]\,dt \qquad (2.8)$$

The above equation includes the ozone exposure and OH radical exposure, as well as the second-order reaction rate constants of the microorganism with ozone and hydroxyl radical.

If it is assumed that hydroxyl radicals do not play a major role in disinfection, then Equation 2.8 is reduced to:

$$\ln\left(\frac{N}{N_O}\right) = -k_{O3}\int[O_3]\,dt \qquad (2.9)$$

2.3.4 Factors affecting disinfection of MWWE with ozone

2.3.4.1 Transferred ozone dose

The transferred ozone dose (TOD) is the mass of the applied ozone dose that dissolves in the MWWE (i.e. product of applied ozone dose and ozone transfer efficiency). It is the most important parameter that affects ozone treatment (Paraskeva et al., 1998). The MWWE characteristics and the disinfection target dictate the TOD required. As per USEPA (1986b), good quality secondary or tertiary treated effluent require 4 to 10 mg/L of TOD to achieve the disinfection criterion of 200 fecal coliform MPN per 100 mL (approximately equal to 126 cfu *E. coli* per 100 mL as per Black & Veatch (2010)). However, TOD of 15 to 42 mg/L may be required to meet California's stringent Title 22 standard of 2.2 total coliform per 100 mL. For practical disinfection applications, Gehr et al. (2003) consider an ozone dose up to 20 mg/L reasonable. In Japan, the typical dose for disinfection of MWWE is usually between 2 and 5 mg/L (Hashimoto et al., 2006).

Researchers have reported the all-or-none effect of ozone on microorganisms. They have noted measurable disinfection only beyond a threshold dose of ozone (Bancroft et al., 1984). USEPA (1986b) defines this ozone dose as the initial ozone demand (IOD). It is difficult to determine the IOD of MWWE experimentally. However, it is possible to get an estimate of this value from the dose-response curve as suggested by USEPA (1986b). The IOD has a great impact on the effectiveness of disinfection by ozone (USEPA, 1986b).

Studies have reported the presence of residual ozone in MWWE only beyond a certain ozone dose. Xu et al. (2002) have referred to this dose as the immediate ozone demand (ImOD) of the MWWE, and have defined it as the minimum ozone dose required to obtain measurable residual ozone. Researchers have reported inactivation of microorganisms even in the absence of residual ozone in effluent (Paraskeva et al., 1999; Xu et al., 2002; Gehr et al., 2003). Xu et al. (2002) have observed up to 3-log reduction of fecal coliform at residual ozone concentration less than measureable level. Figure 2.2 shows the effect of TOD on measureable disinfection and residual ozone.

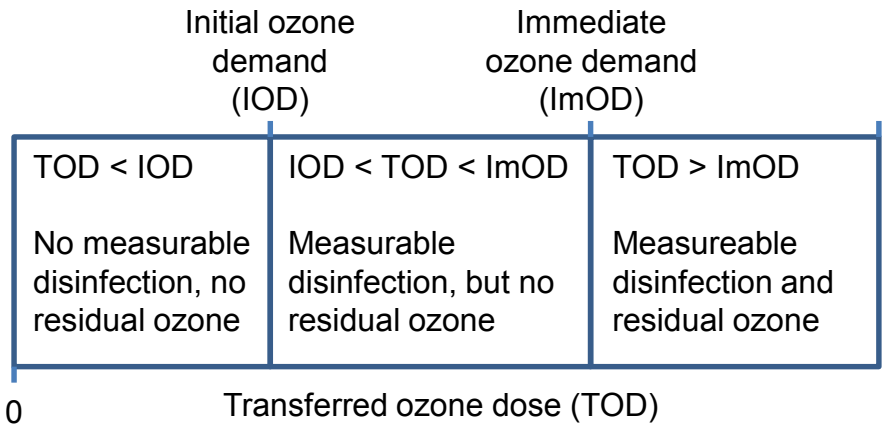


Figure 2.2 Effect of TOD on disinfection and residual ozone in reference to ozone demand

As shown in Figure 2.2, the total transferred ozone dose can be hypothetically divided into three zones: (a) TOD less than initial ozone demand, (b) TOD more than initial ozone demand but less than immediate ozone demand, and (c) TOD more than immediate ozone demand. In the first zone, when the TOD is less than the initial ozone demand, researchers have observed that there is no measurable inactivation of the microorganisms. It is possible that in this zone, the compounds in the MWWE matrix with higher second-order reaction rate constants (with oxidants) than that of the microorganisms react with and scavenge the oxidants. This shielding of microorganisms leads to their negligible inactivation that is difficult to measure.

The second zone relates to the ozone dose at which the TOD is more than the initial ozone demand but less than the immediate ozone demand. In this zone, the oxidants first react with compounds with comparatively higher reaction rates than the disinfection indicator microorganisms. The oxidants remaining then react with the microorganisms and compounds that have similar reaction rates. This results in measurable inactivation of the microorganisms. The rate of disinfection will depend on the characteristics of the MWWE. The rate of reaction between the oxidants and reactants such as the microorganisms and the compounds, would still be in the magnitude of 10^4 to 10^6 M^{-1} s^{-1}, resulting in the oxidants being consumed quickly. Hence, there is measurable disinfection but not measurable residual ozone in the effluent in this zone.

In the third zone, the TOD is more than the immediate ozone demand and the ozone demand of the effluent is significantly less. Hence, an increase in ozone dose will result in an increase in the residual ozone concentration. If considerable disinfection has already occurred before fulfillment of the immediate ozone demand, then with an

increase in ozone dose the inactivation of microorganism may increase, however the rate of disinfection would be lower.

2.3.4.2 MWWE characteristics

The quality and the quantity of organic matter present in the MWWE can have a great impact on the efficacy of disinfection by ozone. In this context, organic matter includes natural organic matter (NOM), dissolved organic matter (DOM), dissolved organic carbon (DOC), and total organic carbon (TOC).

Bancroft et al. (1984) have proposed that in water above pH 6.5, disinfection with ozone might include the following steps:

Ozone mass transfer; O_3 (g) → O_3 (aq) (2.10)

Ozone decomposition; O_3 (aq) → Oxidants (including OH•) (2.11)

Competitive reactions: (a) Oxidants + TOC → products (2.12 a)

(b) Oxidants + bacteria → disinfection (2.12 b)

The mass transfer step is the slowest and rate limiting in the above reactions as per Bancroft et al. (1984). They indicate that in the presence of high organic load, the reaction between TOC and the oxidants get preference and the microorganism inactivation is lower. Hence, a larger ozone dose is required to meet the ozone demand of the organics as well as to achieve disinfection. Organic carbon in MWWE thus negatively affects the disinfection ability of ozone (Sawyer, 1976; Bancroft et al., 1984). The refractory materials that are present in the effluent can contain carbon-carbon double bonds and increase the ozone demand of effluent (Nebel et al., 1973). Drury et al. (2006)

noted in their experiments that most of the ozone demand was due to total organic carbon. Inorganics and suspended solids can also exert ozone demand (Gehr et al., 2003). Finch and Smith (1989) have observed that the secondary treated effluent required 960 times more ozone than the ozone demand-free water for 99.99% inactivation of *E. coli*. In their experiment, the effluent had initial ozone demand of 1 mg/L. Even after this initial demand was fulfilled and disinfection was apparently favoured, they observed competing reactions for ozone. They concluded that the effectiveness of disinfection at a given TOD would also depend on the characteristics of the competing compounds present in the effluent. The concentration and composition of dissolved organic carbon can also affect the rate of decomposition of aqueous ozone (Buffle et al., 2006a), which can in turn affect disinfection.

The microorganisms can also be shielded by the organic matter or flocs from direct attack of oxidants and the low residual ozone concentration may not be sufficient to cause their inactivation (Xu et al., 2002; Huber et al., 2005). Based on their hydrophobicity characteristics, 30 to 85% of the *E. coli* strains in activated sludge liquor may bind to the sludge flocs (Zita and Hermansson, 1997).

Besides the organic matter, other effluent characteristics such as temperature, pH, and alkalinity can affect the reaction rate and the decomposition rate of ozone. Hence, they can affect the disinfection efficacy. A later section in this chapter discusses in detail their effects on the stability of ozone.

2.3.4.3 Hydraulic retention time

Studies have been made on the effect of hydraulic retention time (HRT) in the ozone dissolution chamber on disinfection. Nebel et al. (1973) observed that disinfection occurred within 3 to 8 seconds of contact time. Liberti et al. (2000) observed that the mass of the inactivation of microorganism occurred within the initial 6 seconds of contact time with a sharp initial inactivation rate. They did not observe an increase in microorganism inactivation after 5 minutes of contact time. Xu et al. (2002) found that the HRT of the dissolution chamber did not have a major impact on the inactivation of *E. coli* and fecal coliform. In their experiments, the inactivation of microorganism was identical with dissolution chambers having 2 and 10 minutes of HRT. Ried et al. (2009) have reported similar disinfection levels with 10 to 30 minutes HRT in the contact column.

As the HRT in the dissolution chamber does not have a major effect on the disinfection, the volume of the dissolution chamber should be just sufficient for efficient ozone transfer from gaseous phase to the aqueous phase. An increase in the ozonation rate (product of feed gas flow rate and concentration of ozone in the feed gas) results in a higher ozone mass transfer (Paraskeva et al., 1998). For similar TOD, this will result in a decrease in feed gas consumption as well as the size of dissolution chamber. Ried et al. (2009) also suggest ozonation with low feed gas flow rate and high ozone concentration for economic reasons.

2.3.5 Monitoring and control of disinfection by ozone

Ozone dissipates quickly in the effluent and does not leave a residual for long (Sawyer, 1976). Since a typical ozone dose for disinfection of MWWE may not produce a measurable residual ozone in the MWWE, studies have attempted to correlate disinfection with surrogate parameters. Absi et al. (1993) have reported that disinfection efficiency cannot be predicted by monitoring parameters such as BOD, COD, TOC, pH, oxidation-reduction potential (ORP), ozone dose, suspended solids and turbidity. Buffle et al. (2006a) have observed a weak correlation between TOD and ozone exposure since the ozone exposure varied by a factor of more than two at the same TOD. Hence, they do not recommend TOD as a surrogate parameter to predict disinfection or oxidation of micropollutants. Venosa and Meckes (1983) and Rakness et al. (1984) have proposed the use of concentration of ozone in the off-gas for process control of disinfection because of ease in continuous monitoring and quick feedback in case of change in the effluent characteristic and flow-rate. Residual ozone in the liquid or in the off-gas (vent gas) is currently used as a technical control parameter in ozone treatment (Bahr et al., 2007).

Since, the rate of reaction between disinfection indicator microorganisms and oxidants is fast, residual ozone can indicate attainment of a certain degree of inactivation of microorganisms. It implies fulfillment of the immediate ozone demand of the MWWE and the availability of oxidants to react with microorganisms. While residual ozone in the effluent leaving the dissolution chamber as well as the first contact chamber can be used as a surrogate parameter for monitoring disinfection, the residual at the outlet of the first contact chamber is a better indicator. Residual ozone of 0.2 to 1 mg/L can indicate fulfillment of disinfection criterion of 100 MPN *E. coli* per 100 mL (Paraskeva et al., 1998). As discussed earlier, a typical ozone dose for disinfection may not produce

residual ozone in the MWWE. Paraskeva et al. (1998) observed that the residual ozone concentration was less than the detectable level within 20 to 120 seconds of contact time at the disinfection ozone dose of around 5 mg/L. Buffle et al. (2006a) also observed that the TOD of 1.5, 2, and 2.5 mg/L failed to produce residual ozone after 20 seconds of contact time. Hence, an ozone dose higher than that typically required for disinfection is required to produce residual ozone in the MWWE.

Bahr et al. (2007) envisaged that it is difficult to measure and hence use as a process control parameter the concentration of ozone in the vent gas and MWWE when the TOD is low. They observed strong correlation between inactivation of microorganisms and reduction in UV absorption at 254 nm (UVA) of the effluent. The coefficient of correlation (R^2 value) between UVA and inactivation of total coliform, and UVA and inactivation of fecal coliform was 0.764 and 0.572, respectively. They proposed the use of UVA as a process control parameter as it can be easily and continuously monitored. Ried et al. (2009) have confirmed the availability of instruments that can measure UVA of MWWE inline.

2.4 OXIDATION OF CECs IN MWWE BY OZONE

2.4.1 Background on the CECs

The CECs consist of pharmaceutically active compounds (PhACs), personal care products (PCPs), antibiotics, hormones, endocrine disruptive chemicals (EDCs), plasticizers, surfactants, fire retardants, pesticides, herbicides, insecticides, industrial and household chemicals, and nanomaterials (Bhandari et al., 2009). Their presence in drinking source water is a major concern. While the long term effects of these CECs on

human health is still not clear, studies have linked them to feminization of vertebrates such as fish. Municipal wastewater plant effluent is a major contributor for many of these CECs. Earlier research has shown that ozonation is an effective method for transformation of these compounds in water and wastewater matrices. However, studies with actual wastewater matrix are limited. In addition, these studies have covered only a fraction of known CECs. With an ever-increasing list of emerging chemicals, there is a need to study their transformation with advanced oxidation processes including ozonation.

2.4.2 Introduction of the CECs into the environment

The use of chemicals and other compounds in everyday life in households, industries, animal farms, and agricultural farms, results in release of the CECs in the environment and water bodies. Figure 2.3 shows the origin and transportation of the CECs in the environment. The municipal wastewater treatment plants (MWWTPs), industries, and landfills are important point sources while animal and agricultural farms are some of the non-point sources.

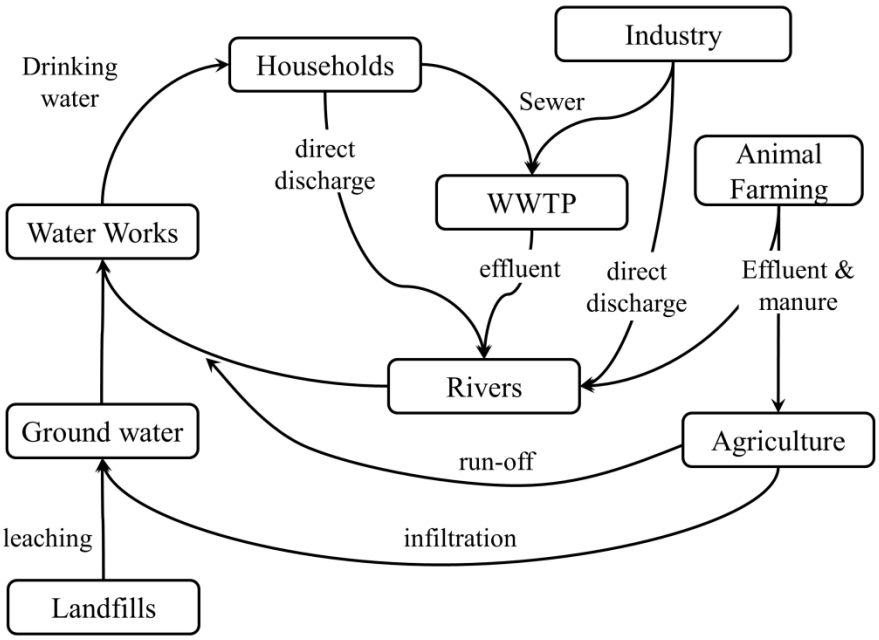


Figure 2.3 **Origin and transportation of micropollutants**
(Adapted from Petrovic et al. 2003)

PhACs and EDCs are two main groups of the CECs. The use of pharmaceuticals results in release of PhACs in the environment. Their main use is to treat or prevent diseases in the human body. Veterinary pharmaceuticals have a similar application but for animals. The pharmaceuticals are designed with biologically active sites and are supposed to be eliminated from the host body quickly (Daughton and Ternes, 1999). The body excretes the transformed and untransformed drugs from the body in feces and urine, in the form of parent compound, metabolites, or conjugates. The human body excretes up to 90% of some drugs in unchanged form (Table 2.1).

Table 2.1 Maximum excretion rate of some pharmaceuticals in unchanged form

Category	Pharmaceuticals	Max Excretion rates (%) Unchanged	Metabolites	Reference
Antiphlogistics	Acetaminophen	2 – 3	NA	MN
	Diclofenac	6–39	NA	MN
	Ibuprofen	1–8	NA	MN
	Indomethacin	15 ± 8	NA	MN
	Ketoprofen	< 10	53 - 65	IZ
	Naproxen	< 1	NA	MN
Antibiotics	Chloramphenicol	≤5, 5 - 10	NA	MN
	Chlortetracycline	> 70	NA	MN
	Ciprofloxacin	45 – 60, ≥70	40 - 45	MN
	Doxycycline	41 ± 19	NA	MN
	Erythromycin	12 - 15	NA	MN
	Lincomycin	4 – 7	40	EM
	Norfloxacin	40 - 69	NA	MN
	Oxytetracycline	> 80	NA	MN
	Penicillin G	50 - 70	30 - 70	MN
	Roxithromycin	74	NA	PU
	Sulfadiazine sodium	50	22	AD
	Sulfadimethoxine	7	86	WS
	Sulfamethazine	20 - 89		PL
	Sulfamethoxazole	10 - 30	55 - 75	MN
	Sulfathiazole	63	34	WP
	Tetracycline	80 - 90	NA	MN
	Trimethoprim	50 - 60	NA	MN
Antiepileptic, Antidepressant	Carbamazepine	1 - 2	NA	MN
Anitcoagulant	Warfarin	<2		AN, PL
Lipid regulators	Bezafibrate	40 - 69	NA	MN
	Gemfibrozil	< 2	70	MN
Ovulation Inhibitors	17-α-Ethynyl-Estradiol	23 - 59	30 - 53	MN
Reproductive Hormones	17-β-Estradiol (E2)	<1	50 - 80	AN
	Progesterone	5 - 10	50 - 60	AN

References:

AD Andreasen et al. (1978)

AN Anderson et al. (2002)

EM EMEA (1998)

IZ Ishizaki et al. (1980)

MN Various sources, refer to Monteiro and Boxall (2010)

PL Pagliaro and Benet (1975)

PU Puri and Lassman (1987)

WP Williams and Parke (1964)

WS Williams (1971)

Sewage contains the PhACs and EDCs discharged from the human body in the solid and liquid waste, as well as the expired or unwanted drugs disposed directly into the sewage system (Daughton and Ternes, 1999). As per a survey in the USA, up to 35% of the general public flush medication down the drain (Kuspis and Krenzelok, 1996). In the same country, health care facilities probably dispose 250 million pounds of drugs each year by flushing them down the drain or throwing them in trash (Gorman, 2010). The municipal wastewater treatment plants (MWWTPs) treat the sewage that contains conventional pollutants as well as the CECs, before discharging it to receiving water bodies. The MWWTPs are effective in removing only the conventional pollutants and hence are a major point source in introducing the CECs in the aquatic ecosystem (Daughton and Ternes, 1999; Petrović et al., 2003; Ternes et al., 2004).

2.4.3 Occurrence of PhACs in MWWE

The use of pharmaceuticals results in release of PhACs in the environment. Some categories of widely used pharmaceuticals are antiphlogistics, antibiotics, antiepileptic, and lipid regulators. The following section discusses in detail the use and application of these drugs, their removal in the conventional sewage treatment process and their occurrence (ratio of detects to total number of samples) in the MWWE.

2.4.3.1 Antiphlogistics

This group consist of analgesics, antipyretics, and anti-inflammatory agents.

Use and consumption

Many of the drugs in this category have high consumption rate, and some of them are available without prescription (Ternes, 1998). Some important antiphlogistics are

acetaminophen (paracetamol), diclofenac, ibuprofen, indomethacin, ketoprofen, naproxen, and phenazone. The main use of these drugs is as medicine for humans. Diclofenac and naproxen have additional application as veterinary medicine (Stumpf et al., 1999; Swan et al., 2006). All of the drugs have analgesic and antipyretic properties. Acetaminophen is the only drug in the earlier mentioned list that does not have anti-inflammatory property. The other drugs are non-steroidal anti-inflammatory drugs (NSAIDs).

Paracetamol is the other common name of acetaminophen. It is mainly used to treat pain and fever (Anderson et al., 2002). Diclofenac is an NSAID pharmaceutical prescribed to humans and livestock to reduce inflammation and to manage pain. The exposure of this drug to vultures, when they consume the carcasses of the cattle treated with diclofenac, has resulted in their death and a major decrease in their global population (Swan et al., 2006). Diclofenac is a more toxic drug compared to naproxen, ketoprofen, and ibuprofen as per Mehinto (2009). Their study has shown that continuous exposure to diclofenac in environmentally relevant concentrations can cause damage to the kidney and intestine of fish, and can disrupt key functional processes controlling metabolism and cell cycle.

Acetaminophen is a widely used analgesic drug in Canada, with nearly 740 tonnes of this drug sold in 2001 (Metcalfe et al., 2004), which is equivalent to 24.7 g per capita per annum consumption. It is a popular analgesic in the United States (Sedlak and Pinkston, 2001). Table 2.2 compiles the data related to consumption of some of the drugs of the antiphlogistics group of several studies. Acetaminophen is widely used in France

and UK and its consumption is more than 3300 tonne/yr, which is approximately equal to 50 g per capita per annum.

Zhang et al. (2008) have estimated the worldwide consumption of diclofenac to be 940 tonnes in 2008. In Canada, the sale of this drug in 2001 was approximately 3.5 tonnes (Metcalfe et al., 2004).

Ibuprofen is a NSAID that is available without prescription in Canada (Lévesque et al., 2005). The sale of this drug in Canada in the year 2001 was 176 tonnes (Metcalfe et al., 2004). As per Table 2.2, the sale of ibuprofen in France, Germany, Spain, and UK exceeds 200 tonne/yr. High consumption can indicate high occurrence and concentration in raw sewage. The occurrence and concentration in MWWE will depend on the removal of the compound in the MWWTP.

The literature research did not reveal data related to consumption of ketoprofen in Canada. If per capita consumption of this drug in other countries may give any indication, Sadezky et al. (2008) have reported 0.018 and 0.025 g per capita per annum consumption of this drug in Germany and UK. They also report 0.337 and 0.366 g per capita per annum consumption of this drug in France and Poland, which translates into a total consumption of 22 and 13 t/yr, respectively. As per Table 2.2, the annual consumption of this drug in most of the other listed countries was below 2 tonnes.

Naproxen is a widely used NSAID in Canada. Its consumption in Canada in year 2001 was 25 tonnes as per Metcalfe et al. (2004). From data in Table 2.2, the annual consumption of naproxen in European countries such as France, UK, Spain, and Poland exceeds 30 tonnes each. The annual consumption in Australia was nearly 24 tonnes in 2004.

Table 2.2 Consumption of antiphlogistics in various countries

Compound	Country	Year	Sale (tonne/yr)	Reference
Acetaminophen (Paracetamol)	Canada	2001	740	Metcalfe et al. (2004)
	France	2004	3303	Besse et al (2008)
	France	1999-2006	2799	Sadezky et al (2008)
	Germany	1999-2006	367	Sadezky et al (2008)
	Norway	2006	185	Grung et al. (2008)
	Poland	1999-2006	186	Sadezky et al (2008)
	Spain	1999-2006	147	Sadezky et al (2008)
	UK	1999-2006	821	Sadezky et al (2008)
	UK	2004	3535	Monteiro et al (2010)
	Australia	1998	296	Khan et al (2004)
Diclofenac	Canada	2001	3.5	Metcalfe (2004)
	Austria	1997	6	Zhang et al (2008)
	Finland	2005	1.07	Vieno et al. (2007)
	France	2004	9.9	Besse et al (2008)
	France	1999-2006	9.90	Sadezky et al (2008)
	Germany	1999	82	Zhang et al (2008)
	Germany	1999-2006	72.7	Sadezky et al (2008)
	Norway	2006	1.3	Grung et al. (2008)
	Poland	1999-2006	19. 5	Sadezky et al (2008)
	Spain	2003	32.3	Monteiro et al (2010)
	Spain	1999-2006	2.42	Sadezky et al (2008)
	Switzerland	2004	3.9	Tauxe-Wuersch et al (2005)
	UK	2000	26	Zhang et al (2008)
	UK	2004	35.4	Monteiro et al (2010)
	UK	1999-2006	28.2	Sadezky et al (2008)
	Australia	1998	4.4	Khan et al (2004)
	China	2005	328	Sui et al. (2010)
	Worldwide	2008	940	Zhang et al (2008)
Ibuprofen	Canada	2001	176	Metcalfe (2004)
	Finland	2005	94	Vieno et al. (2007)
	France	2004	240	Besse et al (2008)
	France	1999-2006	203	Sadezky et al (2008)
	Germany	1999-2006	261	Sadezky et al (2008)
	Norway	2006	29	Grung et al. (2008)
	Poland	1999-2006	193	Sadezky et al (2008)
	Spain	2003	276	Monteiro et al (2010)
	Spain	1999-2006	108	Sadezky et al (2008)
	Switzerland	2004	18	Tauxe-Wuersch et al (2005)
	UK	2004	330	Monteiro et al (2010)
	UK	1999-2006	149	Sadezky et al (2008)
	Australia	1998	14.2	Khan et al (2004)
	Japan	2002	99	Nakada et al. (2006)

Table 2.2 continued (Consumption of antiphlogistics in various countries)

Compound	Country	Year	Sale (tonne/yr)	Reference
Indomethacin	Canada	2001	0.86	Metcalfe (2004)
	Germany	1999-2006	3.40	Sadezky et al (2008)
	Poland	1999-2006	0.855	Sadezky et al (2008)
	UK	1999-2006	1.06	Sadezky et al (2008)
	China	2005	277	Sui et al. (2010)
Ketoprofen	Finland	2005	11	Vieno et al. (2007)
	France	2004	21.7	Besse et al (2008)
	France	1999-2006	21.7	Sadezky et al (2008)
	Germany	1999-2006	1.48	Sadezky et al (2008)
	Poland	1999-2006	12.93	Sadezky et al (2008)
	Spain	1999-2006	0.21	Sadezky et al (2008)
	Switzerland	2004	0.254	Tauxe-Wuersch et al (2005)
	UK	1999-2006	1.30	Sadezky et al (2008)
	Australia	1998	4.4	Khan et al (2004)
	China	2005	92	Sui et al. (2010)
	Japan	2002	71	Nakada et al. (2006)
Naproxen	Canada	2001	25	Metcalfe (2004)
	Finland	2005	6.05	Vieno et al. (2007)
	France	2004	37.3	Besse et al (2008)
	France	1999-2006	38.2	Sadezky et al (2008)
	Germany	1999-2006	5.19	Sadezky et al (2008)
	Poland	1999-2006	38.8	Sadezky et al (2008)
	Spain	2003	42.6	Monteiro et al (2010)
	Spain	1999-2006	10.6	Sadezky et al (2008)
	UK	2004	33.6	Monteiro et al (2010)
	UK	1999-2006	32.2	Sadezky et al (2008)
	Australia	1998	23	Khan et al (2004)
	Japan	2002	22-33	Nakada et al. (2006)

Legends:

UK United Kingdom

Abatement in conventional MWWTPs

Conventional MWWTPs are effective in removing acetaminophen from sewage (Ternes, 1998; Heberer, 2002; Lee et al., 2003; Pedrouzo et al., 2011). Ternes (1998) have reported 98% elimination of this drug in the MWWTPs.

Ternes (1998) have also reported 50 to 65% reduction in the concentration of diclofenac in the MWWTPs. However, Heberer (2002) found only 17% reduction in the concentration of diclofenac on passage through a MWWTP. They have reported it as difficult to degrade by conventional MWWTPs and have termed it as one of the most important PhACs in the water cycle. Joss et al. (2006) have reported the biological degradation constant of diclofenac to be low. Joss et al. (2006) and Radjenovic et al. (2009) have reported less than 25% reduction in its concentration after treatment of sewage in MWWTP. Zwiener and Frimmel (2003) also found diclofenac to be resistant to biodegradation. Lee et al. (2003) and Pedrouzo et al. (2011) found in their studies that diclofenac was not removed by the MWWTPs. Lishman et al. (2006) have observed negative removal of this compound. The results from various studies indicate that diclofenac is difficult to degrade biologically, and hence may have high occurrence in MWWE.

The efficacy of removal of ibuprofen from sewage by conventional MWWTPs is high as per various studies. Radjenovic et al. (2009) and Lishman et al. (2006) have observed minimum 95% reduction in concentration of this drug after sewage treatment. Pedrouzo et al. (2011) have reported reduction of 80%. From the data compiled by Monteiro and Boxall (2010), while most studies have reported high removal of 75 to 97%, a study has also reported low removal of 22%. Zwiener and Frimmel (2003), and

Joss et al. (2005) have found ibuprofen to be biodegradable in conventional MWWTPs. Joss et al. (2006) indicate that the biological degradation constant of ibuprofen is high and hence more than 90% removal of this drug during sewage treatment is possible. Castiglioni et al. (2006) have observed higher removal of ibuprofen in MWWTPs in summer compared to in winter.

Indomethacin is not an easily biodegradable compound (Joss et al., 2006). Lee et al. (2003) have reported 40% transformations of this drug in the MWWTPs. Lishman et al. (2006) and Rosal et al. (2010) have reported less than 25% removal. Radjenovic et al. (2009) observed that the secondary treatment of sewage did not reduce the concentration of this compound. The findings from these studies indicate that indomethacin is resistant to degradation during the sewage treatment process.

Results of various studies show low removal of ketoprofen by conventional sewage treatment processes. Lee et al. (2003) have observed 18% reduction of this drug. In a study covering 13 MWWTPs, Lishman et al. (2006) found the median removal of this drug to be 44%. Radjenovic et al. (2009) have reported 55% removal of this drug in a conventional MWWTP. The data compiled from various sources by Monteiro and Boxall (2010) shows 65 to 77% removal of this drug in MWWTPs having activated sludge process.

Naproxen has a low biodegradation constant and hence it is difficult to transform by conventional sewage treatment (Joss et al., 2006). Monteiro and Boxall (2010) have reported 15% removal of this drug from sewage after secondary treatment. Carballa et al. (2004) have found 40 to 55% reduction in the concentration of this drug after biological

treatment of sewage. However, Lee et al. (2003) and Lishman et al. (2006) have observed 70% and 93% degradation of naproxen in the MWWTPs.

Occurrence and concentration in MWWE

Studies have frequently detected antiphlogistics in the MWWE in varying concentrations. Table 2.3 and Table 2.4 summarize pertinent data from some of the studies for the MWWE discharged in Canada and in other countries.

Data in Table 2.2 shows that acetaminophen is one of the most consumed drugs in Canada. However, Lee et al. (2003) did not detect this drug in any of the 44 MWWE samples collected from nine WWTPs in Ontario. Brun et al. (2006) have reported less than 40% occurrence, and median concentration of 5 ng/L of acetaminophen in the MWWE samples collected from eight MWWTPs in Canada. However, in one sample they detected this drug at concentration of 9000 ng/L. The low concentration and occurrence may be due to high efficacy of conventional sewage treatment plants in removing acetaminophen from sewage. Sporadic high concentrations of 3,300 ng/L and 6,000 ng/L have been reported by Hope et al. (2012) and Ternes (1998). As per data in Table 2.4, most of the studies in other countries have reported less than 20% occurrence of this drug in MWWE. The only exception to this trend is the study by Reungoat et al. (2012). They detected this compound in all the nine MWWE samples taken from three MWWTPs, in concentrations between < 5 ng/L and 154 ng/L.

Studies have detected diclofenac in concentrations between 5 ng/L and 748 ng/L in the MWWE in Canada (Table 2.3). They have reported occurrence in the range of 40 to 100%. However, Metcalfe et al. (2003a) did not detect diclofenac in any of the

MWWE samples collected from 18 STPs located in five provinces. One of the reasons for this low occurrence can be the high method detection limit (MDL) of 250 ng/L of the compound in the study. Studies from Europe, Australia, and Asia have reported close to 100% occurrence of diclofenac in MWWE (Table 2.4). Bahr et al. (2007) and Ternes et al. (2003) have reported a mean concentration of 4360 ng/L and 1300 ng/L, respectively. Many other studies from Europe also have found this drug in effluent in concentrations in excess of 1000 ng/L. Hence, the concentration of diclofenac in MWWE in Europe seems high. Comparison of the data in Table 2.3 and Table 2.4 shows that the occurrence and concentration of diclofenac in MWWE in Canada is lower than that in Europe.

In MWWE in Canada, Metcalfe et al. (2003a) have detected ibuprofen in concentrations up to 24,600 ng/L. Brun et al. (2006) have also detected this drug at similar concentrations in the MWWE in Atlantic Canada. Metcalfe et al. (2003b), Sosiak et al. (2005), Comeau et al. (2008), and Crouse et al. (2012) have found this drug in concentrations more than 1000 ng/L and their occurrence in the range of 50 to 100%. However, Lishman et al. (2006) and Tabe et al. (2009) have found less than 50% occurrence of ibuprofen. From the drug consumption data, Sedlak and Pinkston (2001) have estimated the average concentration of ibuprofen in raw sewage in the United States to be 37,000 ng/L. Hence, high occurrence of this drug in MWWE even after its high removal during sewage treatment is expected. However, Hope et al. (2012) found less than 5% occurrence of this drug in the MWWE of 52 MWWTPs in Oregon (USA). The high method detection limit of 223 ng/L of the drug can be a reason for the low occurrence. The concentration of the drug when detected in their samples was between 2630 ng/L and 17000 ng/L. Conversely, Snyder et al. (2006) and Wert et al. (2009a) have

reported 100% occurrence but less than 90 ng/L concentration of this drug in MWWE. Studies from Europe, Australia, and Asia have reported high occurrence of ibuprofen in MWWE (Table 2.4). In Europe, Vieno (2007), Ruel et al. (2011), Ternes (1998), Muñoz et al. (2010) and Radjenovic et al. (2007) have detected ibuprofen in MWWE in concentrations more than 3000 ng/L. The data in Table 2.3 and Table 2.4 indicates that the concentration of ibuprofen in MWWE in Canada and in many European countries is higher than that in Australia, Japan, and Korea. This can indicate the consumption pattern of this drug in these countries.

From Table 2.3, various studies have reported 75 to 100% occurrence of indomethacin in the MWWE in Canada. However, Hua et al. (2006) did not detect this drug in any of the 11 MWWE collected by them. Studies have found this drug in MWWE in Canada in concentrations in the range of 10 ng/L to 803 ng/L. In countries other than Canada, Ternes (1998) has found occurrence of 100% and median concentration of 270 ng/L of indomethacin in MWWE in Germany (Table 2.4). Stumpf et al. (1999) have reported a concentration of 1000 ng/L in a MWWE in Brazil. Reungoat et al. (2012) from Australia have reported 100% occurrence but less than 30 ng/L concentration of this drug in the effluent.

Lee et al. (2003) and Comeau et al. (2008) have reported more than 50% occurrence of ketoprofen in MWWE in Canada (Table 2.3). Majority of the other studies have reported less than 25% occurrence. Brun et al. (2006) have detected this drug in concentrations up to 310 ng/L. Studies from Germany, Australia, and Japan have reported high occurrence of ketoprofen in MWWE (Table 2.4). Ruel et al. (2011) from France have reported a mean concentration of 640 ng/L of this drug in the effluent. Radjenovic

et al. (2007) have detected this drug in concentrations up to 1650 ng/L. Studies from Japan have reported concentrations up to 1400 ng/L.

The data in Table 2.3 shows that six studies have reported close to 100% occurrence of naproxen in MWWE in Canada. Seven studies have reported the maximum concentration of the drug in MWWE in excess of 1000 ng/L. Metcalfe et al. (2003a) have detected this drug in the MWWE in concentrations up to 33,900 ng/L. The high occurrence and concentration of this drug in MWWE makes it one of the potential drugs that should be monitored in future in Canada. The data from Table 2.4 indicates a high occurrence and concentration of naproxen in MWWE in North America, Europe, Australia, and Asia. The concentrations reported of this drug in MWWE in United States are between 13 ng/L and 106 ng/L. In studies from Europe, Rosal et al. (2010), Carballa et al. (2004) and Radjenovic et al. (2007) have reported maximum concentrations in the range of 2,208 ng/L to 3,495 ng/L. Stumpf et al. (1999) have detected this drug in MWWE in Brazil in concentrations up to 3000 ng/L.

Table 2.3 Occurrence of antiphlogistics in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Acetaminophen	Ontario	0/16	10					Lee et al. (2003)
	Ontario	3/8	12.3	5	18			Tabe et al. (2009)
	Atl Canada	6/16	10	27	9000		4471 ± 2903	Brun et al. (2006)
Diclofenac	Ontario	4/4	5	5	359			Metcalfe et al. (2003b)
	Ontario	16/16	10	20	210			Lee et al. (2003)
	Ontario	24/39	62		748	140	194	Lishman et al. (2006)
	Ontario	11/11	15				538 ± 370	Hua et al. (2006)
	Ontario	2/8	5.8	225	230			Tabe et al. (2009)
	Alberta	2/7	≤ 25	359	429			Sosiak et al. (2005)
	Nova Scotia	6/7	3	25	190			Comeau et al. (2008)
	Atl Canada	6/16	30	37	500	15	171 ± 176	Brun et al. (2006)
	Canada	0/18	250					Metcalfe et al. (2003a)
Ibuprofen	Ontario	4/4	5-20	79	1885			Metcalfe et al. (2003b)
	Ontario	16/16	10	40	970			Lee et al. (2003)
	Ontario	16/39	61		773	353	384	Lishman et al. (2006)
	Ontario	6/11	15				90 ± 47	Hua et al. (2006)
	Ontario	3/8	6.4	157	203			Tabe et al. (2009)
	Alberta	4/7	≤ 25	383	1759			Sosiak et al. (2005)
	Nova Scotia	5/5	6	140	6300			Comeau et al. (2008)
	Nova Scotia	6/8	7	12	2200			Crouse et al. (2011)
	Atl Canada	15/16	30	37	22000	2305	5523 ± 6795	Brun et al. (2006)
	Canada	12/18	50	300	24600			Metcalfe et al. (2003a)
Indomethacin	Ontario	3/4	5-10	10	378			Metcalfe et al. (2003b)
	Ontario	16/16	20	30	240			Lee et al. (2003)
	Ontario	9/39	100		507	149	190	Lishman et al. (2006)
	Ontario	0/11	10					Hua et al. (2006)
	Ontario	8/8	6.4	19	46			Tabe et al. (2009)
	Alberta	3/7	≤ 25	105	803			Sosiak et al. (2005)
	Nova Scotia	4/6	44	41	120			Comeau et al. (2008)
	Atl Canada	12/16	30	35	310	54	92 ± 75	Brun et al. (2006)
Ketoprofen	Ontario	1/4	5-13		13			Metcalfe et al. (2003b)
	Ontario	16/16	10	30	150			Lee et al. (2003)
	Ontario	9/39	88		210	114	125	Lishman et al. (2006)
	Ontario	5/11	150				348 ± 240	Hua et al. (2006)
	Ontario	4/8	2.3	11	17			Tabe et al. (2009)
	Alberta	0/7	≤25					Sosiak et al. (2005)
	Nova Scotia	5/7	11	18	120			Comeau et al. (2008)
	Atl Canada	5/16	30	52	310	15	178 ± 116	Brun et al. (2006)
	Canada	0/18	50					Metcalfe et al. (2003a)

Table 2.3 continued (Occurrence of antiphlogistics in secondary treated MWWE in Canada)

Compound	Region	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Naproxen	Ontario	4/4	5-20	21	524			Metcalfe et al. (2003b)
	Ontario	16/16	10	210	1110			Lee et al. (2003)
	Ontario	21/39	74		1189	351	452	Lishman et al. (2006)
	Ontario	10/11	100				414 ± 246	Hua et al. (2006)
	Ontario	8/8	2.4	126	555			Tabe et al. (2009)
	Alberta	2/7	≤ 25	1785	2668			Sosiak et al. (2005)
	Nova Scotia	6/6	5	210	6900			Comeau et al. (2008)
	Nova Scotia	8/8	41	61	2400			Crouse et al. (2011)
	Canada	15/16	30	220	14000	1450	3483 ± 4020	Brun et al. (2006)
	Canada	3/18	100	7200	33900			Metcalfe et al. (2003a)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Atl Canada Atlantic Canada

Min Minimum Max Maximum

SD Standard Deviation VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.4 Occurrence of antiphlogistics in secondary treated MWWE in other countries

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Acetaminophen	USA	1/4			46			Barber et al. (2011)
	USA	0/12	50				< 50	Yang et al. (2011)
	USA	2/102	223	2610	3300	2955	2955	Hope et al. (2012)
	France	NA/6	0.5-2				380 ± 170	Ruel et al. (2011)
	Germany	4/49	500		6000	< 500		Ternes (1998)
	Spain	NA/8	5.35	48	418		207	Radjenovic et al. (2007)
	Spain	2/13	2	9	30			Pedrouzo et al. (2011)
	Switzerland	0/11	590					Hollender et al. (2009)
	Australia	NA/4	10	120	390	260		Reungoat et al. (2010)
	Australia	NA/16		90	580			Reungoat et al. (2011)
	Australia	9/9		< 4.7	154			Reungoat et al. (2012)
	Japan		43		1700			Okuda et al. (2008)
	Korea	3/7	1	1.8	19		9.5	Kim et al. (2007)
	Korea	2/12	5	6	9			Choi et al. (2008)
	Korea	NA/5	1.7	0	27		10	Behera et al. (2011)
Diclofenac	USA	3/3	1	54	73			Snyder et al. (2006)
	USA	3/3		47	150	81		Wert et al. (2009)
	USA	2/3	0.53	110	220		165	Gerrity et al. (2011)
	USA	NA/12	50	27	130		99	Yang et al. (2011)
	Austria	5/5	20	780	1680			Clara et al. (2005b)
	Austria	3/3	20	970	2300	2000		Schaar et al. (2010)
	Finland	13/13	5	140	620	320	350	Vieno et al. (2007)
	France	NA/6	0.5-2				630 ± 310	Ruel et al. (2011)
	Germany	49/49	50		2100	810		Ternes et al.(1998)
	Germany	NA/6	50				1300 ± 100	Ternes et al.(2003)
	Germany	NA/10					4360 ± 1360	Bahr et al. (2007)
	Greece	11/11	2	10	365			Koutsouba et al. (2003)
	Spain	NA/8	40	786	1991		1241	Radjenovic et al. (2007)
	Spain	NA/17					1700	Muñoz et al (2010)
	Spain	NA/17					1500	Muñoz et al (2010)
	Spain	> 4/12	1	6	431		220	Rosal et al. (2010)
	Spain	13/13	2	130	1032	368	418 ± 273	Pedrouzo et al. (2011)
	Sweden	NA/3	2.3				485 ± 30	Zorita et al. (2009)
	Switzerland	NA/15		500	1250			Joss et al. (2005)
	Switzerland	11/11	50	501	1731	1096	1099 ± 323	Hollender et al. (2009)

Table 2.4 continued (Occurrence of antiphlogistics in secondary treated MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Diclofenac	Australia	NA/4	10	140	270	200		Reungoat et al. (2010)
(cont'd)	Australia	NA/16		80	290			Reungoat et al. (2011)
	Australia	9/9		139	316			Reungoat et al. (2012)
	China	4/4	4.7	130	260			Sui et al. (2010)
	Korea	7/7	1	8.8	127		40	Kim et al. (2007)
	Korea	11/11	1	7.8	26	14	14	Ryu et al. (2011)
	Korea	5/5	0.24	13	49		24	Behera et al. (2011)
	Brazil	NA/10	50		1415	400		Stumpf et al. (1999)
Ibuprofen	USA	0/2	2.6					Boyd et al. (2003)
	USA	3/3	1	5.6	19			Snyder et al. (2006)
	USA	3/3		5	85	75		Wert et al. (2009)
	USA	1/3	1		13			Gerrity et al. (2011)
	USA	0/4	42					Barber et al. (2011)
	USA	5/102	223	2630	17000	3350	6120	Hope et al. (2012)
	USA	NA/12	50	49	78		64	Yang et al. (2011)
	Austria	3/5	20	20	2400			Clara et al. (2005b)
	Austria	2/3	20	< 20	31			Schaar et al. (2010)
	Finland	12/13	5	< 5	3910	120	650	Vieno et al. (2007)
	France	NA/6	0.5-2				2500 ± 3400	Ruel et al. (2011)
	Germany	42/49	50		3400	370		Ternes et al.(1998)
	Germany	NA/6	50				130 ± 30	Ternes et al.(2003)
	Germany	NA/10					20 ± 10	Bahr et al. (2007)
	Greece	0/11	1.6					Koutsouba et al. (2003)
	Spain	NA/17					4700	Muñoz et al (2010)
	Spain	NA/17					1.7	Muñoz et al (2010)
	Spain	> 4/12	4	< 4	653		135	Rosal et al. (2010)
	Spain	9/13	7	15	955	137	261 ± 301	Pedrouzo et al. (2011)
	Spain	NA/8	20	336	6268		2559	Radjenovic et al. (2007)
	Spain	3/3	20	910	2100	970		Carballa et al. (2004)
	Sweden	NA/3	2.7				88.5 ± 4.5	Zorita et al. (2009)
	Switzerland	NA/15		0.1	175			Joss et al. (2005)
	Switzerland	3/11	80	56	86	80	74 ± 16	Hollender et al. (2009)

Table 2.4 continued (Occurrence of antiphlogistics in secondary treated MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Ibuprofen	Australia	NA/4	40	80	160	90		Reungoat et al. (2010)
(cont'd)	Australia	NA/16		< 10	161			Reungoat et al. (2011)
	Australia	8/9		< 16	88			Reungoat et al. (2012)
	Japan	16/16	1	1.4	177	18	33 ± 44	Nakada et al. (2006)
	Japan	4/4	0.3-21	4.3	15			Nakada et al. (2007)
	Korea	5/7	1	10	137		65	Kim et al. (2007)
	Korea	7/11	1	< 1	11	1.9	3.4	Ryu et al. (2011)
	Korea	5/5	3	15	75		40	Behera et al. (2011)
	Brazil	NA/10	50		3625	600		Stumpf et al. (1999)
Indomethacin	Germany	49/49	50		600	270		Ternes et al.(1998)
	Germany	NA/6	50				100 ± 40	Ternes et al.(2003)
	Spain	NA/8	31	< RL	124		88	Radjenovic et al. (2007)
	Australia	NA/4	10	30	40	30		Reungoat et al. (2010)
	Australia	NA/16		< 10	30			Reungoat et al. (2011)
	Australia	9/9		6	28			Reungoat et al. (2012)
	China	4/4	1.3	70	130			Sui et al. (2010)
	Brazil	NA/10	50		1000	50		Stumpf et al. (1999)
Ketoprofen	Finland	12/13	25	< 25	1240	320	370	Vieno et al. (2007)
	France	NA/6	0.5-2				640 ± 390	Ruel et al. (2011)
	Germany	37/49	50		380	200		Ternes et al.(1998)
	Germany	NA/10					130 ± 130	Bahr et al. (2007)
	Spain	NA/8	74	518	1650		777	Radjenovic et al. (2007)
	Australia	NA/16		< 0.2	70			Reungoat et al. (2011)
	Australia	9/9		< 6.7	86			Reungoat et al. (2012)
	China	0/4	5.5					Sui et al. (2010)
	Japan	16/16	0.3	68	219	110	120 ± 46	Nakada et al. (2006)
	Japan	4/4	0.03-15	96	299			Nakada et al. (2007)
	Japan	12/12	43	ND	1400			Okuda et al. (2008)
	Korea	NA/5	1.65	0	37		12	Behera et al. (2011)
	Brazil	NA/10	50		656	168		Stumpf et al. (1999)

Table 2.4 continued (Occurrence of antiphlogistics in secondary treated MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Naproxen	USA	2/2	0.4	81	106			Boyd et al. (2003)
	USA	3/3	1	13	71			Snyder et al. (2006)
	USA	3/3		23	51	48		Wert et al. (2009)
	USA	3/3	0.5	52	100		72 ± 25	Gerrity et al. (2011)
	Finland	13/13	25	170	1930	500	690	Vieno et al. (2007)
	France	NA/6	0.5-2				60 ± 30	Ruel et al. (2011)
	Germany	10/10	50		520	300		Ternes et al.(1998)
	Germany	NA/6	50				100 ± 10	Ternes et al.(2003)
	Germany	NA/10					130 ± 80	Bahr et al. (2007)
	Spain	3/3	20	800	2600	1850		Carballa et al. (2004)
	Spain	NA/8	20	491	3495		1682	Radjenovic et al. (2007)
	Spain	>4/12	24	359	2208		923	Rosal et al. (2010)
	Spain	13/13	7	15	691	85	175 ± 194	Pedrouza et al. (2011)
	Sweden	NA/3	2				340 ± 15	Zorita et al. (2009)
	Switzerland	NA/15		190	600			Joss et al. (2005)
	Switzerland	11/11	175	181	329	223	249 ± 53	Hollender et al. (2009)
	Australia	NA/4	100	240	510	290		Reungoat et al. (2010)
	Australia	NA/16		100	587			Reungoat et al. (2011)
	Australia	9/9		83	587			Reungoat et al. (2012)
	Japan	16/16	0.3	12	139	56	62 ± 41	Nakada et al. (2006)
	Japan	4/4	0.24-27	33	85			Nakada et al. (2007)
	Korea	7/7	1	20	483		128	Kim et al. (2007)
	Korea	11/11	1	1.8	80	21	26	Ryu et al. (2011)
	Korea	5/5	4.7	37	166		111	Behera et al. (2011)
	Brazil	NA/10	50		3000	610		Stumpf et al. (1999)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA	United States of America		
Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency		
RL	Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)		

2.4.3.2 Antibiotics

Antibiotics are compounds that can inhibit and/or destroy bacteria or single-celled organisms. They are used to treat bacterial infection. The main use of antibiotics is in human and veterinary medicines. McArdell et al. (2003) have reported that of the total antibiotics consumed in Switzerland in 1997, 38% was in human medicine and 62% was in veterinary medicine. Göbel et al. (2005a) report 5 g per person per year consumption of antimicrobials in Germany and Switzerland. The data regarding the consumption of the antibiotics in Canada and USA was not available in the published literature during literature research.

The main sub-groups of antibiotics are fluoroquinolones, macrolides, penicillin, sulfonamides, and tetracyclines (Monteiro and Boxall, 2010). Table 2.5 compiles the data related to the consumption of antibiotics in other countries from various sources. The comparison of the data in Table 2.2 and Table 2.5 shows that the consumption of the antibiotics is lower by one to two orders than that of the antiphlogistics.

Table 2.5 Consumption of antibiotics in various countries

Compound	Country	Year	Sale (tonne/yr)	Reference
Fluoroquinolones				
Ciprofloxacin	Finland	2005	0.85	Vieno et al. (2007)
	France	2004	12.2	Besse et al (2008)
	France	1999-2006	12.2	Sadezky et al (2008)
	Germany	1999-2006	14.2	Sadezky et al (2008)
	Norway	2006	0.885	Grung et al. (2008)
	Poland	1999-2006	4.85	Sadezky et al (2008)
	Spain	1999-2006	3.75	Sadezky et al (2008)
	UK	2004	16.4	Monteiro et al (2010)
	UK	1999-2006	6.51	Sadezky et al (2008)
Enrofloxacin	UK	2000	0.80	Sarmah et al. (2006)
Norfloxacin	Finland	2005	0.261	Vieno et al. (2007)
	Germany	1999-2006	3.04	Sadezky et al (2008)
	Poland	1999-2006	3.03	Sadezky et al (2008)
	UK	1999-2006	0.393	Sadezky et al (2008)
Macrolides				
Erythromycin	Germany	1999-2006	21.12	Sadezky et al (2008)
	Poland	1999-2006	6.37	Sadezky et al (2008)
	Spain	2003	8.1	Monteiro et al (2010)
	Switzerland	1999	0.22	Gobel et al (2005b)
	UK	2004	48.7	Monteiro et al (2010)
	UK	1999-2006	28.03	Sadezky et al (2008)
	Australia	1998	11	Khan et al (2004)
Lincomycin	UK	2000	0.721	Sarmah et al. (2006)
Roxithromycin	France	2004	3.4	Besse et al (2008)
	France	1999-2006	9.5	Sadezky et al (2008)
	Germany	1999-2006	7.10	Sadezky et al (2008)
	Poland	1999-2006	1.88	Sadezky et al (2008)
	Switzerland	1999	0.15	Gobel et al (2005b)
	UK	1999-2006	0	Sadezky et al (2008)
	Australia	1998	3.75	Khan et al (2004)
Tylosin	UK	2000	5.14	Sarmah et al. (2006)
Sulfonamides				
Sulfadiazine	Germany	1999-2006	2.55	Sadezky et al (2008)
	Switzerland	1999	0.070	Gobel et al (2005b)
	UK	2000	14.2	Sarmah et al. (2006)*
	UK	2004	0.362	Monteiro et al (2010)
	UK	1999-2006	0.007	Sadezky et al (2008)
Sulfamerazine	Germany	1999-2006	0.923	Sadezky et al (2008)

Table 2.5 continued (Consumption of antibiotics in various countries)

Compound	Country	Year	Sale (tonne/yr)	Reference
Sulfamethoxazole	Finland	2005	0.269	Vieno et al. (2007)
	France	2004	16.7	Besse et al (2008)
	France	1999-2006	20	Sadezky et al (2008)
	Germany	1999-2006	54	Sadezky et al (2008)
	Norway	2006	0.26	Grung et al. (2008)
	Poland	1999-2006	7	Sadezky et al (2008)
	Spain	2003	12.7	Monteiro et al (2010)
	Switzerland	1999	2.6	Gobel et al (2005)
	UK	2004	3.13	Monteiro et al (2010)
	UK	1999-2006	1	Sadezky et al (2008)
	Australia	1998	7.3	Khan et al (2004)
Tetracyclines				
Chlortetracycline	Germany	1999-2006	0.28	Sadezky et al (2008)
	UK	2000	6.26	Sarmah et al. (2006)
Doxycycline	France	2004	6.24	Besse et al (2008)
	France	1999-2006	6.24	Sadezky et al (2008)
	Germany	1999-2006	11.25	Sadezky et al (2008)
	UK	1999-2006	1.41	Sadezky et al (2008)
	Australia	1998	1.8	Khan et al (2004)
Oxytetracycline	Germany	1999-2006	2.03	Sadezky et al (2008)
	UK	1999-2006	24.90	Sadezky et al (2008)
Tetracycline	Germany	1999-2006	1.40	Sadezky et al (2008)
	Norway	2006	1.09	Grung et al. (2008)
	Poland	1999-2006	3.26	Sadezky et al (2008)
	UK	2004	2.1	Monteiro et al (2010)
	UK	1999-2006	1.49	Sadezky et al (2008)
Miscellaneous				
Chloramphenicol	Germany	1999-2006	0.32	Sadezky et al (2008)
	UK	1999-2006	0.104	Sadezky et al (2008)
	China	2005	1929	Sui et al. (2010)
Trimethoprim	France	2004	3.35	Besse et al (2008)
	France	1999-2006	3.35	Sadezky et al (2008)
	Germany	1999-2006	12.1	Sadezky et al (2008)
	Norway	2006	0.68	Grung et al. (2008)
	Spain	2003	3.7	Monteiro et al (2010)
	Switzerland	1999	0.52	Gobel et al (2005b)
	UK	2004	11.2	Monteiro et al (2010)
	UK	1999-2006	7.34	Sadezky et al (2008)
	Australia	1998	2.7	Khan et al (2004)
	China	2005	2352	Sui et al. (2010)

* Sale for veterinary medicine

Antibiotics - Fluoroquinolones

Use and consumption

The fluoroquinolone class of anti-bacterial drugs can treat infections that affect different parts of the body as well as bacterial diarrhea and gonorrhea (Sweetman, 2009). Some of these drugs also have veterinary use.

The data in Table 2.5 shows that the consumption of ciprofloxacin is three to four times higher than that of norfloxacin in European countries. The average consumption of ciprofloxacin in selected European countries is between 0.09 and 0.21 g per capita per annum (Sadezky et al., 2008).

Abatement in conventional MWWTPs

As per Xu et al. (2007), sorption to the sludge is the main elimination process of fluoroquinolones in MWWTPs. They observed 66% reduction in concentration of norfloxacin during the sewage treatment process. Gulkowska et al. (2008) have reported -16 to 78% removal of norfloxacin in secondary wastewater treatment plants. Ghosh et al. (2009) have observed of 75 to 95% reduction in concentration of norfloxacin and 60 to 83% reduction in ciprofloxacin. The reduction in concentration of enrofloxacin was comparatively lower, in the range of 38 to 74%.

Occurrence in MWWE

Table 2.6 contains the data regarding the occurrence data of fluoroquinolones in MWWE in Canada. Studies have reported occurrences of 50 to 85% for ciprofloxacin and norfloxacin. The reported concentration of ciprofloxacin in effluent is between 132 and

888 ng/L, while that of norfloxacin is in the range of 78 to 821 ng/L. Miao et al. (2004) and Sosiak et al. (2005) did not detect enrofloxacin in any of their sampling events.

Table 2.7 compiles the occurrence data of fluoroquinolones in MWWE in countries other than Canada. The data indicates a high occurrence of ciprofloxacin in MMWE of most of the countries. Occurrence of enrofloxacin and norfloxacin is close to zero in USA and Australia. However, it is close to 100% in China and Japan.

Table 2.6 Occurrence of fluoroquinolones in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Ciprofloxacin	Ontario	7/8	22.7	132	344			Tabe et al. (2009)
	Alberta	7/7	≤ 15	207	888			Sosiak et al. (2005)
	Canada	7/8	1		400	118		Miao et al. (2004)
Enrofloxacin	Alberta	0/7	≤ 15					Sosiak et al. (2005)
	Canada	0/8	8					Miao et al. (2004)
Norfloxacin	Alberta	6/7	≤ 15	78	821			Sosiak et al. (2005)
	Canada	4/8	5		112	50		Miao et al. (2004)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends: Det. Freq. Detection Frequency
Min Minimum
Max Maximum
SD Standard Deviation
VS Various Sources
RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.7 Occurrence of fluoroquinolones in secondary treated MWWE in other countries

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Ciprofloxacin	USA	4/10	50		140	60		Karthikeyan et al. (2006)
	USA	8/8	43				440 ± 118	Batt et al. (2007)
	USA	3/4	5/50	28	522	91		Barber et al. (2011)
	USA	NA/12	50	70	240		130	Yang et al. (2011)
	Finland	20/21	29	30	130	70	60	Vieno et al. (2007)
	Spain	NA/17					710	Muñoz et al (2010)
	Spain	NA/17					850	Muñoz et al (2010)
	Spain	> 4 / 12	10	<10	5692		2378	Rosal et al. (2010)
	Sweden	9/10	6	7	60	14	20 ± 17	Lindberg et al. (2005)
	Sweden	NA/3	4.9				94 ± 12	Zorita et al. (2009)
	Australia	NA/4	10	<10	30	20		Reungoat et al. (2010)
	Australia	0/8	10					Reungoat et al. (2011)
	Japan	4/4	1-10	9	65	98	41 ± 22	Ghosh et al. (2009)
	Various			< 6	90			VS, Lee-Minh et al. (2010)
	Various			< 20	251			VS, Monteiro et al. (2010)
	Various			7	970			VS, Zhang et al. (2011)
Enrofloxacin	USA	0/10	50					Karthikeyan et al. (2006)
	Australia	NA/4	10	<10	10			Reungoat et al. (2010)
	Australia	0/8	10					Reungoat et al. (2011)
	Japan	4/4	1-10	3	26	14	15 ± 9	Ghosh et al. (2009)
	Various				10			VS, Zhang et al. (2011)
Norfloxacin	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	5/50					Barber et al. (2011)
	Finland	1/21	24	< 24	30	< 24	< 24	Vieno et al. (2007)
	Sweden	9/10	7	7	37			Lindberg et al. (2005)
	Sweden	NA/3	5.5				19 ± 1.5	Zorita et al. (2009)
	Australia	NA/4	10	<10	40	30		Reungoat et al. (2010)
	Australia	0/8	10					Reungoat et al. (2011)
	China	4/4	10	27	85			Xu et al. (2007)
	China	4/4	16	85	320			Gulkowska et al. (2008)
	Japan	4/4	1-10	8	56	37	33 ± 17	Ghosh et al. (2009)
	Various			< 7	320			VS, Lee-Minh et al.,2010
	Various			30	112			VS, Monteiro et al. (2010)
	Various			< 6	120			VS, Zhang et al. (2011)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA United States of America

Min Minimum Max Maximum

SD Standard Deviation VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Antibiotics - Macrolides

Use and consumption

Macrolides do not kill the bacteria but prevent them from multiplying (Monteiro and Boxall, 2010). As per Ebadi (2008) and Monteiro and Boxall (2010), macrolides can treat streptococcal infections, syphilis, respiratory and mycoplasmal infection, Lyme disease, and tetanus.

The most prescribed macrolides in Canada are azithromycin, clarithromycin, and erythromycin (Karlowsky et al., 2009). Table 2.8 shows the prescription rate for the macrolides in Canada. The data shows a decrease in consumption of erythromycin in Canada. In addition, the absence of roxithromycin in the list of most prescribed macrolides indicates that its consumption is less than that of erythromycin.

Table 2.8 Annual macrolide prescription rate in Canada in 1995 and 2005

Compound	Prescriptions/1000 persons per year	
	1995	2005
Azithromycin	4.8	52.5
Clarithromycin	24.7	58.5
Erythromycin	77.2	12.3
Total Macrolides	106.7	123.2

Reference: Karlowsky et al. (2009)

The average consumption of erythromycin in five European countries is in the range of 0.166 to 0.536 g per capita per annum, which is the highest in the macrolides group (Sadezky et al., 2008). Data in Table 2.5 indicates that consumption of roxithromycin is less than that of erythromycin in many of the European countries as well as in Australia.

Abatement in conventional MWWTP

Literature indicates that conventional MWWTPs do not remove effectively some of the macrolides. Joss et al. (2005) have also found roxithromycin to be resistant to biodegradation during wastewater treatment. Gulkowska et al. (2008) have observed less than 20% reduction in concentration of erythromycin in MWWTP. Xu et al. (2007) have reported reduction of 26% and 48% in the concentration of erythromycin and roxithromycin during the sewage treatment process. Castiglioni et al. (2006) have reported close to zero percent removal of erythromycin and lincomycin by conventional wastewater treatment. Ghosh et al. (2009) have reported almost similar reduction of -32 to 59% and -39 to 57% in the concentration of roxithromycin and lincomycin in MWWTP.

Occurrence in MWWE

Majority of the studies in Canada have reported 75% or higher occurrence of macrolides in MWWE in Canada (Table 2.9). Miao et al. (2004) have detected erythromycin in effluent in concentrations up to 536 ng/L. The maximum reported concentration of lincomycin and roxithromycin in MWWE in Canada is 21 and 18 ng/L.

Table 2.10 compiles the data related to the occurrence and concentration of macrolides in MWWE in other countries. Erythromycin is one of the most frequently detected antibiotics in the environment (Monteiro and Boxall, 2010). Most of the studies have reported high occurrence of erythromycin. Studies have reported maximum concentration of 561 ng/L and 760 ng/L of this drug in effluents in USA and Europe. From China, Xu et al. (2007) have reported concentrations up to 2,054 ng/L. However,

Monteiro and Boxall (2010) show that a study has reported concentration of 6,000 ng/L of erythromycin in MWWE.

Studies have reported low occurrence and low concentration of lincomycin in MWWE in USA. Studies from other countries have reported low to high occurrence and low concentration of lincomycin. However, Behera et al. (2011) have detected lincomycin in MWWE in Korea in concentrations up to 21,278 ng/L.

Hope et al. (2012) have reported zero occurrence of roxithromycin in MWWE in over 100 sampling events. However, most of the other studies from Europe and Asia have reported 50 to 100% occurrence. The data compiled by Monteiro and Boxall (2010) shows that a study has reported maximum concentration of 1,000 ng/L of this compound in effluent.

Table 2.9 Occurrence of macrolides in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Erythromycin	Ontario	6/8	39.2	91	281			Tabe et al. (2009)
	Canada	6/8	1		536	87		Miao et al. (2004)
Lincomycin	Ontario	8/8	2.7	4	21			Tabe et al. (2009)
Roxithromycin	Ontario	0/8	20.3					Tabe et al. (2009)
	Canada	6/8	1		18	8		Miao et al. (2004)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends: Det. Freq. Detection Frequency
Min Minimum
Max Maximum
SD Standard Deviation
VS Various Sources

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.10 Occurrence of macrolides in secondary treated MWWE in other countries

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Erythromycin	USA	3/3	1	133	162			Snyder et al. (2006)
	USA	3/10	50		300	270		Karthikeyan et al. (2006)
	USA	4/8	10-100	180	561			Barber et al. (2011)
	USA	NA/12	100	140	410		270	Yang et al. (2011)
	Austria	3/3	20	170	210	170		Schaar et al. (2010)
	Germany	NA/6	50				620 ± 240	Ternes et al. (2003)
	Spain	NA/8	2	43	205		104	Radjenovic et al. (2007)
	Spain	NA/17					570	Muñoz et al (2010)
	Spain	NA/17					750	Muñoz et al (2010)
	Spain	> 4 / 12	99	<99	760		331	Rosal et al. (2010)
	Sweden	0/10	160					Lindberg et al. (2005)
	Switzerland	7/11	75	15	73	32	36 ± 22	Hollender et al. (2009)
	Australia	NA/4	10	180	460	260		Reungoat et al. (2010)
	Australia	NA/8		50	390			Reungoat et al. (2011)
	Australia	8/8		20	324			Reungoat et al. (2012)
	China	4/4	5	216	2054			Xu et al. (2007)
	China	4/4	12	510	850			Gulkowska et al. (2008)
	Japan	1/1	0.0012		92			Nakada et al. (2007)
	Korea	5/7	1	8.9	294		130	Kim et al. (2007)
	Various			10	6000			VS, Monteiro et al. (2010)
	Various			145	620			VS, Zhang et al. (2011)
Lincomycin	USA	0/10	50					Karthikeyan et al. (2006)
	USA	1/4	5/50		8			Barber et al. (2011)
	USA	NA/12	10	10	20		14	Yang et al. (2011)
	Australia	NA/4	10	< 10	60	30		Reungoat et al. (2010)
	Australia	9/9		<0.2	3.1			Reungoat et al. (2012)
	Japan	4/4	1-10	8	28	17	18 ± 6	Ghosh et al. (2009)
	Korea	5/5	2.5	1437	21278		9089	Behera et al. (2011)
	Various				31			VS, Monteiro et al. (2010)
	Various			13	60			VS, Zhang et al. (2011)
Roxithromycin	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	10/100					Barber et al. (2011)
	USA	0/102	8.9					Hope et al. (2012)
	Austria	5/5	20	36	69			Clara et al. (2005b)
	Austria	3/3	10	< 20	160	27		Schaar et al. (2010)
	France	NA/6	1-2				10 ± 10	Ruel et al. (2011)
	Germany	NA/6	50				540 ± 40	Ternes et al. (2003)
	Switzerland	NA/15		7	33			Joss et al. (2005)
	Switzerland	6/11	3	4	26	7	9 ± 8	Hollender et al. (2009)
	Australia	NA/4	10	230	370	290		Reungoat et al. (2010)
	Australia	NA/16		40	220			Reungoat et al. (2011)
	Australia	9/9		60	703			Reungoat et al. (2012)

Table 2.10 continued (Occurrence of macrolides in secondary treated MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Roxithromycin (cont'd)	China	4/4	5	36	278			Xu et al. (2007)
	Japan	1/1	0.00018		22			Nakada et al. (2007)
	Japan	4/4	1-10	14	276	71	90 ± 87	Ghosh et al. (2009)
	Various			10	870			VS, Lee-Minh et al. (2010)
	Various				1000			VS, Monteiro et al. (2010)
	Various				540			VS, Zhang et al. (2011)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA	United States of America		
Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency	NA	Not available
RL	Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)		

Antibiotics - Sulfonamides

Use and consumption

Sulfonamides have anti-bacterial property due to the sulphur that is directly linked to the benzene ring, and they inhibit the growth of bacteria by inhibiting their DNA synthesis (Monteiro and Boxall, 2010). This category of drugs can treat urinary tract infections and burns (Ebadi, 2008). They also have veterinary use (Sweetman, 2009).

The use of sulfathiazole has been reduced significantly due to its toxicity (Sweetman, 2009). Sulfamethoxazole is one of the most common sulfonamide used in human medicine (García-Galán et al., 2008). The data in Table 2.5 confirms that consumption of sulfamethoxazole for human medicine is higher than other sulfonamides.

Abatement in conventional MWWTP

Joss et al. (2005) have found a huge variation in transformation efficiency of sulfamethoxazole. They have reported transformation in the range of 0 to 90%. Xu et al. (2007) have reported 0 to 64% reduction of sulfamethoxazole during sewage treatment. Pedrouzo et al. (2011) have found the reduction of sulfamethoxazole and sulfathiazole in the range of 70 to 85%. Ghosh et al. (2009) have observed 9 to 62% removal of sulfamethoxazole. In their study, the removal of sulfadimethoxine was in the range of 38 to 100% while that of sulfamerazine was between 41 and 44%.

Occurrence in MWWE

Table 2.11 compiles the occurrence data of sulfonamides in MWWE in Canada from various studies. The occurrence of six of the eight drugs in this table is zero or close

to zero. The occurrence of sulfamethazine is between 0 and 30%. Miao et al. (2004) have detected it in one sample in concentration of 363 ng/L. Three studies have reported 100% occurrence of sulfamethoxazole. Sosiak et al. (2005) have detected this drug in MWWE in concentrations up to 3,278 ng/L.

The Table 2.12 summarizes the occurrence data of sulfonamides in MWWE in countries other than Canada. In the USA and other European countries, the occurrence and concentration of most of these drugs except sulfamethoxazole is low. Studies from different parts of the world have reported nearly 100% occurrence of sulfamethoxazole in MWWE. Hope et al. (2012) have detected this drug in concentrations up to 5,280 ng/L. The data compiled by Zhang and Li (2011) shows that studies have reported up to 6,000 ng/L concentration of sulfamethoxazole in MWWE.

Table 2.11 Occurrence of sulfonamides in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Sulfachloro-pyridazine	Ontario	0/8	17.7					Tabe et al. (2009)
	Canada	0/8	1					Miao et al. (2004)
Sulfadiazine	Ontario	0/8	28.3					Tabe et al. (2009)
	Canada	1/8	3		19	19		Miao et al. (2004)
Sulfadimethoxine	Ontario	0/8	5.7					Tabe et al. (2009)
	Canada	0/8	1					Miao et al. (2004)
Sulfamerazine	Ontario	0/8	4.9					Tabe et al. (2009)
	Canada	0/8	3					Miao et al. (2004)
Sulfamethazine	Ontario	0/8	3.4					Tabe et al. (2009)
	Alberta	2/7	≤ 15	23	72			Sosiak et al. (2005)
	Canada	1/8	1		363	363		Miao et al. (2004)
Sulfamethizole	Ontario	0/8	7.1					Tabe et al. (2009)
	Canada	0/8	2					Miao et al. (2004)
Sulfamethoxazole	Ontario	8/8	6.2	229	516			Tabe et al. (2009)
	Alberta	7/7	≤ 15	193	3278			Sosiak et al. (2005)
	Canada	8/8	1		871	243		Miao et al. (2004)
Sulfathiazole	Ontario	0/8	9.7					Tabe et al. (2009)
	Canada	0/8	4					Miao et al. (2004)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency		
RL	Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)		

Table 2.12 Occurrence of sulfonamides in secondary treated MWWE in other countries

Compound	Country	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Sulfachloropyridazine	USA	0/10	100					Karthikeyan et al. (2006)
	USA	0/4	5/50					Barber et al. (2011)
	Korea	4/12	30	50	149			Choi et al. (2008)
Sulfadiazine	USA	3/4	5/50	90	260	110		Barber et al. (2011)
	Switzerland	3/11	100	17	127	127	90 ± 64	Hollender et al. (2009)
	Australia	0/4	10					Reungoat et al. (2010)
	Australia	NA/8			20			Reungoat et al. (2011)
	China	1/4	1		36			Xu et al. (2007)
	Various			< 1	< 150			VS, Lee-Minh et al. (2010)
	Various				19			VS, Monteiro et al. (2010)
Sulfadimethoxine	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/12	10				< 10	Yang et al. (2011)
	USA	1/4	5/50		5			Barber et al. (2011)
	Switzerland	0/11	60					Hollender et al. (2009)
	Japan	1/1	0.012		0.15			Nakada et al. (2007)
	Japan	4/4	1-10	4	44	14	19 ± 17	Ghosh et al. (2009)
	Korea	4/12	10	13	70			Choi et al. (2008)
	Various				< 30			VS, Lee-Minh et al. (2010)
Sulfamerazine	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	5/50					Barber et al. (2011)
	Japan	1/1	0.018		0.48			Nakada et al. (2007)
	Japan	1/4	1-10		9			Ghosh et al. (2009)
	Various				< 30			VS, Lee-Minh et al. (2010)
Sulfamethazine	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	5/50					Barber et al. (2011)
	Spain	0/13	10					Pedrouza et al. (2011)
	Switzerland	4/11	5	7	20	8	11 ± 6	Hollender et al. (2009)
	Japan	1/1	0.3		0.35			Nakada et al. (2007)
	Korea	NA/5	0.5	0	408		114	Behera et al. (2011)
	Various				< 30			VS, Lee-Minh et al. (2010)
	Various				363			VS, Monteiro et al. (2010)
	Various				19			VS, Zhang et al. (2011)
Sulfamethizole	USA	0/10	100					Karthikeyan et al. (2006)
	Japan	1/1	0.06		1.11			Nakada et al. (2007)
	Various				180			VS, Lee-Minh et al. (2010)
Sulfamethoxazole	USA	3/3	1	669	841			Snyder et al. (2006)
	USA	6/10	50		370	200		Karthikeyan et al. (2006)
	USA	8/8	27				460 ± 180	Batt et al. (2007)
	USA	3/3		330	1200	970		Wert et al. (2009)
	USA	3/3	0.25	260	600		443 ± 172	Gerrity et al. (2011)
	USA	4/4	5/50	137	813	406	232 ± 297	Barber et al. (2011)
	USA	1/4	64		178			Barber et al. (2011)
	USA	8/10	10				907	Oppenheimer et al. (2011)
	USA	NA/12	10	130	1600		420	Yang et al. (2011)
	USA	94/102	11.2	136	5280	1040	1261	Hope et al. (2012)

Table 2.12 continued (Occurrence of sulfonamides in secondary treated MWWE in other countries)

Compound	Country	Det. Freq.	RL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Sulfamethoxazole	Austria	4/5	20	18	91			Clara et al. (2005b)
(cont'd)	Austria	3/3	10	73	140	100		Schaar et al. (2010)
	France	NA/6	1-2				180 ± 270	Ruel et al. (2011)
	Germany	NA/6	50				620 ± 50	Ternes et al. (2003)
	Spain	1/1			250			Carballa et al. (2004)
	Spain	NA/8	3.1	65	264		139	Radjenovic et al. (2007)
	Spain	NA/17					550	Muñoz et al (2010)
	Spain	NA/17					270	Muñoz et al (2010)
	Spain	> 4 / 12	15	104	370		231	Rosal et al. (2010)
	Spain	8/13	10	44	670	260	286 ± 247	Pedrouza et al. (2011)
	Sweden	4/10	80	135	304	248`	234 ± 84	Lindberg et al. (2005)
	Switzerland	NA/15		90	900			Joss et al. (2005)
	Switzerland	11/11	25	84	434	155	197 ± 122	Hollender et al. (2009)
	Australia	NA/4	10	110	240	220		Reungoat et al. (2010)
	Australia	NA/8		60	330			Reungoat et al. (2011)
	Australia	9/9		39	1701			Reungoat et al. (2012)
	China	4/4	1	9	78			Xu et sl. (2007)
	Japan	1/1	0.018		40			Nakada et al. (2007)
	Japan	4/4	1-10	67	162	97	112 ± 40	Ghosh et al. (2009)
	Korea	4/7	1	3.8	407		136	Kim et al. (2007)
	Korea	12/12	5	25	492			Choi et al. (2008)
	Korea	11/11	1	92	330	160	193	Ryu et al. (2011)
	Korea	5/5	0.9	20	162		57	Behera et al. (2011)
	Various			0.3	964			VS, Lee-Minh et al. (2010)
	Various				2140			VS, Monteiro et al. (2010)
	Various			< 5	6000			VS, Zhang et al. (2011)
Sulfathiazole	USA	0/10	100					Karthikeyan et al. (2006)
	USA	0/4	5/50					Barber et al. (2011)
	Spain	2/13	10	161	205			Pedrouza et al. (2011)
	Australia	0/4	10					Reungoat et al. (2010)
	Australia	0/16	10					Reungoat et al. (2011)
	Australia	9/9		< 0.6	< 2.6			Reungoat et al. (2012)
	Japan	1/1	0.015		0.50			Nakada et al. (2007)
	Korea	0/12	30					Choi et al. (2008)
	Various				< 30			VS, Zhang et al. (2011)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA United States of America

Min Minimum

Max Maximum

SD Standard Deviation

VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Tetracyclines

Use and Consumption

As per Ebadi (2008), tetracyclines are bacteriostatic and have the broadest spectrum of activity. They are effective against the Gram-positive and Gram-negative bacteria (Ebadi, 2008). Some of the important drugs in this category are chlortetracycline, doxycycline, meclocycline, oxytetracycline, and tetracycline.

Data in Table 2.5 indicates that the consumption of the drug tetracycline is the lowest in this group. Oxytetracycline is the most widely used tetracyclines in UK. If normalized by capita, the average consumption of this drug in UK is 0.476 g per capita per annum (Sadezky et al., 2008).

Abatement in conventional MWWTPs

Gulkowska et al. (2008) have reported -88 to 73% reduction in the concentration of tetracycline in secondary wastewater treatment plants. Ghosh et al. (2009) have reported 40 to 73% reduction of this drug.

Occurrence in MWWE

In Canada, studies have reported zero or close to zero occurrences of tetracyclines such as chlortetracycline, doxycycline, meclocycline, and oxytetracycline; and 40 to 100% occurrence of tetracycline (Table 2.13). Miao et al. (2004) have reported concentrations up to 977 ng/L of these drugs in MWWE in Canada.

From the data compiled in Table 2.14, the occurrence of chlortetracycline, doxycycline, and oxytetracycline in MWWE in various countries is almost zero. The

maximum reported concentration of chlortetracycline and oxytetracycline in MWWE is 60 ng/L and < 30 ng/L as per Le-Minh et al. (2010). Lindberg et al. (2005) have reported concentration of 915 ng/L of doxycycline in effluent in Sweden. Most of the studies from China, Japan, and USA have reported close to 100% occurrence of tetracycline in MWWE. From Australia, two studies have reported zero occurrence of this compound. The maximum reported concentration of tetracycline in MWWE is around 1000 ng/L as per Monteiro and Boxall (2010) and Zhang and Li (2011).

Table 2.13 Occurrence of tetracyclines in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Tetracyclines								
Chlortetracycline	Ontario	0/8	55.8					Tabe et al. (2009)
	Alberta	0/7	≤ 15					Sosiak et al. (2005)
	Canada	0/8	4					Miao et al. (2004)
Doxycycline	Ontario	0/8	17.7					Tabe et al. (2009)
	Alberta	1/7	≤ 15		102			Sosiak et al. (2005)
	Canada	2/8	2		46	38		Miao et al. (2004)
Meclocycline	Ontario	0/8	21.3					Tabe et al. (2009)
Oxytetracycline	Ontario	0/8	24					Tabe et al. (2009)
	Alberta	0/7	≤ 15					Sosiak et al. (2005)
	Canada	0/8	6					Miao et al. (2004)
Tetracycline	Ontario	8/8	32.9	48	103			Tabe et al. (2009)
	Alberta	3/7	≤ 15	81	320			Sosiak et al. (2005)
	Canada	7/8	2		977	151		Miao et al. (2004)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency		

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.14 Occurrence of tetracyclines in secondary treated MWWE in other countries

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Tetracyclines								
Chlortetracycline	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	10/100					Barber et al. (2011)
	Australia	0/4	100					Reungoat et al. (2010)
	Australia	0/8						Reungoat et al. (2011)
	Various			40	60			VS, Lee-Minh et al. (2010)
Doxycycline	USA	0/10	100					Karthikeyan et al. (2006)
	USA	1/4	10/100		180			Barber et al. (2011)
	USA	0/12	20				< 20	Yang et al. (2011)
	Sweden	7/10	64	64	915	227	380 ± 376	Lindberg et al. (2005)
Meclocycline								No data available
Oxytetracycline	USA	0/10	50					Karthikeyan et al. (2006)
	USA	0/4	10/100					Barber et al. (2011)
	Australia	0/4	100					Reungoat et al. (2010)
	Australia	0/8	100					Reungoat et al. (2011)
	Various				< 30			VS, Lee-Minh et al. (2010)
	Various				20			VS, Zhang et al. (2011)
Tetracycline	USA	8/10	50		850	170		Karthikeyan et al. (2006)
	USA	8/8	52				181 ± 69	Batt et al. (2007)
	USA	3/4	10/100	34	411	131		Barber et al. (2011)
	USA	0/12	50				< 50	Yang et al. (2011)
	Australia	0/4	100					Reungoat et al. (2010)
	Australia	0/8	10					Reungoat et al. (2011)
	China	4/4	14	180	620			Gulkowska et al. (2008)
	Japan	4/4	1-10	4	39	25	23 ± 15	Ghosh et al. (2009)
	Various				1,000			VS, Monteiro et al. (2010)
	Various				977			VS, Zhang et al. (2011)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA	United States of America		
Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency		
RL	Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)		

Miscellaneous antibiotics

The antibiotics not covered under the fluoroquinolones, macrolides, tetracyclines, and sulfonamides categories are included in this group.

Use and consumption

Carbadox is a veterinary medicine, antibiotic, added to swine feed to prevent dysentery and promote growth (Aga, 2008). Some European countries have banned its application because of its carcinogenic property (Sweetman, 2009). Chloramphenicol is a bacteriostatic antibiotic, and is useful in the treatment of ampicillin resistant influenza, rickettsial infections, typhoid fever and vancomycin-resistant enterococci (Anderson et al., 2002). Lasalocid A is an antibiotic and an antiprotozoal. It can prevent and treat parasitic disease that infects intestinal tracts of (Sweetman, 2009). As per Sweetman (2009), trimethoprim is an antibacterial used in the treatment of stomach flu, respiratory tract, and urinary tract infections. In combination with sulfamethoxazole, it is used to manage pneumonia. It also has use as a veterinary antibiotic (Sarmah et al., 2006).

Limited data are available related to the consumption of the drugs such as carbadox, chloramphenicol, and Lasalocid-A. Table 2.15 shows the data related to consumption of trimethoprim in some countries. The annual consumption in most of the listed countries is less than 10 tonnes. However, China consumed nearly 2,352 tonnes of this drug in 2005.

Table 2.15 Consumption of antibiotic - trimethoprim in various countries

Compound	Country	Time period	Sale (tonne/yr)	Reference
Trimethoprim	France	2004	3.35	Besse et al (2008)
	France	1999-2006	3.35	Sadezky et al (2008)
	Germany	1999-2006	12.1	Sadezky et al (2008)
	Norway	2006	0.68	Grung et al. (2008)
	Spain	2003	3.7	Monteiro et al (2010)
	Switzerland	1999	0.52	Gobel et al (2005)
	UK	2004	11.2	Monteiro et al (2010)
	UK	1999-2006	7.34	Sadezky et al (2008)
	Australia	1998	2.7	Khan et al (2004)
	China	2005	2352	Sui et al. (2010)

Abatement in conventional MWWTPs

Gulkowska et al. (2008) have reported -42 and 62% reduction in concentration of trimethoprim. Xu et al. (2007) have observed 45% removal of chloramphenicol during sewage treatment. Plósz et al. (2010) have reported increase in the concentration of trimethoprim in the MWWE after biological treatment, most probably due to the deconjugation process.

Occurrence in MWWE

Table 2.16 shows the data related to detection of the miscellaneous antibiotics in MWWE in Canada. Table 2.17 represents similar data for MWWE other countries.

In Canada, studies have reported zero or close to zero occurrence of carbadox, chloramphenicol, Lasalocid A, and penicillin G. In contrast, studies have reported 100% occurrence of trimethoprim in the MWWE. Sosiak et al. (2005) have reported up to 3,528 ng/L concentration of this drug in the MWWE.

From studies outside Canada, Reungoat et al. (2012) have reported 100% occurrence but low concentration of chloramphenicol in MWWE in Australia. The

maximum concentration of this drug in their study is 3.1 ng/L. Most of the studies listed in Table 2.17 have reported 100% occurrence of trimethoprim in the MWWE. Studies from USA have reported 35 to 720 ng/L concentration of this drug in effluent. Lindberg et al. (2005) have detected this drug in concentration up to 1,340 ng/L. Studies have reported concentrations in the range of 10 to 780 ng/L of this drug in MWWE in Asia.

Table 2.16 Occurrence of miscellaneous antibiotics in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Miscellaneous								
Carbadox	Ontario	0/8	46.3					Tabe et al. (2009)
	Canada	0/8	5					Miao et al. (2004)
Chloramphenicol	Ontario	0/8	8.8					Tabe et al. (2009)
Lasalocid A	Ontario	2/8	54.9	24	32			Tabe et al. (2009)
Penicillin-G	Ontario	0/8	16.9					Tabe et al. (2009)
Trimethoprim	Ontario	4/4	5-9	9	194			Metcalfe et al. (2003b)
	Ontario	11/11	0.6				265 ± 122	Hua et al. (2006)
	Ontario	8/8	5	164	486			Tabe et al. (2009)
	Alberta	7/7	≤ 15	514	3,528			Sosiak et al. (2005)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Min Minimum Max Maximum

SD Standard Deviation VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.17 Occurrence of miscellaneous antibiotics in secondary treated MWWE in other countries

Compound	Country	Detection Frequency	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Miscellaneous								
Carbadox	USA	0/10	100					Karthikeyan et al. (2006)
	USA	0/3	5/50					Barber et al. (2011)
Chloramphenicol	Australia	0/4	100					Reungoat et al. (2010)
	Australia	NA/16		0.3	<100			Reungoat et al. (2011)
	Australia	9/9		< 0.3	3.1			Reungoat et al. (2012)
	China	1/4	5		17			Xu et al. (2007)
	China	1/4	1		19			Sui et al. (2010)
	Various				560			VS, Monteiro et al. (2010)
Lasalocid A								No data available
Penicillin-G	USA	0/4	10/100					Barber et al. (2004)
	China	0/4	4					Gulkowska et al. (2008)
	Various				< 2			VS, Lee-Minh et al. (2010)
	Various				ND			VS, Monteiro et al. (2010)
	Various			ND	300			VS, Zhang et al. (2011)
Trimethoprim	USA	3/3	1	35	229			Snyder et al. (2006)
	USA	6/10	50		550	170		Karthikeyan et al. (2006)
	USA	8/8	68				993 ± 891	Batt et al. (2007)
	USA	3/3		36	370	83		Wert et al. (2009)
	USA	3/3	0.25	550	720		620 ± 89	Gerrity et al. (2011)
	USA	3/4	5/50	61	641	367		Barber et al. (2011)
	USA	4/4	13	130	327	186	207 ± 92	Barber et al. (2011)
	USA	NA/12	100	69	530		280	Yang et al. (2011)
	Austria	3/3	20	150	320	240		Schaar et al. (2010)
	Germany	NA/6	50				340 ± 40	Ternes et al. (2003)
	Spain	> 4 / 12	29	< 29	148		99	Rosal et al. (2010)
	Sweden	10/10	8	66	1340	396	499 ± 386	Lindberg et al. (2005)
	Switzerland	11/11	30	71	234	108	119 ± 47	Hollender et al. (2009)
	Australia	NA/4	10	150	210	200		Reungoat et al. (2010)
	Australia	NA/16		10	380			Reungoat et al. (2011)
	Australia	9/9		27	141			Reungoat et al. (2012)
	China	4/4	6	120	230			Gulkowska et al. (2008)
	China	4/4	1	20	200			Sui et al. (2010)
	Japan	1/1	0.027		16			Nakada et al. (2007)
	Japan	4/4	1-10	24	72	41	43 ± 16	Ghosh et al. (2009)
	Korea	5/7	1	10	188		58	Kim et al. (2007)
	Korea	7/12	10	13	174			Choi et al. (2008)
	Korea	11/11	1	27	780	70	134	Ryu et al. (2011)
	Korea	5/5	0.14	13	154		63	Behera et al. (2011)
	Various			9	1760			VS, Monteiro et al. (2010)

Note: If the study has detected the analyte only once, it is reported as maximum detected concentration in the above table.

Legends: USA = United States of America VS = Various sources

RL = Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

2.4.3.3 Antiepileptic/antidepressant

Use and consumption

Carbamazepine is an antiepileptic/antidepressant drug, and used to control and prevent seizures as well as other medical conditions (Ebadi, 2008). Sadezky et al. (2008) have reported the average consumption of this drug in five European countries in the range of 0.61 to 0.98 g per capita per annum. Table 2.18 summarizes the annual consumption of this drug in different countries. Metcalfe et al. (2004) and Miao et al. (2005) have reported 19 to 28 tonnes of consumption of carbamazepine in Canada in the year 2001. Zhang et al. (2008) have estimated the total worldwide consumption of this drug to be approximately 1014 tonnes in 2008.

Table 2.18 Consumption of antiepileptic/antidepressant in various countries

Compound	Country	Year	Sale (tonne/yr)	Reference
Carbamazepine	Canada	2001	19	Metcalfe et al. (2004)
	Canada	2001	28	Miao et al (2005)
	USA	2000	43	Zhang et al (2008)
	USA	2003	35	Zhang et al (2008)
	Austria	1997	6	Zhang et al (2008)
	Finland	2005	4.35	Vieno et al. (2007)
	France	2004	33.5	Besse et al (2008)
	France	1999-2006	36.4	Sadezky et al (2008)
	Germany	1999	87	Zhang et al (2008)
	Germany	1999-2006	80.9	Sadezky et al (2008)
	Poland	1999-2006	32.2	Sadezky et al (2008)
	Spain	2003	20	Monteiro et al (2010)
	UK	2000	40	Zhang et al (2008)
	UK	2004	52.2	Monteiro et al (2010)
	UK	1999-2006	40.1	Sadezky et al (2008)
	Australia	1998	10	Khan et al (2004)
	China	2005	395	Sui et al. (2010)
	Japan	2002	107-162	Nakada et al. (2002)
	World	2008	1014	Zhang et al (2008)

Abatement in conventional WWTP

Carbamazepine is resistant to biodegradation and its concentration remains unchanged during conventional activated sludge treatment process (Clara et al., 2005b; Joss et al., 2005). Study by Andreozzi et al. (2002) shows that carbamazepine is persistent in the environment. In water, it degrades only when exposed to solar irradiation. They found its half-life to be 907 sunlight hours. As per their study, nitrate promotes the degradation of the compound while humic acid has the opposite effect.

Occurrence in the MWWE

Studies have reported 87 to 100% occurrence of carbamazepine in MWWE in Canada. Table 2.19 compiles the pertinent data from some studies. Sosiak et al. (2005) have reported the concentration of this drug in the range between 702 and 3,287 ng/L. Table 2.20 compiles the data of occurrence and concentration of carbamazepine in MWWE in other countries. Most of the studies referred to in this table have reported high occurrence of the drug. In addition, the data shows higher concentration of this drug in MWWE in Europe and Australia than in Asian countries. In Germany, Ternes (1998) have detected this drug in concentration up to 6,300 ng/L. Joss et al. (2005) and Vieno (2007) have reported maximum concentration of this drug to be more than 2,000 ng/L.

Table 2.19 Occurrence of antiepileptic/antidepressant in secondary treated MWWE in Canada

Compound	Region	Det. Freq.	DL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Carbamazepine	Ontario	4/4	5-7	7	126			Metcalfe et al. (2003b)
	Ontario	10/11	0.1				291 ± 71	Hua et al. (2006)
	Ontario	8/8	4.3	361	735			Tabe et al. (2009)
	Alberta	7/7		702	3287			Sosiak et al. (2005)
	Atl Canada	14/16	20	24	240	79	100 ± 61	Brun et al. (2006)
	Canada	18/18	100	100	2300			Metcalfe et al. (2003a)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Atl Canada Atlantic Canada

Min Minimum Max Maximum

SD Standard Deviation VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Table 2.20 Occurrence of antiepileptic/antidepressant in MWWE in other countries

Compound	Country	Det. Freq.	DL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Carbamazepine	USA	3/3	1	139	210			Snyder et al. (2006)
	USA	3/3		170	350	260		Wert et al. (2009)
	USA	3/3	0.5	170	190		180 ± 10	Gerrity et al. (2011)
	USA	4/4	11	90	230	122	141 ± 63	Barber et al. (2011)
	USA	16/16	5				416	Oppenheimer et al. (2011)
	USA	NA/12	50	100	550		250	Yang et al. (2011)
	USA	84/102	11.2	133	577	206	219	Hope et al. (2012)
	Austria	5/5	20	465	1594			Clara et al. (2005)
	Austria	3/3	1	500	900	900		Schaar et al. (2010)
	Finland	21/21	1.4	290	2440	500	720	Vieno et al. (2007)
	France	NA/6	0.5-2				640 ± 650	Ruel et al. (2011)
	Germany	30/30	50		6300	2100		Ternes et al. (1998)
	Germany	NA/6	50				2100 ± 40	Ternes et al. (2003)
	Germany	NA/10					1760 ± 420	Bahr et al. (2007)
	Spain	NA/8	0.6	65	305		237	Radjenovic et al. (2007)
	Spain	NA/17					260	Muñoz et al. (2010)
	Spain	NA/17					290	Muñoz et al. (2010)
	Spain	>4 / 12	1	69	173		117	Rosal et al. (2010)
	Spain	13/13		8	170			Pedrouza et al. (2011)
	Switzerland	NA/15		210	2300			Joss et al. (2005)
	Switzerland	11/11	15	186	714	570	512 ± 187	Hollender et al. (2009)
	Australia	NA/4		390	950	700		Reungoat et al. (2011)
	Australia	NA/16		330	1650			Reungoat et al. (2011)
	Australia	8/9		119	1192			Reungoat et al. (2012)
	China	4/4	1	69	120			Sui et al. (2010)
	Japan	16/16	6	11	163	49	60 ± 45	Nakada et al. (2006)
	Japan	4/4	1.5-36	2.32	46			Nakada et al. (2007)
	Korea	6/7	1	73	729		226	Kim et al. (2007)
	Korea	10/12	5	6	195			Choi et al. (2008)
	Korea	11/11	1	140	270	190	196	Ryu et al. (2011)
	Korea	5/5	0.09	40	74		55	Behera et al. (2011)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

USA United States of America

Min Minimum Max Maximum

SD Standard Deviation VS Various Sources

Det. Freq. Detection Frequency

RL Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

2.4.3.4 Lipid Regulators

Use and consumption

In human blood, the fibrates/lipid regulators decrease the synthesis of triglycerides and very-low-density lipoprotein cholesterol that is harmful to human health, and increase the production of high-density lipoprotein cholesterol that is good for human health (Anderson et al., 2002). Clofibric acid is the active metabolite of several fibrate drugs (Stumpf et al., 1999). It can act as a plant growth regulator by inhibiting plant hormone auxin (Emblidge and DeLorenzo, 2006). Clofibric acid is recalcitrant in nature (Winkler et al., 2001) and can persist in the environment for up to 21 years (Zuccato et al., 2000). It can adversely affect the reproduction of the Fathead minnow fish (Runnalls et al., 2007). Based on the bioassay test results, Ferrari et al. (2003) have concluded that clofibric acid has a more adverse effect than carbamazepine and diclofenac on the receiving water bodies.

Fenofibrate is the most commonly prescribed fibrate drug in Canada, accounting for 90.2 % of the total fibrate drug prescriptions in year 2009 (Jackevicius et al., 2011). Gemfibrozil and bezafibrate account for 4.6% and 5.2% of the remaining prescriptions. Fenofibrate is also the most prescribed fibrate drug in USA. Table 2.21 presents the data related to distribution of total fibrate prescriptions in North America. The fibrate prescriptions dispensed in Canada and United States in December 2009 was 474 prescriptions/100,000 population per month and 730 prescriptions/100,000 population per month, respectively (Jackevicius et al., 2011).

Table 2.21 Distribution of total fibrate prescriptions in North America (2005 – 2009)

	Portion of Total Prescription, %				
	2005	2006	2007	2008	2009
Canada					
Bezafibrate	6.8	6.2	5.5	4.9	4.6
Fenofibrate	85.4	86.7	88.3	89.5	90.2
Gemfibrozil	7.8	7.1	6.2	5.6	5.2
United States					
Fenofibrate	62.0	66.2	69.4	71.4	65.2
Gemfibrozil	38.0	33.8	30.6	28.6	26.1
Fenofibric acid	0	0	0	0	8.7

Note: Bezafibrate is only available in Canada, and fenofibric acid is only available in the United States.

Reference: Jackevicius et al. (2011)

Table 2.22 shows the consumption of a few lipid regulators in various countries. In general, the consumption of bezafibrate is higher than gemfibrozil. The annual consumption of bezafibrate in France and Germany is in the range of 27 to 32 tonne/yr, which translates to approximately 0.38 to 0.46 g/capita/annum (Sadezky et al., 2008). However, the consumption of bezafibrate and gemfibrozil is almost equal in Poland, and the annual consumption rate is around 0.007 g/capita/annum (Sadezky et al., 2008).

Table 2.22 Consumption of fibrates/lipid regulators in various countries

Compound	Country	Year	Sale (tonne/yr)	Reference
Bezafibrate	Finland	2005	0.357	Vieno et al. (2007)
	France	2004	20.9	Besse et al (2008)
	France	1999-2006	27.4	Sadezky et al (2008)
	Germany	1999-2006	31.5	Sadezky et al (2008)
	Poland	1999-2006	0.273	Sadezky et al (2008)
	UK	1999-2006	7.66	Sadezky et al (2008)
Clofibric acid	Switzerland	2004	0.143	Tauxe-Wuersch et al (2005)
Gemfibrozil	Canada	2001	1	Metcalfe (2004)
	Germany	1999-2006	5.96	Sadezky et al (2008)
	Poland	1999-2006	0.274	Sadezky et al (2008)
	UK	2004	1.42	Monteiro et al (2010)
	UK	1999-2006	0.902	Sadezky et al (2008)
	Australia	1998	20	Khan et al (2004)
	China	2005	17	Sui et al. (2010)

Abatement in conventional WWTP

As per Cermola et al. (2005), fenofibrate rapidly metabolizes to fenofibric acid. They also report that fenofibric acid is highly susceptible to photo-degradation and converts to phenol, ether, and alcohol. In comparison, bezafibrate and gemfibrozil degrade by only about 10% when exposed to sunlight irradiation (Cermola et al., 2005). As per Clara et al. (2005a), bezafibrate is susceptible to biodegradation and degrades up to 90% in conventional WWTPs. However, they report its lower transformation in the WWTPs that have low sludge retention time (SRT). Joss et al. (2005) did not find any effect of SRT on transformation of antibiotics during wastewater treatment. Lee et al. (2003) observed only 5% transformation of gemfibrozil. Studies have reported that clofibric acid is also not readily biodegradable in municipal treatment plants (Zwiener and Frimmel, 2003; Castiglioni et al., 2006).

Occurrence in MWWE

Table 2.23 presents the data related to occurrence of lipid regulator/bezafibrate in MWWE in Canada. As per the data, most of the studies have reported more than 75% occurrence of bezafibrate and gemfibrozil. Studies have reported maximum concentration of 810 ng/L of bezafibrate and 1493 ng/L of gemfibrozil in MWWE. Lee et al. (2003) did not detect fenofibrate in the 44 municipal sewage plant influent and effluent samples collected in Ontario, Canada. Similarly, Lishman et al. (2006) did not detect fenofibrate in any of the 39 MWWE samples analyzed by them.

Table 2.24 compiles data from various studies concerning the occurrence of the lipid regulators in MWWE in other countries. Majority of the studies have reported close to 100% occurrence of bezafibrate and gemfibrozil. The occurrence of clofibric acid is between 0 and 100%. From the data in the table, studies have reported 4,800 ng/L and 5,223 ng/L as the maximum concentration of bezafibrate and gemfibrozil in MWWE. Studies have reported up to 1,600 ng/L concentration of clofibric acid. For fenofibrate, Ternes (1998) have reported only 10% occurrence and maximum concentration of 30 ng/L in the MWWE in Germany.

Table 2.23 Occurrence of lipid regulators in MWWE in Canada

Compound	Region	Det. Freq.	DL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Bezafibrate	Ontario	4/4	5-12	12	259			Metcalfe et al. (2003b)
	Ontario	11/11	10				325 ± 79	Hua et al. (2006)
	Ontario	8/8	3	145	315			Tabe et al. (2009)
	Alberta	4/7	≤25	144	547			Sosiak et al. (2005)
	Nova Scotia	3/4	12	29	260	120		Comeau et al. (2008)
	Atlantic Canada	14/16	30	42	810	250	290 ± 239	Brun et al. (2006)
	Canada	3/18	50	200	600			Metcalfe et al. (2003a)
Clofibric Acid	Ontario	2/4	5	2	44			Metcalfe et al. (2003b)
	Ontario	0/16	10					Lee et al. (2003)
	Ontario	0/39	66					Lishman et al. (2006)
	Ontario	7/11	45				260 ± 132	Hua et al. (2006)
	Ontario	8/8	5.8	10	43			Tabe et al. (2009)
	Alberta	0/7	≤25					Sosiak et al. (2005)
	Atlantic Canada	1/16	30		38			Brun et al. 2006
	Canada	0/18	50					Metcalfe et al. (2003a)
Fenofibrate	Ontario	0/16	10					Lee et al. (2003)
	Ontario	0/39	26					Lishman et al. (2006)
Gemfibrozil	Ontario	4/4	5	5	1493			Metcalfe et al. (2003b)
	Ontario	16/16	10	20	540			Lee et al. (2003)
	Ontario	17/39	77		436	255	246	Lishman et al. (2006)
	Ontario	11/11	6				52 ± 31	Hua et al. (2006)
	Ontario	8/8	3.1	19	206			Tabe et al. (2009)
	Alberta	7/7	≤25	410	813			Sosiak et al. (2005)
	Atlantic Canada	15/16	30	110	1400	550	591 ± 401	Brun et al. 2006
	Canada	1/18	50		1300			Metcalfe et al. (2003a)

Note: If the study reported only one concentration of the analyte, it is reported as maximum detected concentration in the above table.

Legends:

Min	Minimum	Max	Maximum
SD	Standard Deviation	VS	Various Sources
Det. Freq.	Detection Frequency		
RL	Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)		

Table 2.24 Occurrence of lipid regulators in MWWE in other countries

Compound	Country	Det. Freq.	DL	Concentration, ng/L				Reference
			ng/L	Min	Max	Median	Mean ± SD	
Bezafibrate	Austria	3/5	20	692	4800			Clara et al. (2005b)
	Austria	3/3	20	1500	1600	1500		Schaar et al. (2010)
	Finland	12/13	5	< 5	840	150	240	Vieno et al. (2007)
	Germany	48/49	250		4600	2200		Ternes et al. (1998)
	Germany	NA/10					340 ± 170	Bahr et al. (2007)
	Spain	NA/8	4.35	495	2309		982	Radjenovic et al. (2007)
	Spain	>4/12	8	33	280		128	Rosal et al. (2010)
	Spain	13/13	1	100	510	283	273 ± 105	Pedrouza et al. (2011)
	Switzerland	11/11	65	37	133	67	77 ± 28	Hollender et al. (2009)
	Australia	9/9		<0.5	10			Reungoat et al. (2012)
	China	4/4	0.3	2	7			Sui et al. (2010)
	Japan	12/12	15	26	1100			Okuda et al. (2008)
	Brazil	NA/10	50		1190	1077		Stumpf et al. (1999)
Clofibric Acid	USA	0/2	0.8					Boyd et al. (2003)
	Germany	47/49	50		1600	360		Ternes et al. (1998)
	Germany	NA/6	50				120 ± 20	Ternes et al. (2003)
	Germany	NA/10					90 ± 70	Bahr et al. (2007)
	Greece	1/11	5		5			Koutsouba et al. (2003)
	Spain	NA/8	3.75	18	156		80	Radjenovic et al. (2007)
	Spain	>4/12	6	<6	91		12	Rosal et al. (2010)
	Spain	0/13	2					Pedrouza et al. (2011)
	Sweden	NA/3	1.1				24 ± 1	Zorita et al. (2009)
	Switzerland	6/11	5	11	44	15	20 ± 13	Hollender et al. (2009)
	China	4/4	5.4	8	20			Sui et al. (2010)
	Korea	NA/5	0.74	0	6		2	Behera et al. (2011)
Gemfibrozil	USA	2/2	10	16	567			Snyder et al. (2006)
	USA	3/3		35	1600	1400		Wert et al. (2009)
	USA	3/3	0.25	850	960		890 ± 61	Gerrity et al. (2011)
	USA	1/4	13		318			Barber et al. (2011)
	USA	10/12	5				360	Oppenheimer et al. (2011)
	France	NA/6	0.5-2				1500 ± 1700	Ruel et al. (2011)
	Germany	39/49	50		1500	400		Ternes et al. (1998)
	Spain	NA/8	2.2	1368	3359		2468	Radjenovic et al. (2007)
	Spain	NA/17					6800	Muñoz et al. (2010)
	Spain	NA/17					8200	Muñoz et al. (2010)
	Spain	>4/12	0.1	3	5233		845	Rosal et al. (2010)
	Australia	NA/4	10	140	200	170		Reungoat et al. (2010)
	Australia	NA/16		37	155			Reungoat et al. (2011)
	Australia	9/9		36	191			Reungoat et al. (2012)
	China	4/4	4.2	8	50			Sui et al. (2010)
	Korea	3/7	1	3.9	17		11.2	Kim et al. (2007)
	Korea	10/11	1	<0.25	8	2.7	3.3	Ryu et al. (2011)
	Korea	5/5	1.5	6	26		17	Behera et al. (2011)
	Brazil	NA/10	50		1725	400		Stumpf et al. (1999)

Note: If only one value was detected, it is reported as maximum value in the above table.
Legends: RL = Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

2.4.4 Occurrence of EDCs in MWWE

The USEPA definition of endocrine disruptive chemicals is "an exogenous agent that interferes with the production, release, transport, metabolism, binding, action, or elimination of natural hormones in the body responsible for the maintenance of homeostasis and the regulation of development process." (Kavlock et al., 1996).

Estrogen replacement agents, ovulation inhibitors, and reproductive hormones are some of the groups of potential EDCs based on their application. Perfluorosurfactants and bisphenol-A are also potential EDCs.

Use and consumption

The 17-α-ethinylestradiol (EE2) and 19-norethersterone drugs have a use as oral contraceptive drugs. The 19-norethersterone drug can also treat abnormal uterine bleeding and premenstrual pain when used in estrogen replacement therapy (Anderson et al., 2002). 17-β-Estradiol (E2) is a female sex hormone, and is the most potent among all the naturally occurring estrogens (Bennink, 2004). It is used to treat postmenopausal symptoms, osteoporosis, uterine bleeding and in menopausal hormone therapy. Estrone and estriol are used in menopausal hormone treatments (Ebadi, 2008). Bisphenol-A (BPA) is the mainly used in the production of polycarbonates and epoxy resins. The polycarbonates and the resins have a wide industrial use. They are also used to manufacture food and beverage containers (Environment Canada and Health Canada, 2008).

Of the potential EDCs listed in Table 2.25, the maximum production is of BPA. As per Environment Canada and Health Canada (2008), the worldwide production of this

compound was 4 billion kg in 2006. In Canada, the annual consumption decreased to less than 1,000 tonnes in 2006 from about 12,000 tonnes in 1986. The annual consumption of EE2 in most of the countries is less than 100 kg.

Table 2.25 Sale of potential EDCs

Compound	Country	Year	Sale (tonne/yr)	Reference
Estrogen Replacement Agents				
Bisphenol-A (BPA)	Canada	1986	12,000	Environment. Canada (2008)
	Canada	2006	100 to 1,000	Environment. Canada (2008)
	Worldwide	2006	4,000,000	Environment. Canada (2008)
Reproductive Hormones				
17β-Estradiol	Denmark	1996	0.045	Christensen (1998)
Progesterone	UK	2004	0.75	Monteiro et al (2010)
	France	2004	9.86	Besse and Garric (2009)
Ovulation Inhibitors				
17α-Ethinylestradiol (EE2)	Canada	2001	0.057	Metcalfe et al. (2004)
	United States	2007	0.088	Hannah et al. (2009)
	Belgium	2007	0.008	Hannah et al. (2009)
	Denmark	1996	0.0036	Christensen (1998)
	France	2007	0.034	Hannah et al. (2009)
	Germany	2007	0.051	Hannah et al. (2009)
	Italy	2007	0.020	Hannah et al. (2009)
	Netherland	2007	0.015	Hannah et al. (2009)
	UK	2007	0.026	Hannah et al. (2009)
Norethisterone	France	2004	0.101	Besse and Garric (2009)

Abatement in conventional MWWTP

The physicochemical properties of the EDCs affect their removal in the MWWTP. Some of these properties are their solubility in water, volatilization rate, biological and chemical degradation rate, and adsorption (Langford and Jason, 2002). Most of the EDCs are nonpolar and hydrophobic in nature and are removed mainly by sorption to the solids (Auriol et al., 2006). The octanol-water partition coefficient (K_{ow})

value of the chemicals can give an indication of their sorption potential and hydrophobicity. In general, log $K_{ow} < 2.5$ indicates low sorption potential, $2.5 < \log K_{ow} < 4.0$ indicates medium sorption potential while $\log K_{ow} > 4.0$ indicates high sorption potential (Jones-Lepp and Stevens, 2007). Langford and Jason (2002) indicate that chemicals with large log K_{ow} value have large hydrophobic molecules that bind with solid organic matter, while chemicals with low log K_{ow} value have small hydrophilic molecules. In addition, the main process of removal of chemicals with log K_{ow} greater than 4 during secondary treatment is by sorption to settled sludge. However, as indicated earlier, the removal also depends on other factors besides K_{ow} value. Table 2.26 provides the log octanol-water partition coefficient of few potential EDCs.

Table 2.26 Log octanol/water partition coefficient of few potential EDCs

Compound	Log K_{ow}	Reference
17-α-Ethinylestradiol (EE2)	3.67 – 4.15	Various, ref. Auriol et al. (2006)
17- α-Estradiol	3.94	Almeida and Nogueira (2006)
17-β-Estradiol (E2)	3.94 – 4.01	Various, ref. Auriol et al. (2006)
19-Norethisterone	2.99	Almeida and Nogueira (2006)
BPA	3.32, 3.43	Auriol et al. (2006)
Estrone (E1)	2.45 – 3.43	Various, ref. Auriol et al. (2006)
Estriol (E3)	2.55 – 2.81	Various, ref. Auriol et al. (2006)
Progesterone	3.67	Almeida and Nogueira (2006)

Johnson and Sumpter (2001) indicate that the main mechanism of removal of the EDCs in the MWWTPs can be sorption and biodegradation. As per them, the removal of

weak hydrophobic estrogens such as E1, E2, and E3 may be due to the sorption and biodegradation. In addition, sorption to the sludge may be the most likely mechanism of removal of synthetic estrogen 17-α-ethinylestradiol (EE2), which is recalcitrant and up to 10 times more hydrophobic than E2. However, in batch experiments conducted by Ternes et al. (1999a), the concentration of EE2 did not reduce substantially in conditions similar to an activated sludge process even though it has high log K_{ow} value of 4.2. The sorption effect did not seem to affect the removal of EE2.

Many studies have noted negative removal of estrogens in MWWTPs, i.e. the concentration of estrogens in treated water is higher than that in the raw sewage. The microorganisms present in the activated sludge can cleave the inactive polar conjugates of the estrogens, which results in release of active estrogens and increase in their concentration (Ternes et al., 1999a). In the aerobic batch experiments with activated sludge effluent, Ternes et al. (1999a) have shown that 17-β-estradiol-17 (β-D-glucuronide) and 17-β-estradiol-3 (β-D-glucuronide) converts to 17-β-estradiol in approximately 15 minutes. More than 95% of 17-β-estradiol oxidizes to estrone in a period of 1 to 3 hours (Figure 2.4). Hence, the concentration of some estrogens in the sewage effluent may increase after biological treatment due to the deconjugation process. D'Ascenzo et al. (2003) have shown that the production of estrone in the sewage treatment plants is most probably due to the oxidation of estradiol and deconjugation of the glucuronated and sulfated estrogens.

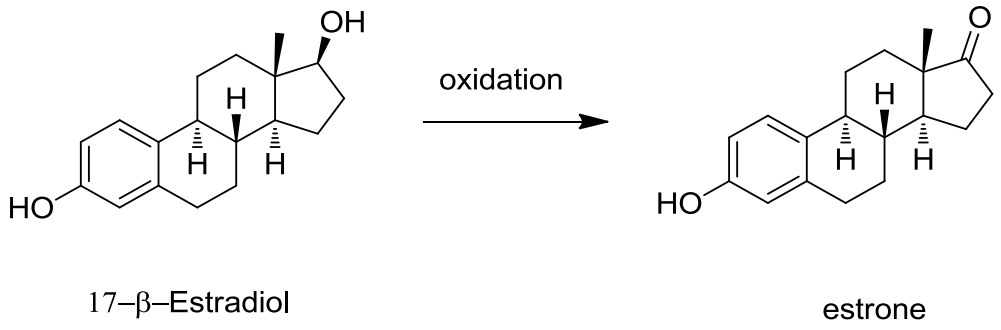


Figure 2.4 **Conversion of 17-β-estradiol to estrone during biological sewage treatment**
(Adapted from Ternes et al. 1999 a)

Ternes et al. (1999b) have reported 64 to 78% reduction in concentration of EE2, above 99.9% reduction in 17-β-estradiol (E2), and 83% reduction of estrone in MWWE in Brazil. However, in their sampling at German MWWTPs, the reduction in E1 and EE2 in MWWE was not substantial while reduction in E2 was close to 64%. They inform that low temperatures (-2 ^{o}C) during the German sampling event may be a reason for the low removal efficiency. Behera et al. (2011) have reported 87 to 100% reduction of estrone, estriol, and estradiol in MWWTPs. D'Ascenzo et al. (2003) have observed high removal of estradiol (85%) and estriol (97%) but low removal of estrone (61%) in the sewage treatment plant. They have concluded estrone to be the most important EDC in the aquatic environment due to its high concentration (nearly 10 times of estradiol) and its estrogenic potency (which is approximately half of estradiol). Clara et al. (2005b) and Nakada et al. (2006) have observed > 90% reduction in the concentration of BPA in MWWTPs having an activated sludge process.

While the activated sludge process can achieve high removal of EDCs, the concentration of the EDCs present in the effluent is still high enough to produce estrogenic activity in fish and aquatic organisms (Auriol et al., 2006). BPA, E2, EE2, and

estrone contribute significantly to the estrogenicity of the effluent (Johnson and Sumpter, 2001; D'Ascenzo et al., 2003).

Occurrence in the MWWE

Table 2.27 summarizes the occurrence and concentration data of potential EDCs in Canadian MWWE from some of the studies. The data show that studies frequently detect most of these EDCs. Fernandez et al. (2007) have reported the highest maximum concentration for all the EDCs. They have reported the highest maximum concentration of 19-norethisterone, E1, E2 and EE2 in the range of 147 ng/L to 178 ng/L. Viglino et al. (2008) and Tabe et al. (2009) did not detect progesterone in any of their sampling events.

Table 2.28 compiles the data related to the occurrence and concentration of EDCs in MWWE in other countries. The data indicate frequent detection of the EDCs in MWWE in various countries. Ternes et al. (1999b) have reported the highest maximum concentration of 15 ng/L of EE2. Conversely, studies have reported concentrations up to 3,480 ng/L of BPA, and 282 ng/L of E1 and 275 ng/L of E3. Comparison of data in Table 2.27 and Table 2.28 indicates higher occurrence and concentration of EE2 in MWWE in Canada than in other countries.

Table 2.27 Occurrence of potential EDCs in MWWE in Canada

Compound	Region	Det. Freq.	DL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Estrogen Replacement Agents								
Bisphenol-A (BPA)	Ontario	4/8	114.9	7	42			Tabe et al. (2009)
	Alberta	7/8		1.3	195			Sosiak et al. (2005)
	BC	5/5	3.2	2.9	76	45	41 ± 30	Nelson et al. (2007)
	Canada	28/29	2.1	33	1054	305	386 ± 296	Fernandez et al. (2007)
Diethylstilbestrol	Ontario	0/8	159					Tabe et al. (2009)
Equilin	BC	0/5	8.9					Nelson et al. (2007)
	Canada	2/29	18	83	207			Fernandez et al. (2007)
Ovulation Inhibitors								
17-α-Ethinylestradiol	Ontario	0/8	118.8					Tabe et al. (2009)
(EE2)	Alberta	1/8			8.5			Sosiak et al. (2005)
	BC	0/5	6.9					Nelson et al. (2007)
	Manitoba	NA/6					14.5	Lee et al. (2004)
	Quebec	0/1	7					Viglino et al. (2008)
	Canada	9/10	1		42	9		Ternes et al. (1999)
	Canada	6/29	7.1	131	178	177	169 ± 19	Fernandez et al. (2007)
19-Norethisterone	Ontario	0/8	159.1					Tabe et al. (2009)
	BC	5/5	11.1	10.4	23	14	14 ± 5	Nelson et al. (2007)
	Quebec	1/1	7		53			Viglino et al. (2008)
	Canada	1/29	38		159			Fernandez et al. (2007)
Reproductive Hormones								
17- α-Estradiol	Ontario	0/8	101.3					Tabe et al. (2009)
	Alberta	1/8			1.8			Sosiak et al. (2005)
	BC	0/5	5.3					Nelson et al. (2007)
	Canada	4/29	6.9	37	38	37	37 ± 1	Fernandez et al. (2007)
17-β-Estradiol (E2)	Ontario	0/34	5					Lishman et al. (2006)
	Ontario	0/8	158.3					Tabe et al. (2009)
	Alberta	4/8	3	0.2	2.7			Sosiak et al. (2005)
	BC	5/5	4.9	0.1	11	2	3 ± 5	Nelson et al. (2007)
	Manitoba	NA/6					0.39	Lee et al. (2004)
	Quebec	1/1			90			Viglino et al. (2008)
	Canada	8/10	1		64	6		Ternes et al. (1999)
	Canada	>27/35	0.8	0.2	14.7		1.8	Servos et al. (2005)
	Canada	14/29	7.1	10	158	25	37 ± 39	Fernandez et al. (2007)
Estrone (E1)	Ontario	17/34	5		38	13	7.6	Lishman et al. (2006)
	Ontario	7/8	140.6	0.4	12			Tabe et al. (2009)
	Alberta	6/8		0.3	10.3			Sosiak et al. (2005)
	BC	5/5	5.4	1.3	27	9	13 ± 12	Nelson et al. (2007)
	Manitoba	NA/6					5.3	Lee et al. (2004)
	Quebec	0/1	10					Viglino et al. (2008)
	Canada	8/10	1		48	3		Terrnes et al. (1999)
	Canada	>27/36	0.7	1	96		17	Servos et al. (2005)
	Canada	18/29	7.6	10	147	43	48 ± 31	Fernandez et al. (2007)

Table 2.27 continued (Occurrence of potential EDCs in MWWE in Canada)

Compound	Region	Det. Freq.	DL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Estriol (E3)	Ontario	0/8	137.4					Tabe et al. (2009)
	Alberta	4/8		2.2	4			Sosiak et al. (2005)
	BC	5/5	5.9	4.9	9	5	6 ± 2	Nelson et al. (2007)
	Quebec	0/1	50					Viglino et al. (2008)
	Canada	12/29	1	4	29	29	23 ± 9	Fernandez et al. (2007)
Progesterone	Ontario	0/8	135.7					Tabe et al. (2009)
	Quebec	0/1	3					Viglino et al. (2008)

Legends: BC = British Columbia Atl Canada = Atlantic Canada

RL = Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

Note:

1) If only one value was detected, it is reported as maximum value in the above table.

2) Only municipal plant data is considered from Fernandez et al. (2007). In addition, while calculating mean and median from this study, the values below MDL were not considered.

Table 2.28 Occurrence of potential EDCs in MWWE in other countries

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Estrogen Replacement Agents								
Bisphenol-A	USA	0/2	0.1					Boyd et al. (2003)
	USA	2/3	5	50	91			Wert et al. (2009)
	USA	3/6			270		117 ± 32	Sowers et al. (2009)
	USA	2/2	5	13	72			Geritty et al. (2011)
	Austria	6/6	20	26	1530	101	419 ± 605	Clara et al. (2005a)
	Austria	3/3	15	36	400	73		Schaar et al. (2010)
	Australia	1/3	1		1.1			Reungoat et al. (2010)
	China	23/23	1-7.5	28.9	56.8	39.8		Jin et al. (2008)
	China	2/2	0.9				86	Zhou et al. (2010)
	Japan	11/11	5	11	143	16	44 ± 50	Nakada et al. (2006)
	Japan	4/4	1.2-30	50	3480			Nakada et al. (2007)
	Korea	2/11	5	<5	26	<5	7.1	Ryu et al. (2011)
Diethylstilbestrol	USA	0/1	1					Barber et al. (2011)
	Spain	0/13	25					Pedrouza et al. (2011)
	China	21/23	1-7.5		6.2	3.8		Jin et al. (2008)
Equilin	USA	0/1	1					Barber et al. (2011)

Table 2.28 continued (Occurrence of potential EDCs in MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L Min	Max	Median	Mean ± SD	Reference
Ovulation Inhibitors								
17-α-Ethinylestradiol	USA	4/5	0.053	0.242	0.759			Synder et al. (1999)
(EE2)	USA	6/6	0.1	0.2	2.4	0.6		Huang et al. (2001)
	USA	0/3	1					Wert et al. (2009)
	USA	9/9		0.1	0.5		0.21 ± 0.13	Sowers et al. (2009)
	USA	0/3	1					Geritty et al. (2011)
	USA	1/3	1		2			Barber et al. (2011)
	USA	0/102	97					Hope et al. (2012)
	USA	0/12	20				< 20	Yang et al. (2011)
	Austria	3/6	1	3	5	4	4 ± 1	Clara et al. (2005a)
	Austria	2/3	0.7	< 4.3	7.4			Schaar et al. (2010)
	France	NA/6	0.5-2				4 ± 1	Ruel et al. (2011)
	Germany	9/16	1		15	1		Ternes et al. (1999)
	Germany	NA/10					1 ± 0.2	Bahr et al. (2007)
	Spain	0/13	70					Pedrouza et al. (2011)
	Sweden	0/3	10					Zorita et al. (2009)
	Switzerland	NA/15		0.1	0.6			Joss et al. (2005)
	UK	NA/56					0.5 ± 0.3	Ifelebuegu et al. (2011) [(a)]
	Australia	0/15	0.1					Braga et al. (2005)
	Australia	0/3	1					Reungoat et al. (2011)
	China	2/2	1.5				62	Zhou et al. (2010)
	Japan	0/20	1.2					Komori et al. (2004)
	Korea	1/7	1		1.3			Kim et al. (2007)
	Korea	0/11	1					Ryu et al. (2011)
19-Norethisterone	USA	0/1	1					Barber et al. (2011)
Reproductive Hormones								
17- α-Estradiol	USA	0/3	1					Barber et al. (2011)
	USA	0/102	20					Hope et al. (2012)
	France	NA/6	0.5-2				< 2	Ruel et al. (2011)
	Spain	0/13	70					Pedrouza et al. (2011)
	China	2/2	1.3				50	Zhou et al. (2010)
	Korea	0/5	1.6					Behera et al. (2011)
	Various				38			VS, ref. Liu et al. (2009)
17-β-Estradiol (E2)	USA	5/5	0.107	0.477	3.66			Snyder et al. (1999)
	USA	8/8	0.1	0.2	4.1	1.9		Huang et al. (2001)
	USA	1/3	0.5		1.8			Wert et al. (2009)
	USA	4/9			2.6		0.42 ± 85	Sowers et al. (2009)
	USA	1/3	0.5		3			Gerrity et al. (2011)
	USA	2/3	1	2	3			Barber et al. (2011)
	USA	4/102	50	8	90	35	42	Hope et al. (2012)
	Austria	3/6	5	4	30	8	14 ± 14	Clara et al. (2005a)
	France	NA/6	0.5-2				4	Ruel et al. (2011)
	Germany	NA/10					0.9 ± 0.2	Bahr et al. (2007)
	Spain	0/13	70					Pedrouza et al. (2011)
	Sweden	NA/3	1.6				2.5 ± 2.7	Zorita et al. (2009)
	Switzerland	NA/15		2	8			Joss et al. (2005)
	UK	NA/70					6.9 ± 6.4	Ifelebuegu et al. (2011) [(a)]

Table 2.28 continued (Occurrence of potential EDCs in MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
17-β-Estradiol (E2)	Australia	NA/15	0.1				0.95 ± 0.55	Braga et al. (2005)
(cont'd)	Australia	0/3	1					Reungoat et al. (2010)
	China	19/23	1-7.5		8.6	4.4		Jin et al. (2008)
	China	2/2	2.1				30	Zhou et al. (2010)
	Japan	NA/20	0.5	< 0.5	11	< 0.5		Komori et al. (2004)
	Japan	11/11	0.1	0.49	17	4	6 ± 5	Nakada et al. (2006)
	Japan	4/4	0.015-1.5	1.34	2.3			Nakada et al. (2007)
	Korea	0/7	1					Kim et al. (2007)
	Korea	2/11	0.5	< 0.5	9.4	< 0.5	1.6	Ryu et al. (2011)
	Korea	0/5	2.7					Behera et al. (2011)
	Various				64			VS, ref. Monteiro et al. (2010)
Estrone (E1)	USA	0/2	0.3					Boyd et al. (2003)
	USA	2/2		5.4	20			Synder et al. (2006)
	USA	3/3		0.44	12	5.4		Wert et al. (2009)
	USA	9/9		0.4	15.9		2.74 ± 4.98	Sowers et al. (2009)
	USA	3/3	0.2	15	140		69 ± 64	Gerrity et al. (2011)
	USA	1/1	1		130			Barber et al. (2011)
	USA	48/102	20	2	282	45	72	Hope et al. (2012)
	Austria	4/6	1	2	72	6	22 ± 34	Clara et al. (2005a)
	Austria	3/3	1.5	<1.1	2	1.6		Schaar et al. (2010)
	France	NA/6	0.5-2				20 ± 30	Ruel et al. (2011)
	Germany	NA/6	3				15 ± 2	Ternes et al. (2003)
	Germany	NA/10					8.7 ± 7.3	Bahr et al. (2007)
	Spain	1/1	1		4.4			Carballa et al. (2004)
	Spain	0/13	25					Pedrouza et al. (2011)
	Sweden	NA/3	3				70 ± 10	Zorita et al. (2009)
	UK	NA/70					39 ± 20	Ifelebuegu et al. (2011) [(a)]
	Australia	NA/15	0.1				8.1 ± 4.2	Braga et al. (2005)
	Australia	0/3	1					Reungoat et al. (2010)
	China	23/23	1-7.5	7.2	31.5	12.6		Jin et al. (2008)
	China	2/2	4.9				123	Zhou et al. (2010)
	Japan	NA/20	0.8	< 0.8	180	12		Komori et al. (2004)
	Japan	11/11	0.6	3	110	42	47 ± 32	Nakada et al. (2006)
	Japan	4/4	0.027-2.1	20	41			Nakada et al. (2007)
	Korea	5/7	1	2.2	36		14	Kim et al. (2007)
	Korea	7/11	5	< 5	120	21	34	Ryu et al. (2011)
	Korea	NA/5	0.84	0	24		6	Behera et al. (2011)

Table 2.28 continued (Occurrence of potential EDCs in MWWE in other countries)

Compound	Country	Det. Freq.	RL ng/L	Concentration, ng/L				Reference
				Min	Max	Median	Mean ± SD	
Estriol (E3)	USA	2/2		< 5	5.7			Synder et al. (2006)
	USA	0/9						Sowers et al. (2009)
	USA	0/3	1					Barber et al. (2011)
	USA	0/102	240					Hope et al. (2012)
	Austria	3/6	1	1	275	17	98 ± 154	Clara et al. (2005a)
	France	NA/6	0.5-2				< 2	Ruel et al. (2011)
	Spain	0/13	25					Pedrouza et al. (2011)
	Australia	0/3	1					Reungoat et al. (2010)
	China	1/23			8.4			Jin et al. (2008)
	China	2/2	0.9				18	Zhou et al. (2010)
	Japan	NA/20	1.4	< 1.4	5.8	1.5		Komori et al. (2004)
	Japan	7/8	0.2	0.31	0.84	0.46	0.51 ± 0.18	Nakada et al. (2006)
	Japan	4/4	0.024-0.6	0.11	0.72			Nakada et al. (2007)
	Korea	3/7	5	8.9	25		16	Kim et al. (2007)
	Korea	0/5	6					Behera et al. (2011)
Progesterone	USA	0/3	0.5					Wert et al. (2009)
	USA	1/9			2.6		0.29 ± 0.87	Sowers et al. (2009)
	USA	0/3	0.5					Gerrity et al. (2011)
	USA	0/1	1					Barber et al. (2011)
	Korea	0/11	0.5					Ryu et al. (2011)

Notes:

a) The data taken from Ifelebuegu et al. (2011) is for secondary treated effluent only.

b) If only one value was detected, it is reported as maximum value in the above table.

Legends: USA: United States of America UK: United Kingdom

RL = Reported limit (i.e. detection limit – DL, or method detection limit – MDL, or limit of detection – LOD, or limit of quantification – LOQ)

2.4.5 Removal of PhACs and EDCs from MWWE

As per the discussion in the earlier sections, the municipal effluent contains a complex cocktail of various chemicals, PhACs and EDCs. The anthropogenic activities have resulted in the omnipresence of these compounds in municipal sewage. The conventional MWWTPs cannot effectively remove these micropollutants and hence are a major contributor for many of the PhACs and EDCs. The concentrations of the

micropollutants are in the range of ng/L to ug/L, and are high enough to produce estrogenic activity in fish and aquatic organisms (Auriol et al., 2006). Studies have linked them to feminization or masculinization of vertebrates such as fish (Ternes et al., 2004). The micropollutants affect the reproduction and growth of fish, amphibians, reptiles, birds, and mammals (Bloetscher and Plummer, 2011). The long-term effect of the micropollutants on human health is still not clear. However, their negative impacts on various aquatic species and mammals are a cause of concern. This concern prompts preventive and precautionary measures to reduce the amount of the micropollutants released into the environment. To protect public health, it is easier to treat the MWWE to remove the micropollutants and address the pollution at source, rather than treating the potable water in which these pollutants have been diluted several orders of magnitude. In addition, removing of the micropollutants from MWWE will have positive effects on the aquatic species in the receiving water bodies.

The molecular size of most of the PhACs and EDCs is in the range of 150 to 500 Daltons (Snyder et al., 2003). Shon et al. (2006) have provided the size range of effluent organic matter (EfOM) removed by various MWWE treatment processes. Figure 2.5 reproduces this data. This figure shows that membrane filtration (reverse osmosis and nanofiltration), activated carbon adsorption, ion exchange, and advanced oxidation are the treatment processes that can remove 150 to 500 Daltons size EfOM.

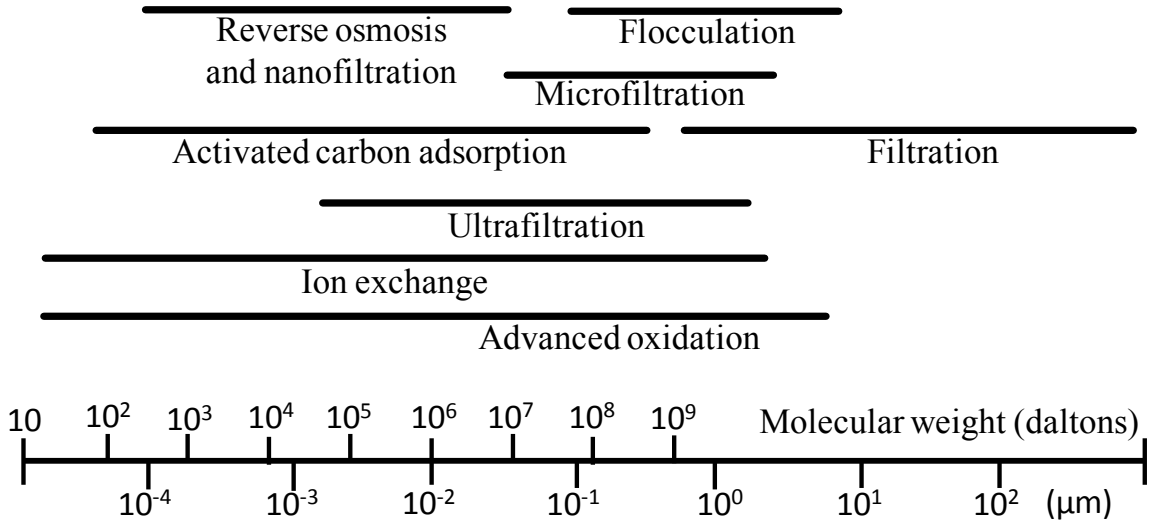


Figure 2.5 **Size range of effluent organic matter removed by various treatment processes** (Adapted from Shon et al. 2006)

Reverse osmosis and nanofiltration membrane processes are effective in the removal of the micropollutants from MWWE (Sedlak and Pinkston, 2001; Yoon et al., 2007; Liu et al., 2009; Lee et al., 2012). Membrane filtration is a physical method of micropollutant removal, and does not produce by-products or metabolites (Liu et al., 2009). However, operation cost and membrane fouling can limit their potential use (Petala et al., 2006). These processes are very energy intensive. In addition, the waste stream can be 15 to 25% of the feed and can have high concentrations of regulated contaminants as well as micropollutants that can make their disposal difficult and expensive (Lee et al., 2012).

Adsorption of micropollutants by activated carbon can be by granular activated carbon (GAC) bed or by adding powdered activated carbon (PAC) to the (Snyder et al., 2003). Ternes et al. (2002) have shown that activated carbon can effectively remove the majority of the micropollutants. However, competition for adsorption by the organic

matter present in MWWE and blockage of the pores of carbon can decrease the adsorption capacity of the target compounds (Koh et al., 2008). In addition, the GAC can release the adsorbed compounds and replace it by more strongly adsorbable compounds (Snyder et al., 2003).When the adsorption capacity is exhausted, the activated carbon in GAC bed needs replacement or regeneration, which is a costly process (Koh et al., 2008).

The ion exchange process is effective in removing the majority of the micropollutants and dissolved organic carbon, and can be less expensive than activated carbon in removing of EfOM (Shon et al., 2006). While this process can produce high quality effluent, it is a costly process when compared to other treatment processes. The waste stream generated during backwash and regeneration can contain high concentration of the micropollutants that can make it difficult and costly to dispose.

Some of the oxidation processes for the transformation of the micropollutants are chlorination, chlorine dioxide oxidation, UV irradiation, and ozonation (Snyder et al., 2003; Koh et al., 2008). The concerns related to the formation of carcinogenic by-products on treatment of MWWE with chlorine-based oxidants makes chlorination and chlorine dioxide oxidation the less sought treatment methods for oxidation of micropollutants. In addition, the ammonia present in the MWWE can react and reduce the reactivity of chlorine (Snyder et al., 2003).

UV radiation disinfects MWWE at reasonable cost (Rice, 1999) and is widely used (Snyder et al., 2003). The typical UV dose for disinfection is from <5 up to 140 mJ/cm^2 (Snyder et al., 2003; Kim et al., 2009). Studies have attempted to use the UV radiation technology to remove pharmaceuticals from MWWE. Kim et al. (2009) found over 90% reductions of some pharmaceuticals at a UV dose of 923 mJ/cm^2 and 5 minutes

of contact time. Out of the 41 pharmaceuticals monitored by them, 29 showed low removal even at high UV dose of 2768 mJ/cm^2 and 15 minutes of contact time. The experimental results show that the removal of the pharmaceuticals will be low at a UV disinfection dose.

As discussed earlier, ozone is a powerful oxidant. It decomposes to form oxidants such as the hydroxyl radical, which is more powerful oxidant than ozone (Hoigné and Bader, 1976). Oxidation reactions directly with ozone are highly selective and slow while those with hydroxyl radicals are nonselective and fast (Hoigné and Bader, 1976; Huber et al., 2003). The second-order reaction rate constant of the pharmaceuticals with ozone is in the range of <1 to 10^6 M^{-1} s^{-1} and with hydroxyl radical is around 10^9 M^{-1} s^{-1} (Huber et al., 2003; Huber et al., 2005; Dodd et al., 2006). Studies have shown that ozonation can effectively mineralize or transform the pharmaceuticals and other chemicals present in water and wastewater matrices (Ternes et al., 2003; Huber et al., 2005; Nakada et al., 2007).

2.4.6 Oxidation of CECs in MWWE by ozonation

The number of studies that have investigated the transformation of CECs present in MWWE by ozonation is limited. The results from these studies indicate that ozonation is effective in transforming antiphlogistics, antibiotics, lipid regulators, antidepressants, estrogen replacement agents, ovulation inhibitors, and natural and synthetic hormones found in the MWWE. Table 2.29 represents the data from some studies that have examined the transformation of antiphlogistics on ozonation of MWWE.

Table 2.29 Transformation of antiphlogistics present in MWWE by ozonation

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/ mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Acetaminophen	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	> 96	RG1
	1	3.2	2			(2 – 402)		> 99	KM
	1	4.5 – 4.7	2	~ 0.5	5	18	< RL	86	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	62.5	< RL	96	LE1, LE2
Diclofenac	2	23	5	~ 0.2	50	1300 ± 100	< RL	> 96	TN
	1	12		0.2		4380	4380	0	BH
	1	12		0.4		4380	2	100	BH
		7.7 ± 0.5	1					93	HU
		7.7 ± 0.5	2					99	HU
	2	7.2	2.1		1	71 – 73		> 99	SN
	1	6.84	7	1		73	< 1	> 98	DS
	4	4.7 – 6.0		0.36 – 0.55	10	501 – 1731	< RL – 15	97 – 100 (99)	HO
	4	5.4		0.6 – 0.67	10	855 – 1236	< RL	98 – 100 (99)	HO
	3	6.6 – 10.3		0.2		47 – 150		25 to > 95	WT
	3	6.6 – 10.3		0.6		47 – 150		> 95	WT
		6.9	< 2.4	< 0.4	1	433	< RL	> 99	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	> 94	RG1
	3	6.5 – 8.1		0.6 – 0.8		194 – 240		> 98	RG2
	3	5.8 – 6.6		0.4 – 0.5		140 – 206		> 98	RG2
	3	4.2 – 5.8		0.2 – 0.3		162 – 316		97 ± 4	RG2
	3	2.7 – 3.4	2			(2 – 402)		97 to > 99	KM
	2	5.8 & 7.4	4.6 & 5		20	970 & 200	< RL	> 99	SC

Table 2.29 continued (Transformation of antiphlogistics present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC	O_3 dose	O_3 dose	RL O_3 samples	Pre ozonated effluent	Post ozonated effluent	% Reduction Range (Median)	Reference
		mg/L	mg/L	mg O_3/ mg C	ng/L	ng/L	ng/L		
Ibuprofen	2	23	5	~ 0.2	50	130 ± 30	67	48	TN
	2	23	10/15		50	130 ± 30	< RL	> 62	TN
	1	12		0.2		30	26	13	BH
	1	12		0.4		30	16	47	BH
	1	12		0.8		30	3	90	BH
	1	12		1.0		30	4	87	BH
	2	7.2	2.1		1	5.6 – 15		< 1	SN
	2	7.2	3.6		1	5.6 – 15		> 82	SN
	3	3.4 – 4.4	3		0.03-1.2	0.4-2.98	0.26-1.07	-156 to > 76 (36)	NK
	1	6.84	7	1		5.6	< 1	> 82	DS
	2	4.7 – 6.0		0.36 – 0.55	20	56 – 86	< RL – 80	-43 & 88	HO
	1	5.4		0.67	20	80	< RL	50	HO
	3	6.6 – 10.3		0.2		5 – 85		10 to 30	WT
	3	6.6 – 10.3		0.6		5 – 85		60 to > 95	WT
	3	6.6 – 10.3		1.0		5 – 85		95 to > 95	WT
	1	7.4	5		20	31	< RL	> 35	SC
Indomethacin	2	23	5	~ 0.2	50	100 ± 40	< RL	> 50	TN
	1	12		0.2		124	29	77	BH
	1	12		0.4		124	20	84	BH
	1	12		0.8		124	7	94	BH
		6.9	< 2.4	< 0.4	2	37	< RL	> 97	RS
Ketoprofen	4	3.4 – 4.4	3		0.03-15	76 – 333	20 – 139	52 – 93 (73)	NK
	1	12		0.2		122	114	7	BH
	1	12		0.4		122	84	31	BH
	1	12		0.8		122	22	82	BH
	1	12		1.0		122	15	88	BH
	1	12		1.2		122	2	98	BH
		6.9	16.3	~ 2.4	2	162	3	98	RS
	3	2.7 – 3.4	2			(2 – 402)		31 – 71	KM
	1	2.7 – 3.4	4			(2 – 402)		91	KM

Table 2.29 continued (Transformation of antiphlogistics present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/ mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Ketoprofen (cont'd)	1	4.5 – 4.7	2	~ 0.5	5	62	55	11	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	6	< RL	58	LE1, LE2
Naproxen	2	23	5	~ 0.2	50	100 ± 10	< RL	> 50	TN
	1	12		0.2		157	78	50	BH
	1	12		0.4		157	3	98	BH
	1	12		0.6		157	4	97	BH
	2	7.2	2.1		1	25 – 71		> 96	SN
	4	3.4 – 4.4	3		0.24-27	28 – 99	< RL – 0.79	> 68 to > 99.5	NK
	1	6.84	7	1		25	< 1	> 96	DS
	4	4.7 – 6.0		0.36 – 0.55	10	194 – 292	< RL	70 – 98 (98)	HO
	4	5.4		0.6 – 0.67	10	215 – 329	< RL – 5	59 – 98 (98)	HO
	3	4.2 – 4.6		0.77 – 1.16	10	181 – 291	< RL	70 – 97 (97)	HO
	3	6.6 – 10.3		0.2		23 – 51		20 to > 95	WT
	3	6.6 – 10.3		0.6		23 – 51		> 95	WT
		6.9	< 2.4	< 0.4	12	109	< RL	> 92	RS
	3	6.5 – 8.1		0.6 – 0.8		188 – 587		> 90	RG2
	3	5.8 – 6.6		0.4 – 0.5		189 – 346		> 98	RG2
	3	4.2 – 5.8		0.2 – 0.3		83 – 142		93 ± 9	RG2
	3	2.7 – 3.4	2			(2 – 402)		43 to > 99	KM
	1	2.7 – 3.4	4			(2 – 402)		83	KM
	1	4.5 – 4.7	2	~ 0.5	10	68	< RL	93	LE1, LE2
	1	4.1 – 4.4	4	~ 1	10	160	< RL	97	LE1, LE2
	1	4.1 – 4.3	8	~ 2	10	260	< RL	98	LE1, LE2

Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

Note: For Reference Legends, refer to page 112.

The data in Table 2.29 indicates that some of the CECs such as acetaminophen, diclofenac, indomethacin, and naproxen are transformed by over 80% at an ozone dose of around 0.5 mg O_3/mg DOC. CECs such as ibuprofen and ketoprofen require an ozone dose of around 0.8 mg O_3/mg DOC or higher for similar transformation.

Table 2.30 shows the data from the literature on the transformation of antibiotics on ozone treatment of MWWE. Studies have reported more than 80% reduction in concentration of erythromycin, lincomycin, roxithromycin, sulfadiazine, sulfamethoxazole, and sulfathiazole. There is limited data regarding transformation of some CECs such as ciprofloxacin and norfloxacin that are consumed in notable quantity.

Table 2.30 Transformation of antibiotics present in MWWE by ozonation

Compound	No. of sample	TOC or DOC	O_3 dose	O_3 dose	RL O_3 samples	Pre ozonated effluent	Post ozonated effluent	% Reduction Range (Median)	Reference
		mg/L	mg/L	mg O_3/mg C	ng/L	ng/L	ng/L		
Carbadox	1	4.5 – 4.7	2	~ 0.5	5	27	< RL	91	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	6.1	< RL	59	LE1, LE2
Chloramphenicol	2	2.7 – 3.4	2			(2 – 402)		63 – 68	KM
Ciprofloxacin		6.9	< 6.2	< 1	5	522	< RL	> 99	RS
	3	2.7 – 3.4	2			(2 – 402)		67 to > 99	KM
	12	4.5	1		10	19 – 30 (23)	<10 – 16		YG
Norfloxacin		6.9	< 4.3	~ 0.6	8	38	< RL	> 89	RS
Erythromycin	2	23	5	~ 0.2	50	620 ± 240	< RL	> 92	TN
		7.7 ± 0.5	1					75	HU
		7.7 ± 0.5	2					98	HU
	2	7.2	2.1		1	149 – 162		98	SN
	1	3.4 – 4.4	3		0.0012	103	11.7	89	NK
	1	6.84	7	1		162	< 1	> 99	DS
	2	4.7 – 6.0		0.36 – 0.55	20	15 – 17	< RL – 73	-387 & 41	HO
	3	5.4		0.6 – 0.67	20	19 – 49	< RL	47 – 80 (69)	HO
	2	4.2 – 4.6		0.77 – 1.16	20	48 – 73	< RL	22 & 86	HO
		6.9	< 4.3	~ 0.6	10	72	< RL	> 99	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	95	RG1
	2	6.5 – 8.1		0.6 – 0.8		153 – 167		97 ± 0.5	RG2
	3	5.8 – 6.6		0.4 – 0.5		250 – 324		86 ± 11	RG2
	3	4.2 – 5.8		0.2 – 0.3		20 – 32		83 ± 13	RG2
	2	2.7 – 3.4	2			(2 – 402)		95 to > 99	KM
	2	5.8 & 7.4	4.6 & 5		20	170 & 210	< RL	> 88	SC
	1	7	7.5		20	170		76	SC
	12	4.5	1		10	13 – 50 (28)	<10 – 15		YG
	1	4.1 – 4.4	4	~ 1	10	18.5	< RL	73	LE1, LE2

Table 2.30 continued (Transformation of antibiotics present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Lincomycin		6.9	< 2.4	< 0.4	3	12	< RL	> 88	RS
	3	2.7 – 3.4	2			(2 – 402)		88 to > 99	KM
Roxithromycin	2	23	5	~ 0.2	50	540 ± 40	< RL	> 91	TN
		7.7 ± 0.5	1					56	HU
		7.7 ± 0.5	2					97	HU
		7.7 ± 0.5	3.5					99	HU
	1	3.4 – 4.4	3		< 0.001	20.9	1.9	91	NK
	3	4.7 – 6.0		0.36 – 0.55	3	6 – 26	< LOQ	76 – 94 (79)	HO
	3	5.4		0.6 – 0.67	3	4 – 7	< LOQ – 1	70 – 80 (75)	HO
	4	10.9 – 11.4	5	~ 0.5	10	> 100		79 – 91 (84)	RG1
	3	6.5 – 8.1		0.6 – 0.8		77 – 154		92 ± 5	RG2
	3	5.8 – 6.6		0.4 – 0.5		456 – 703		86 ± 10	RG2
	3	4.2 – 5.8		0.2 – 0.3		60 – 187		85 ± 15	RG2
	3	2.7 – 3.4	2			(2 – 402)		76 to > 99	KM
	1	7.4	5		10	27	< RL	> 63	SC
	1	7	7.5		10	160	< RL	> 94	SC
Sulfadiazine		7.7 ± 0.5	1					84	HU
		7.7 ± 0.5	2					> 99	HU
	1	6.0		0.47	35	127	50	61	HO
	2	4.2 – 4.6		0.77 – 1.16	35	17 – 127	< RL	-5 & 86	HO
	1	4.5 – 4.7	2	~ 0.5	5	19	< RL	87	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	9.2	< RL	73	LE1, LE2
	1	4.1 – 4.3	8	~ 2	5	16	< RL	84	LE1, LE2
Sulfadimethoxine	3	2.7 – 3.4	2			(2 – 402)		98 to > 99	KM
Sulfamerazine	1	3.2	2			(2 – 402)		> 99	KM
Sulfamethazine	2	5.4		0.6 – 0.67	5	7 – 20	< RL	64 – 88	HO
	2	4.2 – 4.6		0.77 – 1.16	5	7 – 9	< RL	72 – 100	HO

Table 2.30 continued (Transformation of antibiotics present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Sulfamethoxazole	2	23	5	~ 0.2	50	620 ± 50	< RL	> 92	TN
		7.7 ± 0.5	1					67	HU
		7.7 ± 0.5	2					97	HU
		7.7 ± 0.5	3.5					> 99	HU
	2	7.2	2.1		1	669 – 695		93	SN
	2	7.2	3.6		1	669 – 695		> 99	SN
	1	5.6	1	0.2		251	3.2	> 99	DS
	1	6.84	7	1		669	< 1	> 99	DS
	4	4.7 – 6.0		0.36 – 0.55	7	84 – 434	< RL – 29	80 – 99 (86)	HO
	4	5.4		0.6 – 0.67	7	99 – 274	< RL	95 – 98 (97)	HO
	3	4.2 – 4.6		0.77 – 1.16	7	96 – 282	< RL	88 – 98 (97)	HO
	3	6.6 – 10.3		0.2		330 – 1200		30 to ~ 95	WT
	3	6.6 – 10.3		0.6		330 – 1200		95 to > 95	WT
	3	6.6 – 10.3		1.0		330 – 1200		> 95	WT
		6.9	< 10.6	~ 1.5	8	95	< RL	> 96	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	> 93	RG1
	3	6.5 – 8.1		0.6 – 0.8		160 – 272		94 ± 3	RG2
	3	5.8 – 6.6		0.4 – 0.5		39 – 229		96 ± 2	RG2
	3	4.2 – 5.8		0.2 – 0.3		278 – 1701		97 ± 3	RG2
	3	2.7 – 3.4	2			(2 – 402)		94 to 97	KM
	2	5.8 & 7.4	4.6 & 5		10	73 & 100	< RL	> 86	SC
	1	7	7.5		10	140	< RL	> 93	SC
	12	4.5	1		10	210–1200 (670)	35-140 (80)	88	YG
	1	4.5 – 4.7	2	~ 0.5	10	470	250	47	LE1, LE2
	1	4.1 – 4.4	4	~ 1	10	1040	12.5	99	LE1, LE2
	1	4.1 – 4.3	8	~ 2	10	1600	< RL	100	LE1, LE2

Table 2.30 continued (Transformation of antibiotics present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Sulfathiazole		7.7 ± 0.5	1					94	HU
		7.7 ± 0.5	2					> 99	HU
	1	4.5 – 4.7	2	~ 0.5	5	9.2	< RL	73	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	5.4	< RL	54	LE1, LE2
Trimethoprim	2	23	5	~ 0.2	50	340 ± 40	< RL	> 85	TN
	2	7.2	2.1		1	191 – 229		> 99	SN
	1	3.4 – 4.4	3		0.027	5.5	0.22	96	NK
	1	5.6	1	0.2		4.4	< 0.25	> 94	DS
	1	6.84	7	1		191	< 1	> 99	DS
	4	4.7 – 6.0		0.36 – 0.55	5	71 – 234	< RL	93 – 98 (97)	HO
	4	5.4		0.6 – 0.67	5	76 – 165	< RL	91 – 98 (97)	HO
	3	4.2 – 4.6		0.77 – 1.16	5	85 – 125	< RL	88 – 98 (97)	HO
	3	6.6 – 10.3		0.2		36 - 370		55 to ~ 95	WT
	3	6.6 – 10.3		0.6		36 - 370		> 95	WT
		6.9	< 4.3	~ 0.6	2	73	< RL	> 99	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	> 93	RG1
	3	6.5 – 8.1		0.6 – 0.8		27 – 49		> 97	RG2
	3	5.8 – 6.6		0.4 – 0.5		48 – 141		97 ± 2	RG2
	3	4.2 – 5.8		0.2 – 0.3		49 – 94		95 ± 6	RG2
	3	2.7 – 3.4	2			(2 – 402)		94 to > 99	KM
	2	5.8 & 7.4	4.6 & 5		20	150 & 240	< RL	> 93	SC
	1	7	7.5		20	320	< RL	> 97	SC
	12	4.5	1		10	11 – 32	< 10		YG
	1	4.1 – 4.4	4	~ 1	10	79.5	< RL	94	LE1, LE2
	1	4.1 – 4.3	8	~ 2	10	60	< RL	92	LE1, LE2

Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

Note: For Reference Legends, refer to page 112.

The data from some studies related to transformation of antidepressants and lipid regulators is summarized in Table 2.31 and Table 2.32. The data indicates that carbamazepine and gemfibrozil are transformed by more than 90% even at a low ozone dose of around 0.2 mg O_3/mg DOC. At similar ozone dose, transformation of bezafibrate is close to zero while that of clofibric acid is in the range of -6 to 50%. These two drugs are transformed by over 80% at an ozone dose of around 0.8 mg O_3/mg DOC.

Table 2.33 shows the effect of ozonation of MWWE on the transformation of the EDCs. Majority of the listed EDCs are transformed by more than 80% at an ozone dose of around 0.5 mg O_3/mg DOC.

Since it is difficult to measure the actual transformation of the CECs present in MWWE in concentrations close to or below the detection limits, some studies have spiked the MWWE with CECs to study their transformation on ozonation. Appendix-A summarizes the result from some of these studies. Data from Table 2.29 to Table 2.33 and Appendix-A indicates that an increase in the ozone dose generally results in an increase in transformation of the CECs. However, it also increases the cost of ozonation as well as the concentration of harmful disinfection by-products formed (Liberti et al., 2000; Kim et al., 2007a). Ozonation of water or wastewater containing bromide can form potentially toxic bromate (Haag and Hoigné, 1983; von Gunten and Hoigné, 1994). Studies by Bahr et al. (2007) and Kim et al. (2007a) have shown that even if the secondary effluent contains bromide concentration of up to 500 µg/L, the formation of bromate on its ozonation can be limited to around 10 µg/L if the ozone dose is < 1 mg O_3/mg DOC. This ozone dose is sufficient to transform the majority of the CECs by more than 80%.

Table 2.31 Transformation of antiepileptic/antidepressant present in MWWE by ozonation

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Carbamazepine	2	23	5	~ 0.2	50	2100 ± 40	< RL	> 98	TN
	1	12		0.2		2000	1000	50	BH
	1	12		0.4		2000	< 50	99	BH
	2	7.2	2.1		1	139		> 99	SN
	3	3.4 – 4.4	3		1.5 – 21	2.9 – 36	< RL – 33	8.3 to > 81	NK
	1	5.6	1	0.2		48	< 0.5	> 99	DS
	1	6.84	7	1		139	< 1	> 99	DS
	4	4.7 – 6.0		0.36 – 0.55	3	186 - 687	< RL – 6	97 – 100 (99)	HO
	4	5.4		0.6 – 0.67	3	76 – 165	< RL	91 – 98 (97)	HO
	3	4.2 – 4.6		0.77 – 1.16	3	384 – 714	< RL	98 – 100 (100)	HO
	3	6.3 – 10.3		0.2		170 – 350		50 to > 95	WT
	3	6.3 – 10.3		0.6		170 – 350		> 95	WT
		6.9	< 6.2	< 1	1	106	< RL	> 99	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	> 98	RG1
	2	6.5 – 8.1		0.6 – 0.8		468 – 631		98 ± 1	RG2
	3	5.8 – 6.6		0.4 – 0.5		119 – 172		98 ± 1	RG2
	2	4.2 – 5.8		0.2 – 0.3		727 – 1192		90 ± 13	RG2
	3	2.7 – 3.4	2			(2 – 402)		98 to > 99	KM
	2	5.8 & 7.4	4.6 & 5		1	500 & 900		> 99	SC
	12	4.5	1		10	25 – 140 (67)	<10 – 12		YG
	1	4.5 – 4.7	2	~ 0.5	5	450	17	96	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	410	< RL	99	LE1, LE2
	1	4.1 – 4.3	8	~ 2	5	440	< RL	99	LE1, LE2

Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

Note: For Reference Legends, refer to page 112.

Table 2.32 Transformation of lipid regulators present in MWWE by ozonation

Compound	No. of sample	TOC or DOC	O_3 dose	O_3 dose	RL O_3 samples	Pre ozonated effluent	Post ozonated effluent	% Reduction Range (Median)	Reference
		mg/L	mg/L	mg O_3/mg C	ng/L	ng/L	ng/L		
Bezafibrate	1	12		0.2		470	470	0	BH
	1	12		0.4		470	390	17	BH
	1	12		0.8		470	10	98	BH
		7.7 ± 0.5	2					49	HU
		7.7 ± 0.5	3.5					95	HU
		7.7 ± 0.5	5					> 99	HU
	4	4.7 – 6.0		0.36 – 0.55	14	48 – 133	9 - 76	8 – 82 (54)	HO
	4	5.4		0.6 – 0.67	14	55 – 108	<LOQ – 21	81 – 91 (88)	HO
	3	4.2 – 4.6		0.77 – 1.16	14	37 – 67	< RL	51 – 89 (81)	HO
		6.9	16.3	~ 2.4	4	115	4	97	RS
	3	2.7 – 3.4	2			(2 – 402)		47 - 82	KM
	1	2.7 – 3.4	4			(2 – 402)		>99	KM
	2	5.8 & 7.4	4.6 & 5		20	1500 & 1600		76 – 81	SC
	1	7	7.5		20	1500		87	SC
Clofibric acid	2	23	5	~ 0.2	50	120 ± 20	60	50	TN
	2	23	10/15		50	120 ± 20	< RL	> 59	TN
	1	12		0.2		70	74	- 6	BH
	1	12		0.4		70	55	21	BH
	1	12		0.8		70	18	74	BH
	1	12		1		70	11	84	BH
	1	12		1.2		70	2	97	BH
	3	5.4		0.6 – 0.67	3	12 – 44	< RL – 15	50 – 79 (66)	HO
	3	4.2 – 4.6		0.77 – 1.16	3	11 – 18	< RL	8 6 – 86 (86)	HO
	2	2.7 – 3.4	2			(2 – 402)		57 - 74	KM

Table 2.32 continued (Transformation of lipid regulators present in MWWE by ozonation)

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Gemfibrozil	2	7.2	2.1	0.3	10	16 – 567		> 94	SN
	1	5.6	1	0.2		3.5	< 0.25	> 93	DS
	1	6.84	7	1		16	< 1	> 94	DS
	3	6.3 – 10.3		0.2		35 – 1600		30 to > 95	WT
	3	6.3 – 10.3		0.6		35 – 1600		> 95	WT
		6.9	16.3	~ 2.4	1	332	15	95	RS
	4	10.9 – 11.4	5	~ 0.5	10	> 100	< RL	91	RG1
	3	6.5 – 8.1		0.6 – 0.8		84 – 155		97 ± 2	RG2
	3	5.8 – 6.6		0.4 – 0.5		36 – 60		81 ± 0.5	RG2
	3	4.2 – 5.8		0.2 – 0.3		83 – 191		76 ± 15	RG2
	1	4.5 – 4.7	2	~ 0.5	5	9.3	< RL	72	LE1, LE2
	1	4.1 – 4.4	4	~ 1	5	43	< RL	94	LE1, LE2
	1	4.1 – 4.3	8	~ 2	5	85	< RL	97	LE1, LE2

Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

Note: For Reference Legends, refer to page 112.

Table 2.33 Transformation of EDCs present in MWWE by ozonation

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/mg C	RL O_3 samples ng/L	Pre ozonated effluent ng/L	Post ozonated effluent ng/L	% Reduction Range (Median)	Reference
Bisphenol-A	4	3.4 – 4.4	3		1.2 – 30	94 – 205	12.2 – 108	47 – 87	NK
	2	10.3		0.2		50 – 91		62 to 70	WT
	2	10.3		0.6		50 – 91		> 95	WT
	2	5.8 & 7.4	4.6 & 5		15	73 & 400	< RL	> 87	SC
17α-ethinylestradiol		7.7 ± 0.5	0.5					63	HU
		7.7 ± 0.5	1					83	HU
		7.7 ± 0.5	2					> 97	HU
	1	7	7.5		0.7	7.4	< RL	> 72	SC
17β-Estradiol		7.7 ± 0.5	0.5					60	HU
		7.7 ± 0.5	1					82	HU
		7.7 ± 0.5	2					> 97	HU
	3	3.4 – 4.4	3		0.015-1.5	1.58 – 2.63	0.15 – 7.8	> 93 to 97	NK
Estrone (E1)	2	23	5	~ 0.2	3	15 ± 2	< RL	> 80	TN
		7.7 ± 0.5	0.5					57	HU
		7.7 ± 0.5	1					84	HU
		7.7 ± 0.5	2					> 97	HU
	2	7.2	2.1		1	5.4 – 20		44	SN
	4	3.4 – 4.4	3		0.027-0.9	16 – 39	0.15 – 7.8	66 – 87 (95)	NK
	1	6.84	7	1		4.3	< 1	> 77	DS
	1	7.4	5		1.5	1.6	< RL	> 50	SC
	1	7	7.5		1.5	2	< RL	> 60	SC
Estriol	3	3.4 – 4.4	3		0.024-0.6	0.22 – 1.22	0.10 – 0.12	56 to > 77	NK

Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

Note: For Reference Legends, refer to page 112.

Table 2.33 continued (Transformation of EDCs present in MWWE by ozonation)

Reference Legends:

BH	Bahr et al. (2005)	
DS	Dickenson et al. (2009)	
HO	Hollender et al. (2009)	
HU	Huber et al. (2005)	
KM	Kim and Tanaka (2011)	Individual concentration of chemicals not provided. All chemicals were in range of 2 – 402 ng/L.
LE1	Lee et al. (2012)	(while calculating percentage reduction, values < RL is replaced by half of RL values)
LE2	Lee (2010)	
NK	Nakada et al. (2007)	
RG1	Reungoat et al. (2010)	
RG2	Reungoat et al. (2012)	
RS	Rosal et al. (2010)	(while calculating percentage reduction, values < RL is replaced by half of RL values)
SC	Schaar et al. (2010)	
SN	Snyder et al. (2006)	
TN	Ternes et al. (2003)	
WT	Wert et al. (2009a)	
YG	Yang et al. (2011)	

2.4.7 Oxidation kinetics of CECs in MWWE with ozone

On ozonation of MWWE, molecular ozone and hydroxyl radicals can oxidize the CECs. The oxidant that will dominate the oxidation process will depend on various factors as discussed in earlier sections. The oxidation rate equation as per von Gunten (2003b) is:

$$-\frac{dC}{dt} = k_{O3}[C][O_3] + k_{OH}[C][OH\bullet] \qquad (2.13)$$

C	concentration of compound
$[O_3]$	concentration of ozone
$[OH\bullet]$	concentration of hydroxyl radicals
k_{O3}	second-order reaction rate constant of compound with ozone
k_{OH}	second-order reaction rate constant of compound with OH radical
t	time

Integrating the Equation 2.13 and substituting the OH radical concentration with $R_{CT} = [OH\bullet]/[O_3]$ i.e. ratio of hydroxyl and ozone exposure (details in Section 2.3.3), the following equation is obtained:

$$\ln\left(\frac{C}{C_O}\right) = -(k_{O3} + k_{OH}\, R_{CT}) \int [O_3]\, dt \qquad (2.14)$$

C_o	initial concentration of compound (at time t = 0)
C	concentration of compound at time t

This is analogous to the disinfection kinetics earlier (Equation 2.7 and 2.8). From the Equation 2.13 and 2.14, the fraction of a compound that reacts with hydroxyl radical $\left(f_{OH,C}\right)$ and molecular ozone (f_{O3}) is:

$$f_{OH,C} = \frac{k_{OH} R_{CT}}{(k_{O3} + k_{OH} R_{CT})} \tag{2.15}$$

$$f_{O3} = 1 - f_{OH,C} \tag{2.16}$$

In case of ozonation of low pH water or wastewater having high concentration of OH radical scavengers, the oxidation by OH radicals will be ineffective (Hoigné and Bader, 1983a). In this case, ignoring the terms related to OH radicals in Equation 2.14, it can be rewritten as:

$$\ln\left(\frac{C}{C_O}\right) = -k_{O3} \int [O_3]\, dt \tag{2.17}$$

From this equation, the half-life of compound C, due to oxidation with ozone is:

$$t_{1/2} = \frac{0.69}{[O_3] x\, k_{O3}/\eta} \approx \frac{0.69}{[O_3] x\, k_{O3}} \tag{2.18}$$

In the above equation, η is the short-circuiting factor, and is considered as unity for a batch type reactor or a plug flow reactor. If the second-order reaction rate constant of the compound is known, equation 2.18 gives an indication if the compounds will oxidize by ozonation in typical water or wastewater treatment plant. Consider a typical wastewater ozonation unit having a dissolution chamber with 2 minutes of detention

time, typical transferred ozone dose of 4 mg/L and a residual ozone concentration at the outlet of this chamber of 2 mg/L (approximately 4 x 10^{-5} M). Assuming uniform concentration of the compound and ozone in the chamber, ozone concentration drops to below detection limit in the first contact column, and the detention time in dissolution chamber equal to the half-life of the compound, the reaction-rate constant (k_{O3}) of 140 M^{-1} s^{-1} is calculated. This indicates that only the compounds that have reaction-rate constants greater than 140 M^{-1} s^{-1} will oxidize by more than 50% if hydroxyl radicals do not contribute significantly in their oxidation. At typical ozone doses for disinfection of MWWE, since the exposure of oxidant decreases significantly in the chambers following the dissolution chamber, the majority of the oxidation of the compounds will occur in the dissolution chamber itself.

CHAPTER III

DESIGN AND METHODOLOGY

3.1 SOURCE AND QUALITY OF MWWE

A pilot plant was set-up at the Little River Pollution Control Plant (LRPCP), Windsor, Ontario, Canada for ozone treatment of secondary treated MWWE. LRPCP has a treatment capacity of 73,000 m^3/day. Figure 3.1 shows the treatment process of LRPCP. It consists of preliminary and primary treatment, followed by biological treatment (activated sludge process). The treatment process includes the addition of alum after grit removal to enhance coagulation and phosphorus removal. In general, the effluent BOD_5 and TSS values are less than 10 mg/L (personal communication with Chris Manzon, Plant Manager, LRPCP). The plant discharges the effluent with or without disinfection into Little River that leads into the Detroit River. The plant meets the specified disinfection requirement of < 200 MPN *E. coli*/100 mL during the months of April-October with UV disinfection. In the current study, the municipal wastewater plant effluent (MWWE) before disinfection was the feed water (influent) to the pilot unit.

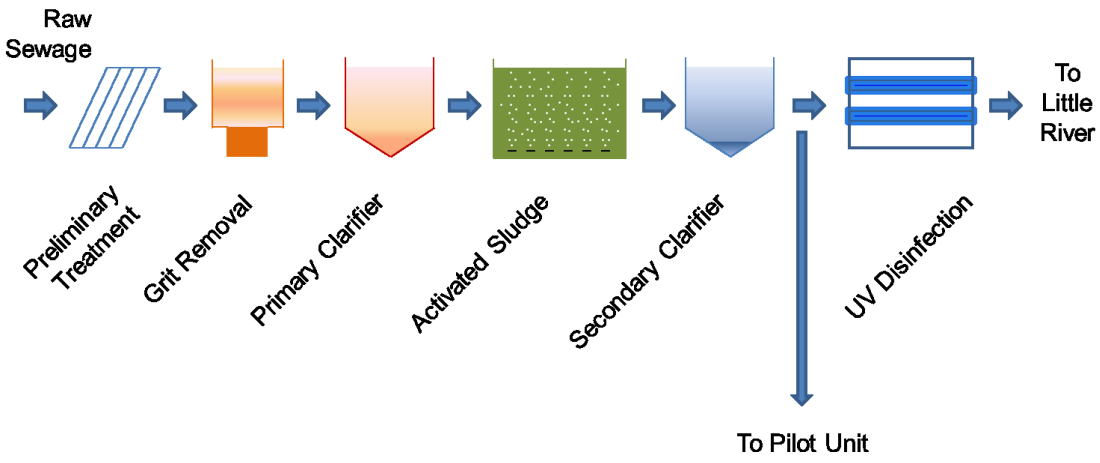


Figure 3.1 Treatment process of LRPCP

3.2 PILOT UNIT

Figure 3.2 shows the schematics while Figure 3.3 shows the picture of the pilot unit. Pilot unit consisted of an ozone contactor, ozone generator (Lab2B, Triogen, Glasgow, UK), and ozone monitor (Model 454, Teledyne, San Diego, USA). Air was the feed gas to generate ozone. The ozone contactor comprised of a dissolution chamber (DC) and four reaction chambers (RC#1 to RC#4). The material of the columns was clear PVC and that of fittings was ozone resistant stainless steel or Teflon. MWWE was collected in a 300 L feed tank, from where it was transferred to the top of the DC by a peristaltic pump. A coarse bubble glass diffuser dispersed the air enriched with ozone at the bottom of the dissolution chamber. The water flowed counter-current to the rising gas bubbles. Ozonated wastewater from the DC entered the first reaction chamber (RC#1) from the bottom and flowed upwards. Similarly, the flow entered the column RC#2 from the top and the columns RC#3 and RC#4 from the bottom. The column RC#4 provided additional contact time to ensure that effluent from the pilot unit did not contain any residual ozone. When operated in continuous flow mode at a flow rate of 4 L/min, the

hydraulic retention time (HRT) in the DC and in RC#1 to RC#3 was 1.7 minutes in each of them. The HRT in RC#4 was 10 minutes. Table 3.1 lists the design parameters of the ozone contactor. Sampling ports were provided at the inlet of the dissolution chamber, and at the outlet of all the five chambers.

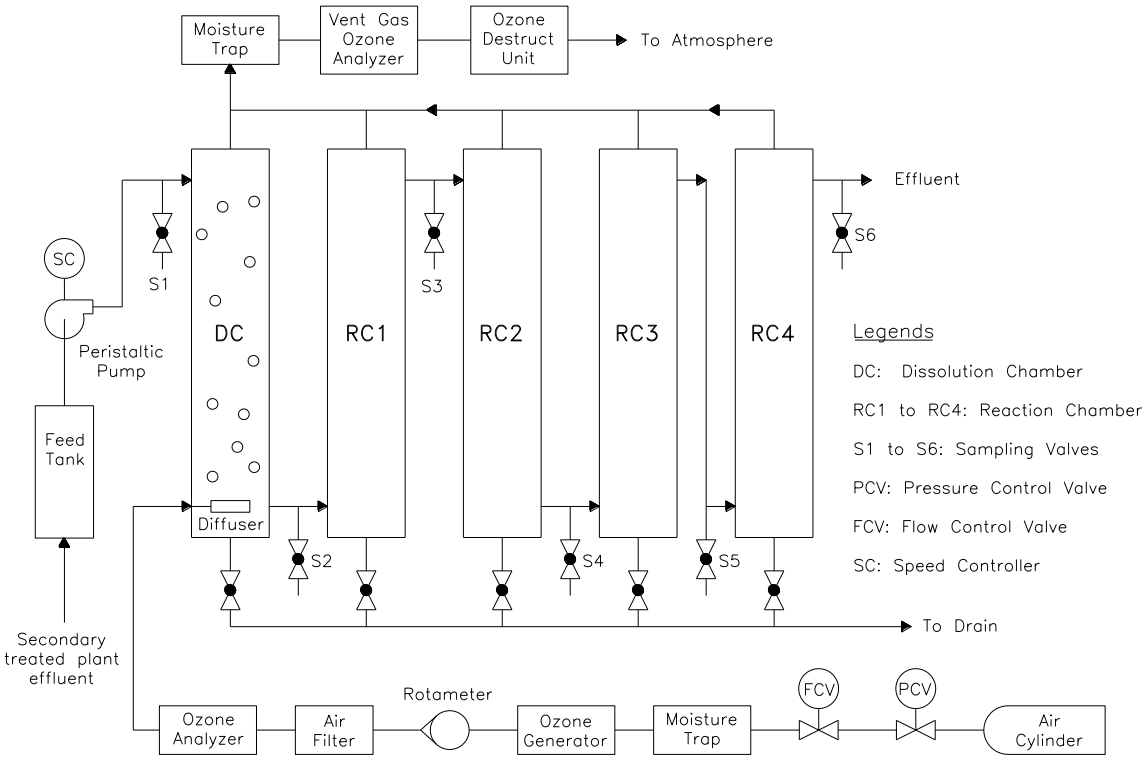


Figure 3.2 Schematic of the pilot unit

Figure 3.3 **Picture of the pilot unit installed at LRPCP**
(inset picture shows the ozone generator and monitor)

Table 3.1 **Design parameters of ozone contactor**

Parameter	Value			
Column #	DC, RC #1, #2, #3		RC#4	
Column internal diameter	88.9 mm (3.5”)		215.9 mm (8.5”)	
Column height (total)	1.8	m	1.8	m
Water height (average)	1.1	m	1.1	m
Volume	6.82	L	40.2	L
Hydraulic retention time @ design flow of 4 L/min	1.7	min	10.0	min

3.3 GRANULAR ACTIVATED CARBON FILTER

To investigate the mutagenicity of ozone treated MWWE filtered through granular activated carbon (GAC), a GAC filter was designed and operated as an adsorption column. The internal diameter of the filter was 89 mm (3.5 inch) and the

carbon bed depth was 490 mm. Calgon make Filtrasorb® 300 activated carbon having effective size of 0.8 to 1 mm was used. Ozone treated MWWE was pumped to the top of the GAC filter by a peristaltic pump at a flow rate of 200 mL/min. The empty bed contact time was around 15 minutes. The filtered MWWE was discharged from the bottom of the filter, and samples were collected for mutagenicity test after minimum 45 minutes of operation of the filter.

3.4 SELECTION OF VARIABLES

As discussed earlier, the disinfection efficiency and removal of CECs by ozonation is dependent on characteristics of MWWE such as temperature, pH, alkalinity, organic carbon content, etc. and transferred ozone dose. In this study conducted with actual MWWE, the only parameter controlled was TOD. The remaining parameters were monitored. The physicochemical characteristics of the sample that change after ozonation, such as turbidity and dissolved oxygen level, were also monitored. Ozonation transforms the characteristics of the CECs present in the MWWE and reduces the aromaticity. The aromaticity of the MWWE was monitored by measuring its UVA. The list of parameters monitored and analyzed in this study is as per Table 3.2. The physicochemical parameters were monitored and analyzed either at the site or in the Environmental Laboratory of University of Windsor. Ontario MOE laboratory carried out the analyses of the CECs.

Table 3.2 List of parameters monitored and analyzed

Parameter	Sampling Point	Purpose
Water flow rate	Outlet of column RC#4	Check system performance
pH	Upstream of DC and downstream of RC#4	- As above
Temperature	- As above	- As above
Dissolved oxygen (DO)	- As above	- As above
Alkalinity	- As above	- As above
Turbidity	- As above	To measure color
UV absorption at 456 nm	- As above	To measure color
Ozone dose Ozone residual	Upstream of DC Downstream of DC, RC#1, 2, 3, 4	Calculate ozone exposure, ozone consumed
Total organic carbon, Dissolved organic carbon	Upstream of DC and downstream of RC#4	Check system performance
UV absorption at 254 nm	- As above	To measure aromaticity
E. coli and total coliform enumeration	Upstream of DC and downstream of RC#2, 4	To monitor disinfection
CEC analysis	Upstream of DC and downstream of RC#4	To determine the transformation of CECs

3.5 SELECTION OF OZONE DOSE

Two different ozone doses were selected based on the literature review and preliminary experiments. The criteria for selection were:

(a) Minimum ozone dose that meets Ontario MOE (2008) disinfection target of < 200 MPN *E. coli* /100 mL,

(b) Ozone dose that consistently meets the disinfection target as well as it produces residual ozone at the outlet of the first reaction chamber (RC#1).

3.6 SAMPLING AND ANALYSIS PROCEDURE

3.6.1 Ozone concentration in the feed gas and vent gas

A microprocessor based ozone monitor (Teledyne, model: 454M) measured ozone concentration in the feed gas and the vent gas. This monitor quantifies the ozone in the air by measuring UV absorption at 254 nm.

3.6.2 Ozone concentration in wastewater

Reagent and material: Commercial grade indigo trisulfonate reagent (Sigma-Aldrich make)

Instrument: Spectronic 20D+ spectrophotometer

Procedure: Wastewater samples were collected from the sampling ports for residual ozone analysis. The sampling lines were flushed thoroughly by discarding the initial flow for a couple of seconds. In addition, while adding the wastewater samples to the flask containing reagent, care was taken to ensure that the samples do not run down the side of the flask as it could cause ozone off-gassing. The ozone residual in wastewater was

measured as per the Standard Methods: 4500-O_3 B, indigo colorimetric method. When the applied ozone concentration was changed, samples for residual ozone analysis were collected only after minimum three hydraulic turnovers in the ozone contactor.

3.6.3 Total organic carbon (TOC)

Reagent & Material: 100-micron nylon mesh, phosphoric acid

Instrument: Shimadzu TOC-V_{CSH} Total Organic Analyzer

Procedure: The TOC concentration in wastewater was measured as per the Standard Methods (5310-B, Combustion-Infrared Method) by APHA (1998), and Method 415.3 by USEPA (2009). The samples were collected in clean amber glass bottles, and immediately stored at 4 deg. C. They were processed and analyzed within 48 hours of collection. Just before analysis, the samples were filtered with 100-micron nylon mesh and acidified to pH $\leq$ 2 by adding concentrated phosphoric acid (H_3PO_4). As the concentration of organic carbon was low (< 10 mg C/L), the NPOC (non purgeable organic carbon) method of the TOC analyzer was selected for analysis. The total hydraulic retention time of the treated MWWE from the wastewater treatment plant was in the range of 10 to 24 hours. After the conventional treatment, it was assumed that there would be a negligible amount of purgeable organic carbon left, hence NPOC method was deemed appropriate to use. The samples were analyzed within 24 hours of collection.

3.6.4 Dissolved Organic Carbon (DOC)

Reagent & Material: 0.45 μm polyethersulfone (PES) filter, phosphoric acid

Instrument: Shimadzu TOC-V_{CSH} Total Organic Analyzer

Procedure: The procedure for DOC analysis is same as that of TOC. The samples were filtered with 0.45 μm PES filter, and acidified to pH ≤ 2 by adding concentrated phosphoric acid (H_3PO_4). The samples were analyzed within 24 hours of collection.

3.6.5 UV absorption at 254 nm (UVA)

Reagent & Material: 0.45 μm polyethersulfone filter

Instrument: Varian Cary 50 UV/Visible Spectrophotometer

Procedure: The sample was filtered with 0.45 μm polyethersulfone filter. The filtrate was not acidified as it might have interfered with UV absorption at 254 nm (UVA). The UVA was measured as per the Standard Methods, Part 5910 B, Ultraviolet Absorption Method (APHA, 1998).

3.6.6 Colour

The colour of municipal wastewater is frequently monitored in the Pt-Co units by visually comparing it with Pt-Co standards. To increase accuracy and reduce reliance on the judgment of the lab analyst for colour measurement, the colour was measured as per the method proposed by Bennett and Drikas (1993). The true colour was measured within 12 hours of collection of the samples.

Reagent & Material: 0.45 μm polyethersulfone filter

Instrument: Varian Cary 50 UV/Visible Spectrophotometer and Turbidity meter (Hach make, Model: 2100 AN)

Procedure: The sample was filtered with 0.45 μm polyethersulfone filter. The filtrate was not acidified. The turbidity in NTU and UV absorption at 456 nm was measured. Colour (Hazen units) was calculated as per the following formula:

$$C_{tc} = \left[\left(\frac{A}{L}\right) - E \bullet t\right] x \frac{1}{\varepsilon_c} \qquad (3.1)$$

C_{tc} = true colour (Hazen units)

A = total absorbance due to dissolved coloured species

L = cell path length (cm)

E = coefficient of scattering ($NTU^{-1}.cm^{-1}$)

= 0.00264 $NTU^{-1}.cm^{-1}$ (at 456 nm)

t = turbidity (NTU)

ε_c = colour absorptivity ($HU^{-1}.cm^{-1}$)

= 0.00027 $HU^{-1}.cm^{-1}$ (at 456 nm)

3.6.7 Alkalinity

The alkalinity was measured as per Standard Methods 2320 (APHA, 1998).

3.6.8 pH, Dissolved Oxygen and Temperature

The above parameters were measured with Hach portable multi-meter (Model HQ40D), and Hach pH and dissolved oxygen probes.

3.6.9 Disinfection of wastewater

E. coli and total coliform enumeration was carried out by USEPA approved Colilert® method.

Reagent & Material: Colilert®- 18, Quanti-Tray® - 2000

Instrument: Quanti-Tray® sealer, UV lamp (365 nm)

Procedure: Samples were collected in sterile bottles containing sodium thiosulphate. Samples expected of containing disinfection-indicator microorganism count of more than 2000 MPN/100mL were diluted with sterilized deionised water. Colilert®- 18 reagent by Idexx Corp. was added to 100mL samples (or diluted sample). The samples were transferred to sterile quantification trays (Quanti-Tray®-2000 by Idexx) and sealed mechanically. The sealed trays were incubated at 37 ^{o}C for 18 to 22 hours. *E. coli* enumeration was performed by counting fluorescent wells under 365-nm UV light. The yellow coloured wells were counted to determine the total coliform count. The *E. coli* and total coliform levels were then reported as most probable number (MPN) per 100 mL.

3.6.10 Mutagenicity of secondary and tertiary treated MWWE

The mutagenicity of the MWWE pre-ozonation, MWWE post-ozonation, and MWWE post-ozonation + GAC filtration, was evaluated with the modified Ames fluctuation test. Rao and Lifshitz (1995) describe the detail about this method and the reagents. The Muta-Chromo Plate kit by Environmental Bio-Detection Products Inc., Canada, was used for this test. The TA 98 and TA 100 strain of *Salmonella typhimurium* were initially tested. TA 100 strain was found to be more sensitive to the MWWE samples and was selected for the mutagenicity test. The MWWE samples to be tested

were filtered-sterilized with 0.22 μm membrane filter. Based on the required concentration of the sample, it was diluted with sterile distilled water to a final volume of 17.5 mL. A 2.5 mL of reaction mixture and 20 μL of bacteria grown overnight in nutrient broth was added to it. The mixture was stirred to mix thoroughly. Using a multi-channel pipette, 200 μL of the mixture was dispensed into 96-well micro-titration plate. The plate was then sealed to prevent evaporation and was incubated at 37^{o}C for six days. The direct acting mutagen, sodium azide, was used as positive control for TA 100 and sterile distilled water as negative control. The background treatment plate consisted of distilled water, reaction mixture, and bacteria.

The plates were scored visually. All yellow, partially yellow, or turbid wells were counted as positive and purple wells were scored negative. The ratio of positive scores of the sample plates with background plate was determined and statistical evaluation carried out using Chi-square analysis (Gilbert, 1980). The samples were considered mutagenic if the positive score of sample plates were significantly higher than the number of positive scores of background plate. In the current study, the samples were analyzed in triplicate. The results are expressed as mutagenicity ratio (MR) and are the average of the triplicates (± standard error).

3.7 CALCULATIONS

3.7.1 Ozone exposure

Ozone exposure, also referred to as CT value, was calculated as per the Extended Integrated CT_{10} method (Rakness et al., 2005). Wert et al. (2009a) have calculated a short-circuiting factor (SCF) of 0.6 for their ozonation pilot unit with pipe contactors.

This SCF was selected in the current study. This value is also in line with the SCF (or T_{10}/T) values given as guidance in the USEPA (1999).

C = concentration of ozone in water (i.e. residual ozone)

T_{10} = time period in which 10% of the water that enters a contactor has passed through

= hydraulic detention time of the contactor (volume/flow rate) x short-circuiting factor (SCF)

3.7.2 Applied Ozone Dose (AOD)

The applied ozone dose is the amount of ozone directed from the ozone generator to unit volume of water treated. The following equation was used to calculate AOD (in mg/L):

$$AOD = (O_3)_{feed} \times \frac{Q_{gas}}{Q_{water}} \qquad (3.2)$$

$(O_3)_{feed}$: ozone concentration in the feed gas, mg/L

Q_{gas} : feed gas flow rate, L/min

Q_{water} : wastewater flow rate, L/min

3.7.3 Transfer Efficiency (TE)

Transfer efficiency is used to define the percentage of the applied ozone dose that has been used and dissolved in the aqueous solution and is not lost in the vent gas. It is affected by various parameters such as contactor design, operating conditions, wastewater characteristics, etc. TE was calculated as under:

$$TE = \frac{\{(O_3)_{feed} - (O_3)_{vent}\}}{(O_3)_{feed}} \times 100\% \quad (3.3)$$

$(O_3)_{vent}$: ozone concentration in the vent gas, mg/L

3.7.4 Transferred Ozone Dose (TOD)

This is the amount of ozone added from the gaseous air containing ozone to the wastewater. The following formula was used to calculate TOD (in mg/L):

$$TOD = \{(O_3)_{feed} - (O_3)_{vent}\} \times \frac{Q_{gas}}{Q_{water}} \quad (3.4)$$

or

$$TOD = AOD \times TE \quad (3.5)$$

In the above formula, it is assumed that the feed gas flow rate and the vent gas flow rate are equal. In addition, there is negligible destruction of ozone in the headspace above the water level in dissolution chamber.

3.7.5 Ozone Consumption (Z)

It is the mass of ozone consumed by the wastewater, and is calculated as:

$$Z = \left[\{(O_3)_{feed} - (O_3)_{vent}\} \times \frac{Q_{gas}}{Q_{water}}\right] - (O_3)_{resi} \quad (3.6)$$

or

$$Z = TOD - (O_3)_{resi} \quad (3.7)$$

$(O_3)_{resi}$: residual ozone in the wastewater, mg/L

3.7.6 Specific Ozone Consumption (Z_{spec})

It is the ratio of the ozone consumption and initial dissolved organic carbon:

$$Z_{spec} = \frac{Z}{DOC_O} \quad (3.8)$$

DOC_o : initial dissolved organic carbon, mg/L

3.7.7 Specific UV Absorbance (SUVA)

Specific UV absorbance (SUVA) is the ratio of UV absorption at 254 nm to initial dissolved organic carbon concentration. This parameter characterizes the effluent organic matter (EfOM). SUVA varies with the type of DOC and is highest in the presence of long-chain humic acids (Bratby, 2006). As per Edzwald and Tobiason (1999),

- SUVA > 4 (L/mg.m) indicates that the DOC in the water matrix is highly hydrophobic and has high molecular weight (MW);
- SUVA in the range of 2 to 4 (L/mg.m) indicates the presence of a mixture of hydrophobic and hydrophilic organic matter;
- SUVA < 2 (L/mg.m) indicates that the organic matter is mostly non-humic, has low hydrophobicity and has low MW.

The molecules with lower MW are generally more biodegradable than molecules with larger MW (Çeçen and Aktas, 2012). SUVA gives an indirect indication of the biodegradability of the raw and ozonated water, and value of < 2 (L/mg.m) indicates that the water contains biodegradable organics that can be removed by biofiltration (Çeçen

and Aktas, 2012). Hence, the lower the SUVA value, the higher is the biodegradability of the organics in the water matrix.

The formula to calculate SUVA is:

$$SUVA\left(\frac{L}{mg.m}\right) = \frac{UV_{254}\left(\frac{1}{cm}\right)}{DOC_O\left(\frac{mg}{L}\right)} \times \frac{100\ cm}{m} \qquad (3.9)$$

3.8 ANALYSIS OF CECs AT ONTARIO MOE LABORATORY

Samples packed in ice to maintain sample temperature to around 4 ^{o}C were shipped to the Mass Spectroscopy Laboratory of Ontario Ministry of the Environment (Toronto, Canada) for the analyses of the target CECs. Solid phase extraction (SPE) was used to extract the samples and liquid chromatography/tandem mass spectrometry and isotope dilution mass spectrometry were used to analyse the samples. Hao et al. (2008) describe details of the methodology and quality control procedure. Table 3.3 shows the list of the CECs targeted in the current study and their detection limits (DLs).

Table 3.3 List of target CECs (PhACs and EDCs)

Antibiotics		DL, ng/L	**Antiphlogistics**		DL, ng/L
1	Carbadox	10	24	Acetaminophen	2
2	Chloramphenicol	2	25	Diclofenac	1
3	Chlortetracycline	10	26	Ibuprofen	0.5
4	Ciprofloxacin	0.5	27	Indomethacin	5
5	Doxycycline	5	28	Ketoprofen	2
6	Enrofloxacin	5	29	Naproxen	2
7	Erythromycin	10	**Antidepressant**		
8	Lasalocid A	10	30	Carbamazepine	1
9	Lincomycin	0.5	**Anticoagulant**		
10	Meclocycline	10	31	Warfarin	5
11	Norfloxacin	10	**Lipid Regulators**		
12	Oxytetracline	5	32	Bezafibrate	0.5
13	Roxithromycin	2	33	Clofibric acid	1
14	Sulfachloropyridazine	5	34	Gemfibrozil	1
15	Sulfadiazine sodium	5	**Estrogen Replacement Agents**		
16	Sulfadimethoxine	1	35	Bisphenol-A (BPA)	2
17	Sulfamerazine	1	36	Diethylstilbestrol	10
18	Sulfamethazine	1	37	Equilin	2
19	Sulfamethizole	2	**Ovulation Inhibitors**		
20	Sulfamethoxazole	2	38	19-Norethersterone	5
21	Sulfathiazole	2	**Reproductive Hormones**		
22	Tetracycline	10	39	17-α-Estradiol	5
23	Trimethoprim	10	40	17-β-Estradiol	2
			41	Estrone	2
			42	Estriol	5
			43	Progesterone	20
			Ionophore		
			44	Monensin sodium	10

Legend: DL: Detection limit

3.9 SUMMARY OF THE PARAMETERS MONITORED

Table 3.4 summarizes the parameters monitored and the instruments used in this study.

Table 3.4 Summary of the parameters monitored

Sr.	Parameter	Instrument and Method
1	pH	Hach pH probe
2	Temperature	Hach pH/DO probe
3	Dissolved Oxygen	Hach DO probe
4	Alkalinity	Standard Methods , Titration, SM-2320
5	Flow Rate (liquid)	Volumetric cylinder and stop-watch
6	Flow Rate (feed gas)	Rotameter
7	Total Organic Carbon (TOC)	Shimadzu TOC Analyzer, Standard Methods 5310
8	Dissolved Organic Carbon (DOC)	
9	UV absorption at 254 nm (UVA)	UV-Vis Spectrophotometer, SM-5910
10	Color	
	- UV absorption at 456 nm	UV-Vis Spectrophotometer
	- Turbidity	Hach 2100 AN Turbidimeter
11	Transferred Ozone Dose (TOD)	
	- Ozone concentration in feed gas	Ozone analyzer, UV 254 Absorption
	- Ozone concentration in vent gas	Ozone analyzer, UV 254 Absorption
12	SUVA (Ratio of UVA to DOC)	US EPA Method 415.3
13	Disinfection	
	- Ozone residual in water	UV Spectrophotometer (Spectronics), SM 4500-O_3 B, Indigo Colorimetric Method
	- Exposure (CT_{10})	Extended Integrated CT_{10} Method
	- *E. coli* enumeration	Colilert® method by IDEXX, Standard Methods 9223 B
14	Concentration of CECs	Mass Spectrophotometer, Analysis by Ontario MOE

CHAPTER IV

ANALYSIS OF RESULTS

This study was conducted to evaluate the effectiveness of ozone treatment on disinfection of municipal effluent and transformation of pharmaceuticals and EDCs. The results from the study are presented in two parts. Part-I of this chapter consists of results from experiments conducted to determine the ozone dose required to achieve the disinfection target and to correlate disinfection with probable process control parameters. The MWWE was treated with different ozone doses. The disinfection indicator microorganisms, total coliform and *E. coli*, and MWWE characteristics were monitored. The Part-II of this chapter consists of results related to the occurrence and concentration of the CECs in MWWE, and their transformation when MWWE is treated with ozone.

PART – I DISINFECTION OF MWWE WITH OZONE

4.1 MWWE CHARACTERISTICS

Four sets of experiments were conducted to study the effect of different ozone dose on disinfection. The characteristics of the MWWE prior to disinfection are presented in Table 4.1.

Table 4.1 Characteristics of secondary treated MWWE before ozone treatment

Experiment	DOC	DO	pH	Temp.	Alkalinity	UVA
	mg/L	mg/L		°C	mg/L as CaCO3	cm^{-1}
Trial #1	5.04	1.59 ± 0.04	7.13 ± 0.02	20.5 ± 0.1	230 – 240	0.1160
Trial #2	5.38 ± 0.11	1.23 ± 0.29	7.11 ± 0.09	20.1 ± 0.2	210	0.1067 ± 0.0015
Trial #3	6.04 ± 0.09	2.08 ± 0.36	7.13 ± 0.14	21.5 ± 0.3	160	0.1065 ± 0.0020
Trial #4	5.33 ± 0.14	2.30 ± 0.21	7.12 ± 0.16	18.8 ± 0.2	170 – 180	0.1075 ± 0.0009

Legends:
DOC: Dissolved organic carbon
DO: Dissolved oxygen
Temp. : Temperature
UVA: UV absorption at 254 nm

The total coliform in the MWWE was in the range of 10^4 to 10^5 MPN/100 mL, which is the typical range for nitrified effluent in North America (USEPA, 1986b). *E. coli* count was in the range of 2,500 to 21,000 MPN/100 mL.

4.2 DISINFECTION OF MWWE WITH OZONE

The secondary treated MWWE was treated with different ozone doses. The goal was to determine the optimum ozone dose required to meet the Ontario MOE disinfection target of < 200 MPN *E. coli*/100 mL for the MWWE of LRPCP.

Table 4.2 represents the results from four experiments. The data indicates that the disinfection criterion was fulfilled sometimes even at low ozone dose of 1.6 to 2.8 mg/L. However, the disinfection target was always achieved at TODs between 3.7 to 4.2 mg/L, and the *E. coli* count in the ozonated MWWE was between 5 and 11 MPN *E. coli*/100 mL.

Table 4.2 Effect of ozone on disinfection

Experiment	DOC	TOD	Residual Ozone		Ozone Exposure (CT_{10})	UVA		Total Coliform		*E coli*	
	mg/L	mg/L	DC	RC #1	mg-min/L	cm^{-1}	% Reduction	MPN/ 100 mL	Log Reduction	MPN/ 100 mL	Log Reduction
Trial #1											
Influent	5.04					0.1160		109,100		21,380	
		1.6	0.10	<0.10	0.04	0.0954	18	365	2.48	48	2.65
		2.3	0.29	<0.10	0.15	0.0835	28	145	2.88	20	3.03
		3.9	0.89	0.14	0.53	0.0744	36	73*	3.17	10	3.35
Trial #2											
Influent	5.38					0.1067		36,940		7,547	
		1.8	<0.10	<0.10	0.02	0.0916	14	> 2420		1613	0.67
		2.8	0.11	<0.10	0.05	0.0768	28	422	1.95	50	2.19
		4.2	0.63	0.05	0.37	0.0649	39	79	2.70	11	2.86
Trial #3											
Influent	6.04					0.1065		46,177		11,403	
		1.4	<0.10	<0.10	0	0.1027	4	> 2420	< 1.28	> 2420	< 0.67
		1.8	<0.10	<0.10	0.015	0.1019	4	> 2420	< 1.28	> 2420	< 0.67
		2.7	<0.10	<0.10	0.06	0.0878	18	> 2420	< 1.28	463	1.41
		3.9	0.24	<0.10	0.07	0.0740	31	56	2.93	10	3.06
Trial #4											
Influent	5.33					0.1075		10,893		2,513	
		1.4	0.10	<0.10	0.04	0.0960	11	3006	0.57	348	1.01
		1.8	<0.10	<0.10	0.06	0.0852	21	283	1.60	17	2.20
		2.6	0.26	<0.10	0.10	0.0764	29	53	2.43	5	2.70
		3.7	0.82	0.14	0.76	0.0672	38	19	2.77	5	2.79
		7.3	3.22	1.75	6.54	0.0537	50	10	3.03	1	3.60

* This data is for sample taken from the outlet of RC#3. All remaining data related to reduction in total coliform and *E. coli* are for sample from outlet of RC#2.

Legends:
DC: Dissolution chamber
RC #1: First reaction chamber

Ozonation of MWWE did not cause a major change in its DOC, pH, and alkalinity parameters. However, the increase in ozone dose resulted in increase of dissolved oxygen, and reduction in UVA and color of the ozonated MWWE. The DOC to TOC ratio was always greater than 0.95. Table 4.3 represents the data related to the effect of ozone dose on dissolved oxygen concentration, UVA, and color of the MWWE.

Table 4.3 Effect of ozone on DO, UVA and color of secondary treated MWWE

	TOD mg/L	DO mg/L	UV254 Absorbance		True Color	
			cm^{-1}	% decrease	Hazen units	% decrease
Trial #1						
Influent		1.59 ± 0.04	0.1160		11.89	
	1.6	n.m.	0.0954	18	3.33	72
	2.3	7.40	0.0835	28	2.90	76
	3.9	7.95	0.0744	36	1.31	89
Trial #2						
Influent		1.23 ± 0.29	0.1067 ± 0.0015		15.98	
	1.8	7.28	0.0916	14	10.51	34
	2.8	7.87	0.0768	28	4.46	72
	4.2	7.92	0.0649	39	2.35	85
Trial #3						
Influent		2.08 ± 0.36	0.1065 ± 0.0020		17.28	
	1.4	7.01	0.1027	4	9.21	47
	1.8	7.18	0.1019	4	7.34	58
	2.7	7.70	0.0878	18	5.63	67
	3.9	7.84	0.0740	31	1.38	92
Trial #4						
Influent		2.30 ± 0.21	0.1075 ± 0.0009		13.91	
	1.4	n.m.	0.0960	11	6.83	51
	1.8	7.45	0.0852	21	6.13	56
	2.6	7.92	0.0764	29	4.48	68
	3.7	8.09	0.0672	38	2.72	80
	7.3	18.84	0.0537	50	1.35	90

Legends: TOD: Transferred ozone dose DO: Dissolved oxygen n.m.: not measured

In three experiments, ozonated MWWE samples were taken from the outlet of the dissolution chamber and reaction chambers, to determine the level of disinfection achieved at different contact times. The results are presented in Table 4.4. Results indicate that disinfection of MWWE with ozone is a fast process. At the transferred ozone doses, the level of disinfection did not increase after the first reaction chamber.

Table 4.4 Effect of contact time on disinfection

Experiments	TOD	Column	Total Contact Time*	Residual ozone	Total coliform		*E. coli*	
	mg/L		min	mg/L	MPN/ 100 mL	Log Reduction	MPN/ 100 mL	Log Reduction
Trial #1								
Influent					109,100		21,380	
	1.6	DC		0.10	488	2.35	59	2.56
		RC#1	1.7	<0.10	365	2.48	48	2.65
		RC#2	3.4	<0.10	435	2.40	66	2.51
		RC#3	5.1	<0.10	365	2.48	61	2.55
	2.3	DC		0.29	161	2.83	34	2.80
		RC#1	1.7	<0.10	145	2.88	20	3.03
		RC#2	3.4	<0.10	173	2.80	26	2.92
		RC#3	5.1	<0.10	130	2.93	34	2.80
	3.9	DC		0.89	121	2.95	18	3.07
		RC#1	1.7	0.14	ND	-	10	3.35
		RC#2	3.4	<0.10	35	3.49	4	3.72
		RC#3	5.1	<0.10	73	3.17	11	3.30
Trial #2								
Influent					36,940		7,547	
	1.8	RC#1	1.7	<0.10	> 2420	< 1.18	1613	0.67
		RC#4	6.8	<0.10	> 2420	< 1.18	1567	0.68
	2.8	RC#1	1.7	<0.10	422	1.95	50	2.19
		RC#4	6.8	<0.10	658	1.75	56	2.14
	4.2	RC#1	1.7	<0.10	79	2.70	11	2.86
		RC#4	6.8	<0.10	90	2.61	13	2.78
Trial #3								
Influent					46,177		11,403	
	1.8	RC#1	1.7	<0.10	> 2420	< 1.28	> 2420	< 0.67
		RC#4	6.8	<0.10	> 2420	< 1.28	> 2420	< 0.67
	2.7	RC#1	1.7	<0.10	> 2420	< 1.28	463	1.41
		RC#4	6.8	<0.10	> 2420	< 1.28	558	1.31
	3.9	RC#1	1.7	<0.10	56	2.93	10	3.06
		RC#4	6.8	<0.10	85	2.74	11	3.06

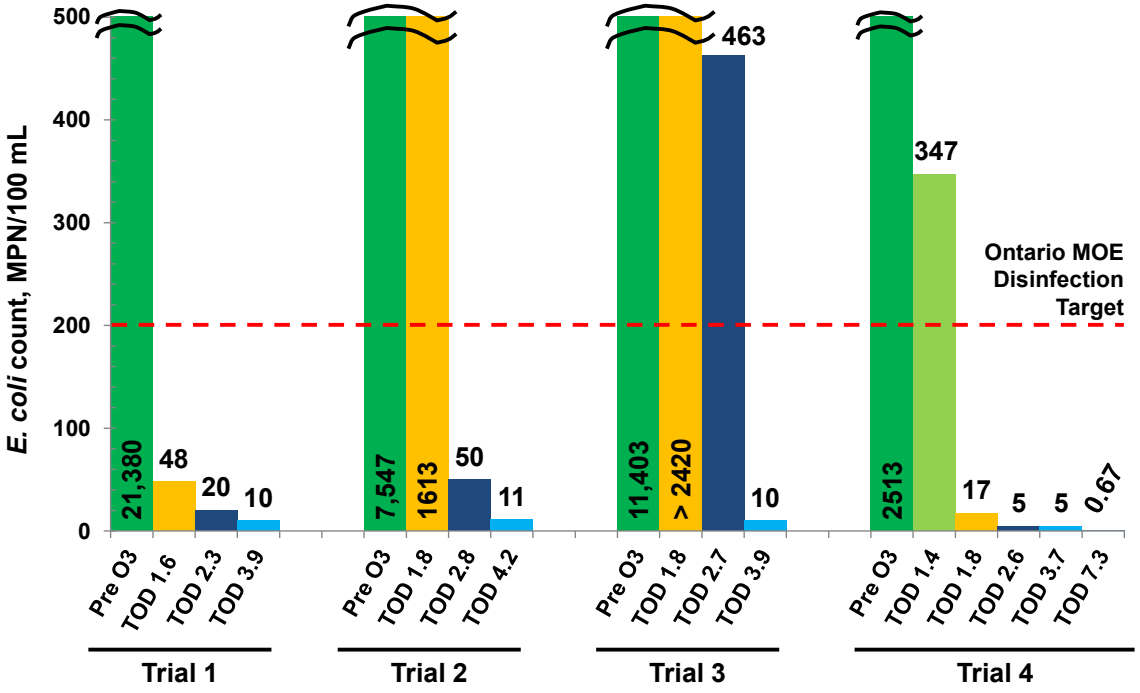
* Total contact time does not include the 1.7 minute of contact time in dissolution chamber

4.3 CORRELATION BETWEEN DISINFECTION AND PROBABLE PROCESS CONTROL PARAMETERS

4.3.1 Transferred Ozone Dose

In the four experiments conducted, at transferred ozone dose of 1.4 to 4.2 mg/L, the total coliform log reduction was in range of <1.28 to 3.17, and the *E. coli* log reduction was in the range of <0.67 to 3.35 (Table 4.2)

Figure 4.1 depicts the graphical presentation of *E. coli* inactivation at different transferred ozone doses.



Legends Pre O3:MWWE before ozonation

TOD: Transferred ozone dose (mg/L), eg. TOD 1.6 = transferred ozone dose of 1.6 mg/L

Figure 4.1 Effect of transferred ozone doses on *E. coli* inactivation

The results indicate that the disinfection target of < 200 MPN *E. coli*/100 mL was achieved even at relatively low ozone doses of 1.6 to 2.8 mg/L. However, on some occasions this ozone dose did not fulfill the disinfection criterion. At TOD of 3.7 to 4.2 mg/L, the log reduction of the disinfection indicating microorganisms was always greater than 2.7 and the disinfection target was achieved consistently. This level of disinfection is similar to the results reported by other studies.

Table 4.5 compiles the disinfection data reported by some studies. The data indicates variation in the disinfection efficiency with ozone, as expected, due to the difference in the MWWE characteristics. However, for an ozone dose of 0.2 to 0.8 mg O_3/mg C, the *E. coli* log reduction is in the range of 1.58 to 4.94. In most cases, the *E. coli* after ozonation is less than 200 MPN/100 mL. The total coliform log reduction is in the range of 1.82 to 3.48.

TOD has been considered the most important parameter in disinfection by ozone treatment (Xu et al., 2002; Paraskeva and Graham, 2005). Some researchers have proposed TOD as process control parameter for disinfection (Stover and Jarnis, 1981; Venosa and Meckes, 1983). The dose/response curve proposed by USEPA (1986a) attempts to correlate the TOD with the reduction of disinfection indicator microorganisms. Figure 4.2 and Figure 4.3 present the data related to the dose/response curve for *E. coli* and total coliform as collected in the present study.

Table 4.5 Effect of ozone dose on disinfection of secondary/tertiary treated MWWE

DOC or TOC mg/L	O_3 dose mg/L	Disinfection indicator microorganism	MPN or cfu/100 mL		Log Reduction	Reference
			Pre O_3	Post O_3		
23	5 mg/L (TOD)	*E. coli*			2.75	Ternes et al. (2003)
23	10 mg/L (TOD)	*E. coli*			3.63	Ternes et al. (2003)
8.3 ± 1	22 mg/L (TOD)	*E. coli*	$10^{7.22}$	7	6.38	Finch et al. (1989)
8.3 ± 1	12 mg/L (TOD)	*E. coli*	$10^{7.22}$	76	5.34	Finch et al. (1989)
8.3 ± 1	6 mg/L (TOD)	*E. coli*	$10^{7.22}$	191	4.94	Finch et al. (1989)
8.3 ± 1	3 mg/L (TOD)	*E. coli*	$10^{7.22}$	10^5	2.22	Finch et al. (1989)
7.7 ± 0.5	2 mg/L (TOD)	*E. coli*	5×10^5	2×10^2	3.4	Huber et al. (2005)
7.7 ± 0.5	5 mg/L (TOD)	*E. coli*	5×10^5	$< 10^2$	> 3.7	Huber et al. (2005)
19.6 ± 1.27	5 mg/L (AOD)	*E. coli*	210,000	16×10^3	1.12	Tripathi et al. (2011)
19.6 ± 1.27	10 mg/L (AOD)	*E. coli*	210,000	6×10^2	2.54	Tripathi et al. (2011)
8.8 – 10.1	2 – 6 mg/L (TOD)	*E. coli*	$4x10^4$-$2.5x10^5$	10^2	2.6 – 3.4	Paraskeva et al. (2005)
3.4	0.8 mg/L (TOD)	*E. coli*	20,000	6935	0.46	Zimmermann et al. (2011)
2.4	1.2 mg/L (TOD)	*E. coli*	5,000	50	2.0	Zimmermann et al. (2011)
4.4	2.6 mg/L (TOD)	*E. coli*	6,000	158	1.58	Zimmermann et al. (2011)
4.7	3.8 mg/L (TOD)	*E. coli*	5,000	50	2.0	Zimmermann et al. (2011)
4.1	5.2 mg/L (TOD)	*E. coli*	4,000	57	1.85	Zimmermann et al. (2011)
12	~ 2.4 (TOD)	T.C.	46,000	24,000	0.28	Bahr et al. (2005)
12	~ 4.8 (TOD)	T.C.	46,000	36	3.1	Bahr et al. (2005)
11.4	~ 5.7 (TOD)	T.C.	$10^{4.38} – 10^{5.04}$		1.82	Bahr et al. (2007)
11.4	~ 11.4 (TOD)	T.C.	$10^{4.38} – 10^{5.04}$		2.86	Bahr et al. (2007)
7.2	2.1 mg/L (TOD)	T.C.	> 1600	30	> 1.73	Wert et al. (2007)
7.2	3.6 mg/L (TOD)	T.C.	> 1600	< 2	> 2.9	Wert et al. (2007)
7.2	4.9 mg/L (TOD)	T.C.	6000	< 2	> 3.48	Wert et al. (2007)
~ 19	3.4 mg/L (AOD)	T.C.			2	Lazarova et al. (1998)
~ 19	10 mg/L (AOD)	T.C.			3.3	Lazarova et al. (1998)
19.6 ± 1.27	5 mg/L (AOD)	T.C.	254,000	19,000	1.12	Tripathi et al. (2011)
19.6 ± 1.27	10 mg/L (AOD)	T.C.	254,000	9×10^2	2.45	Tripathi et al. (2011)
8.8 – 10.1	7 – 10 mg/L (TOD)	T.C.	$4x10^4$-$2.5x10^5$	10	3.6 – 4.4	Paraskeva et al. (2005)
5.0 – 8.3	5 mg/L (TOD)	T.C.	$10^{4.28} – 10^{6.86}$	$10^{2.7}$	~ 1.6 – 4.2	Venosa et al. (1983)
5.0 – 8.3	10 mg/L (TOD)	T.C.	$10^{4.28} – 10^{6.86}$	$10^{1.6}$	~ 2.7 – 5.3	Venosa et al. (1983)

Legends:

DOC: Dissolved organic carbon TOC: Total organic carbon

TOD: Transferred ozone dose AOD: Applied ozone dose

T.C.: Total coliform O_3: Ozone

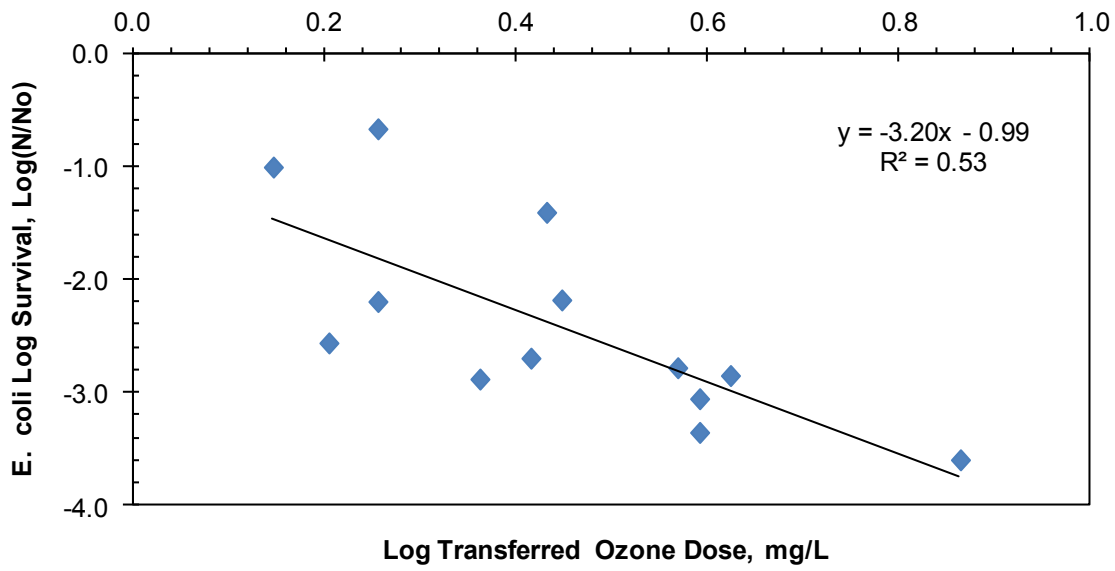


Figure 4.2 **Dose response curve for *E. coli***

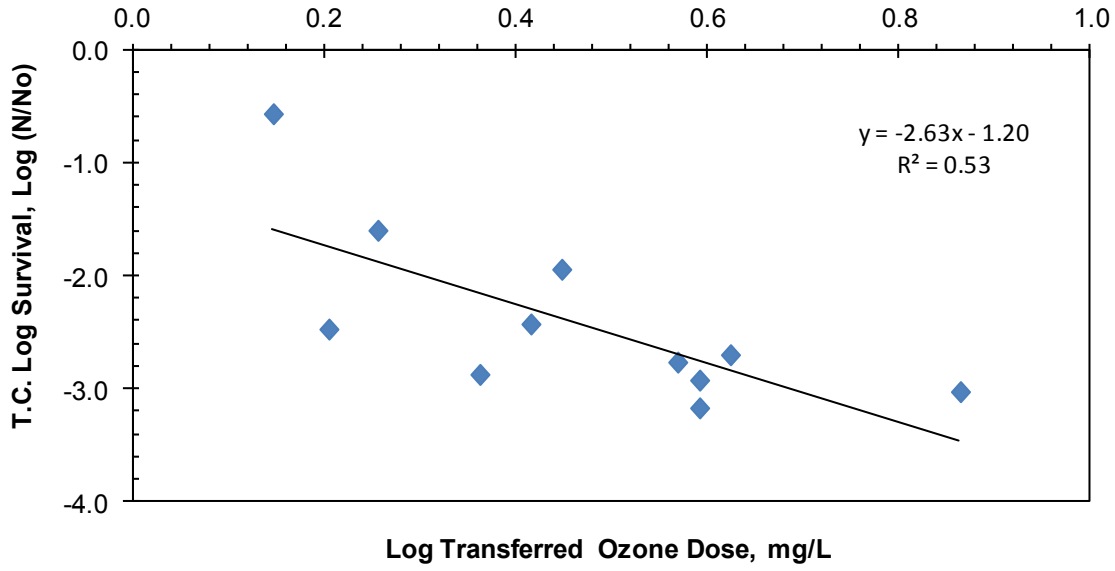


Figure 4.3 **Dose response curve for total coliform**

Table 4.6 compiles the data from the dose/response curve from the current study and from other studies for effluents with initial ozone demand less than 1 mg/L. In the current study, the initial ozone demand of the MWWE was less than 0.5 mg/L, and can be considered as a good quality secondary treated MWWE as the initial ozone demand is less than 1 mg/L (USEPA, 1986b). The data shows that although the TOD is correlated with the reduction in total coliform and *E. coli*, the correlation is not very strong (R^2 value of 0.53 and 0.53). Paraskeva and Graham (2005) have also found a weak correlation between the TOD and level of disinfection (R^2 value of 0.50 to 0.63). This is contrary to the strong correlation (R^2 value of 0.76) reported by USEPA (1986b). As the correlation between the TOD and disinfection is not always strong, it can be concluded that TOD is not be the best process control parameter for disinfection.

Table 4.6 Slope of Dose/Response Curve and Intercept for Ozone Disinfection

Parameter	Slope	Intercept*	Correlation	Reference
E. coli	-3.20	0.49	0.53	Current study
E. coli	-3.44 to - 3.65	0.71 to 0.77	0.54 to 0.63	Paraskeva et al. (2005)
Total Coliform	-2.63	0.35	0.53	Current study
Total Coliform	- 3.04	0.61	0.50	Paraskeva et al. (2005)
Total Coliform	-2.51	0.50	0.76	USEPA (1986b)

* Intercept represents the calculated initial ozone demand.

4.3.2 Residual ozone

In the experiments conducted in this study, different ozone doses were applied and the residual ozone concentrations in effluent leaving the dissolution chamber (DC) and the reaction chambers (RC#1 to RC#4) were measured. Figure 4.4 shows the residual ozone concentration at different time intervals for the four trials. The microbial indicators were also monitored to determine the disinfection achieved. The results are presented earlier in Table 4.2.

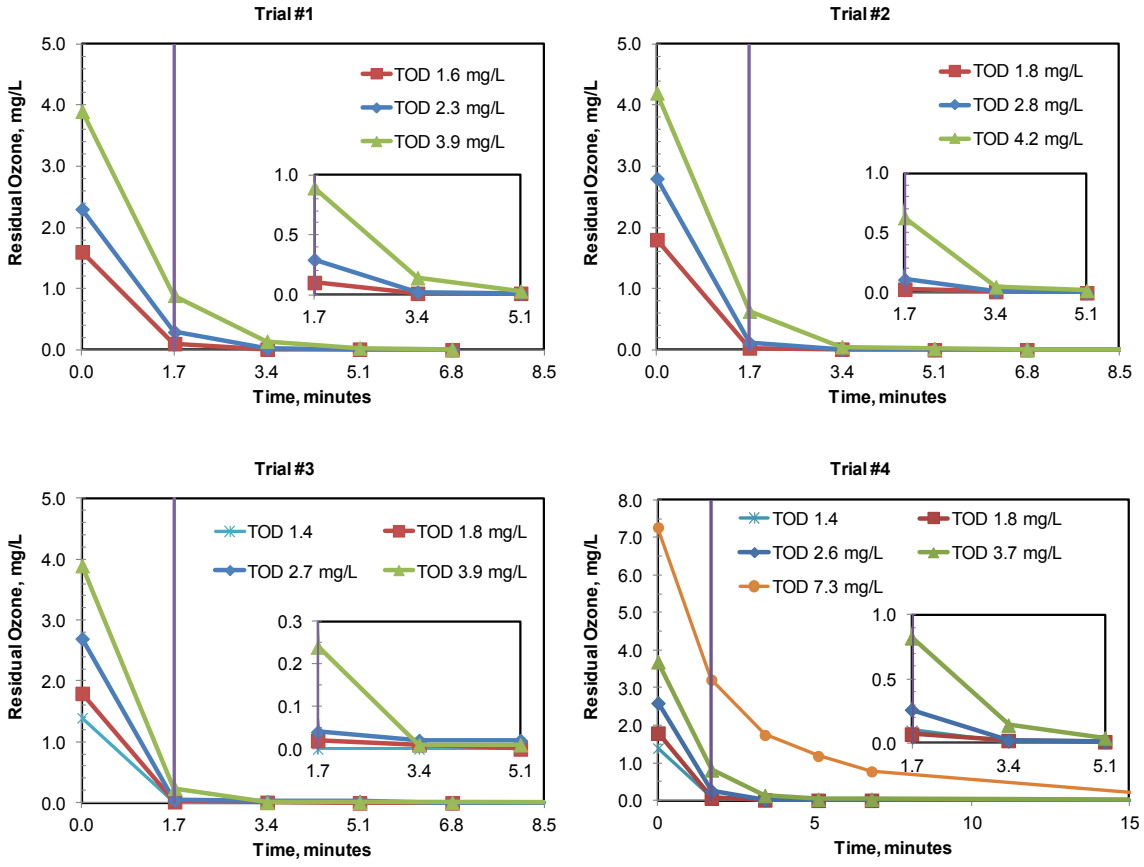


Figure 4.4 Residual ozone concentration at outlet of DC, RC#1, RC#2 and RC#3

Residual ozone at the end of dissolution chamber (DC)

In some of the experiments conducted, the TOD was not sufficient to produce residual ozone in the effluent leaving the dissolution chamber. This can indicate that the TOD was lower than or just equal to the immediate ozone demand (ImOD) of the wastewater matrix. In such cases, the reduction of the microbial indicators was less than 1-log, and the disinfection target of *E. coli* count less than 200 MPN/100mL was not achieved. In most of the cases when the residual ozone at the outlet of the dissolution chamber was greater than 0.1 mg/L, greater than 2-two log reduction of the microbial indicators was observed. At TOD of 3.7 to 4.2 mg/L, the residual ozone was between 0.24 to 0.89 mg/L. Figure 4.5 and Figure 4.6 show the plot of disinfection and corresponding residual ozone in the dissolution chamber.

Residual ozone at the outlet of first reaction chamber (RC#1)

For transferred ozone dose of less than 3 mg/L (approximately 0.5 mg O_3/mg C) or less, the residual ozone at the outlet of the first reaction column (RC#1) was close to zero. The resulting total coliform log reduction was between 0.57 and 2.88 while *E. coli* log reduction was in the range of 0.67 to 3.06. Figure 4.5 and Figure 4.6 show the visual representation of the results. As per the figures, up to 3-log reduction in disinfection parameter was observed at almost zero ozone residual. This result is in line with the findings of other studies (Paraskeva et al., 1999; Xu et al., 2002; Gehr et al., 2003) that have reported greater than 2-log reduction in disinfection parameters at residual ozone concentrations close to zero. At residual ozone concentration close to zero, the ozone exposure (CT value) is almost zero. Hence, the conventional method of correlating ozone

exposure to reduction in disinfection parameter does not apply for wastewater disinfection.

The residual ozone concentration at the outlet of RC#1 was between 0.01 to 0.14 mg/L at transferred ozone dose of approximately 4 mg/L (0.8 mg O_3/mg C). The total coliform log reduction was between 2.7 and 3.13, while *E. coli* log reduction was in the range of 2.79 to 3.35. In all the experiments, the disinfection target was met and total coliform was less than 100 MPN/100 mL while *E. coli* count was less than 15 MPN/100 mL. Ozone exposures for ozone doses from 3.7 to 4.2 mg/L as per the Extended Integrated CT_{10} method were between 0.06 and 0.8 mg-min/L (Table 4.2).

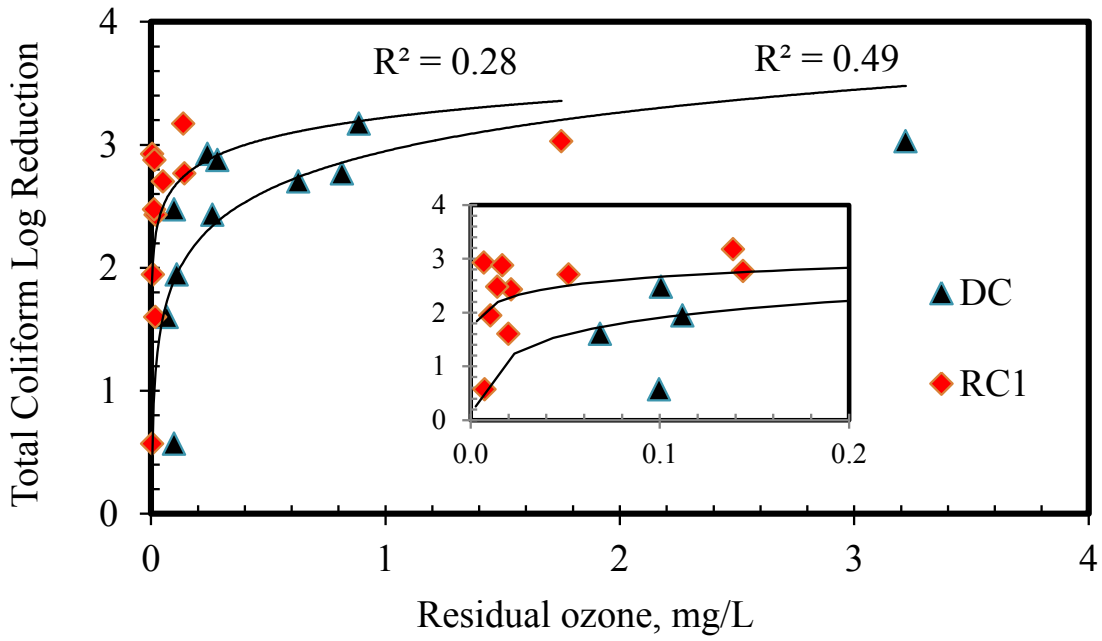


Figure 4.5 **Relationship between residual ozone and total coliform inactivation**

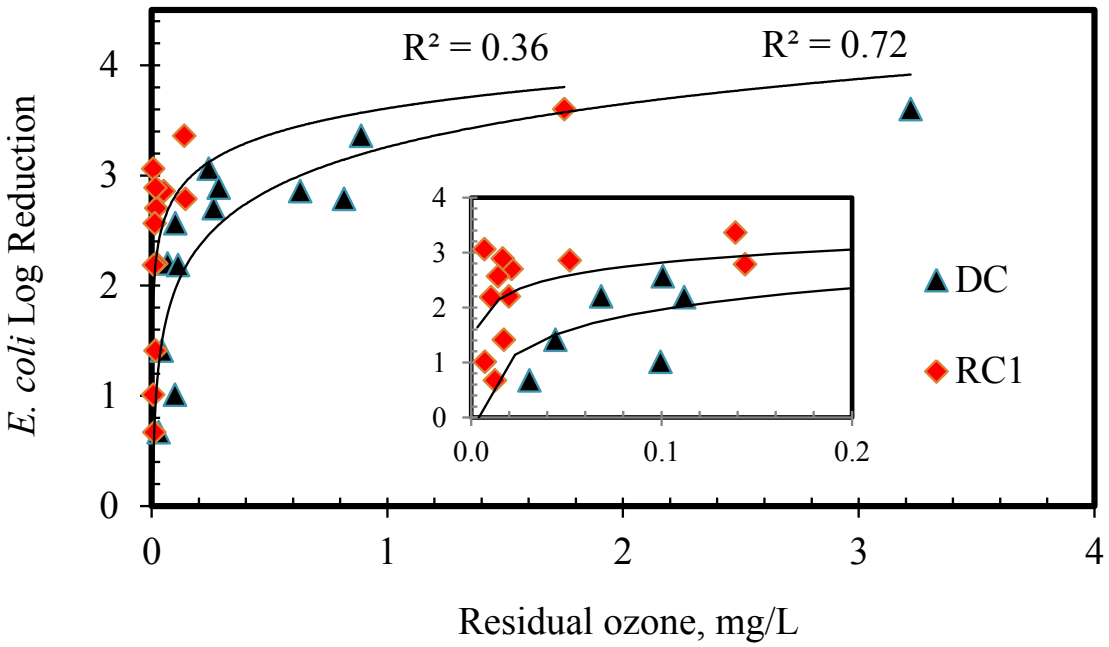


Figure 4.6 **Relationship between residual ozone and *E. coli* inactivation**

As per Figure 4.5 and Figure 4.6, the correlation between residual ozone and inactivation of disinfection indicator microorganisms is not strong. The R^2 value for correlation between reduction of microorganisms and residual ozone at outlet of DC is 0.49 and 0.72, while the value is 0.28 and 0.36 for correlation between reduction in microorganisms and residual ozone at outlet of RC#1. It was observed that greater than 2.5 log reduction in disinfection parameter was achieved when the residual ozone at the outlet of RC#1 was greater than 0.1 mg/L.

From the above, it can be concluded that residual ozone in effluent is not a good disinfection process control parameter. However, residual ozone at the outlet of dissolution chamber and first contact chamber can be monitored to determine if ImOD is fulfilled, and to calculate specific ozone consumption (Z_{spec}). Minimum residual ozone of 0.1 mg/L at the outlet of the first reaction chamber can indicate that a minimum level of disinfection has been achieved. This minimum level of disinfection achieved will depend on the MWWE characteristics. In this study, a minimum of 2.5 log reduction was observed when the residual ozone concentration was 0.1 mg/L.

4.3.3 UV absorption at 254 nm

Studies have shown that the UV absorption at 254 nm (UVA) of MWWE decreases after ozone treatment. Bahr et al. (2007) have attempted to correlate the inactivation of disinfection indicator microorganisms with reduction in UVA. In large-scale ozonation applications, they proposed UVA as a process control parameter for disinfection as well as removal of micropollutants (pharmaceuticals and EDCs) and bromate formation, mainly because of the ease in its analysis and continuous monitoring.

During the literature review, no other study was found that had attempted to correlate disinfection with reduction in UVA. In the current study, an attempt was made to determine the strength of correlation between reduction in UVA and level of disinfection due to ozonation. Figure 4.7 and Figure 4.8 show the results.

For the TOD up to 0.8 mg O_3/mg C, a linear correlation was found to exist between the log reduction in UVA and the log reduction in the microbial indicators. The R^2 values were 0.71 and 0.80 for correlation between reduction in UVA and total coliform, and UVA and *E. coli*. The coefficient of determination (R^2) values from the current study and previous study by Bahr et al. (2007) is presented in Table 4.7.

Table 4.7 Coefficient of determination (R^2) values for correlation between reduction in UVA and inactivation of disinfection indicator microorganisms

Disinfection indicator microorganism	Coefficient of determination (R^2)	Reference
E. coli	0.795	Current study
Total coliform	0.714	Current study
Total coliform	0.764	Bahr et al. (2007)
Fecal coliform	0.572	Bahr et al. (2007)
Intestinal enterococci	0.787	Bahr et al. (2007)

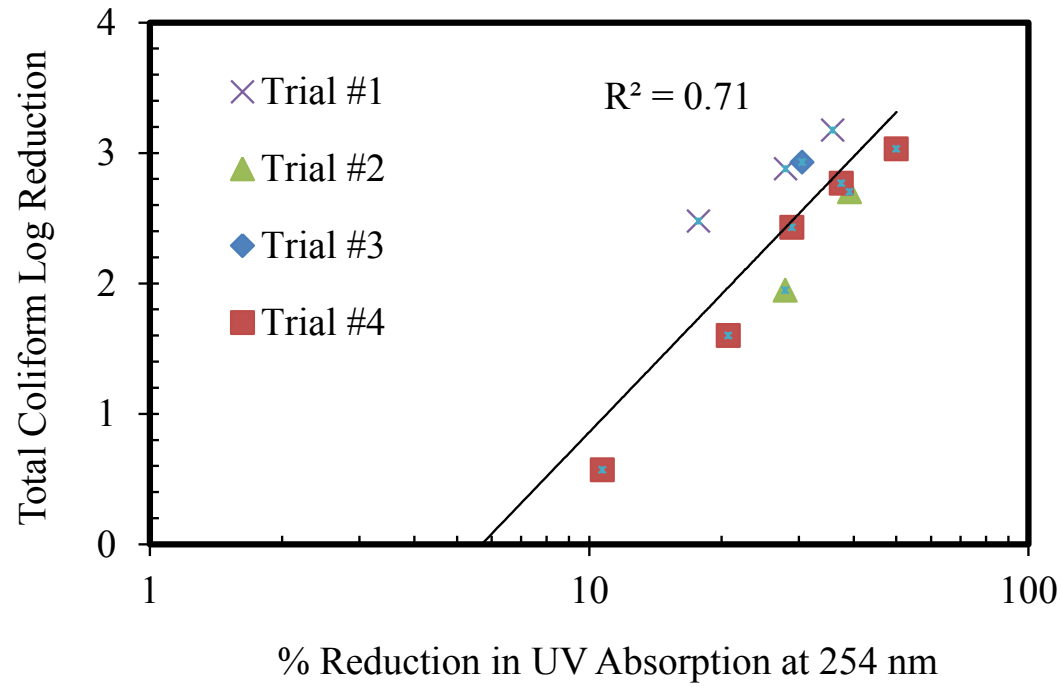


Figure 4.7 **Correlation between reduction in UVA and Total Coliform inactivation**

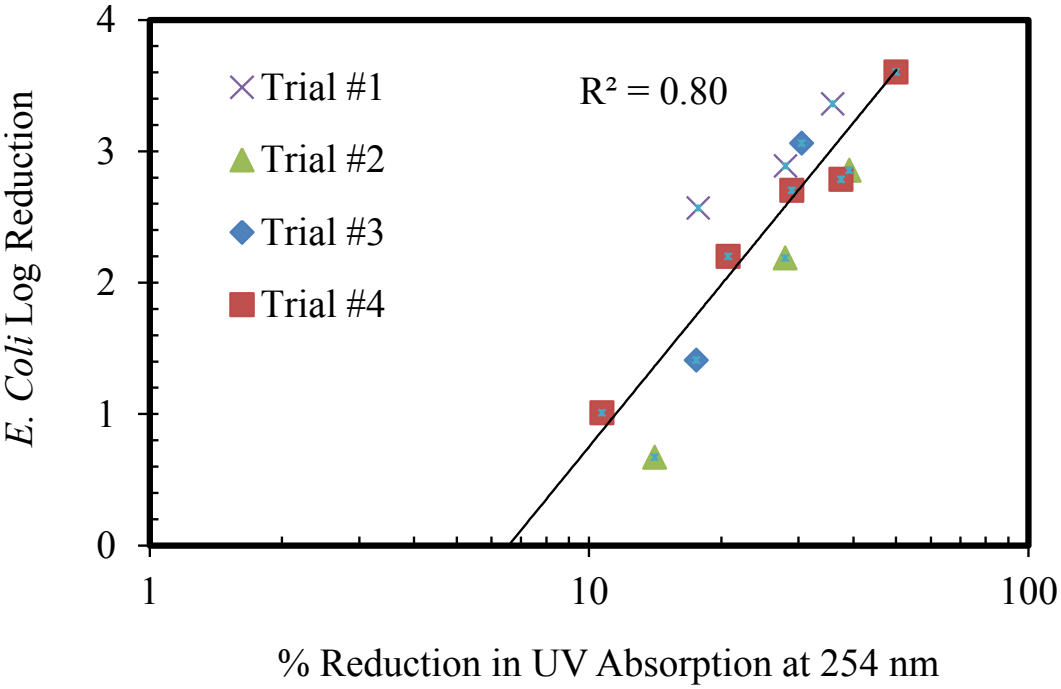


Figure 4.8 **Correlation between reduction in UVA and *E. coli* inactivation**

4.3.4 SUVA

The SUVA was calculated and an attempt was made to correlate disinfection with SUVA (Figure 4.9 and Figure 4.10). The correlation coefficient of 0.58 and 0.77 for correlation between SUVA and total coliform, and SUVA and *E. coli* was obtained. Hence, the correlation of disinfection with SUVA is not as strong as with UVA.

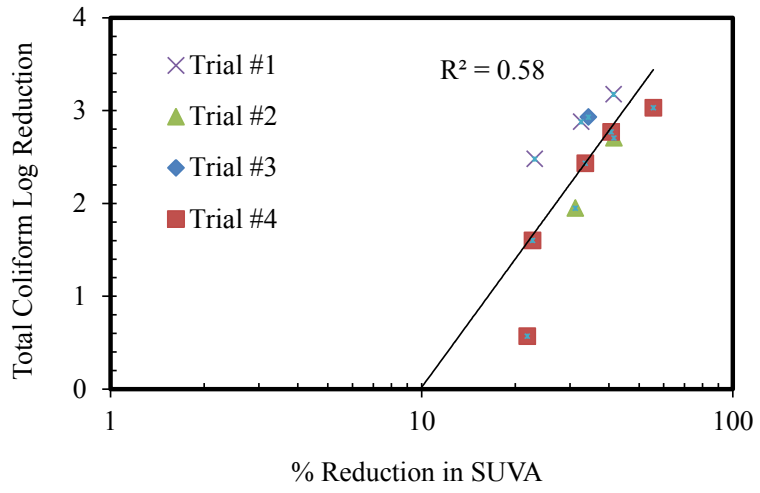


Figure 4.9 Correlation between reduction in SUVA and Total Coliform inactivation

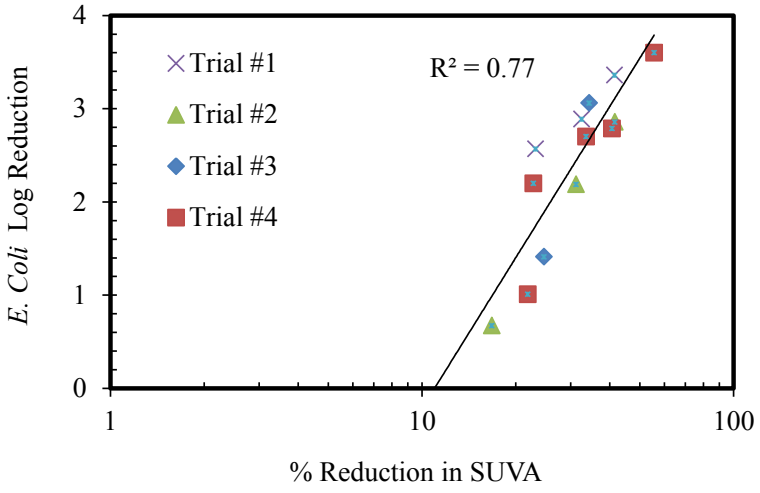


Figure 4.10 Correlation between reduction in SUVA and *E. coli* inactivation

4.3.5 Color

In this study, the reduction in color was measured at the different transferred ozone doses. The results are presented in Table 4.3. At TOD of 1.4 to 2.8 mg/L, the true color reduced by 34 to 76%. At relative higher ozone doses of 3.7 to 4.2 mg/L, the reduction in color was in the range of 80 to 92%. When compared with UVA reduction at similar ozone doses, the reduction in color was comparatively higher. This can indicate that the compounds that contribute to color have higher reaction rate with the oxidants, and oxidation reaction to remove color is favoured over removal of aromatic compounds.

Strong correlation (R^2 value of 0.86 and 0.80) was observed between the true color reduction and inactivation of disinfection indicator microorganisms (Figure 4.11 and Figure 4.12). This is an interesting finding, and the results indicate that the color parameter can be applied as a surrogate parameter to assess disinfection. However, more study is required to confirm the results.

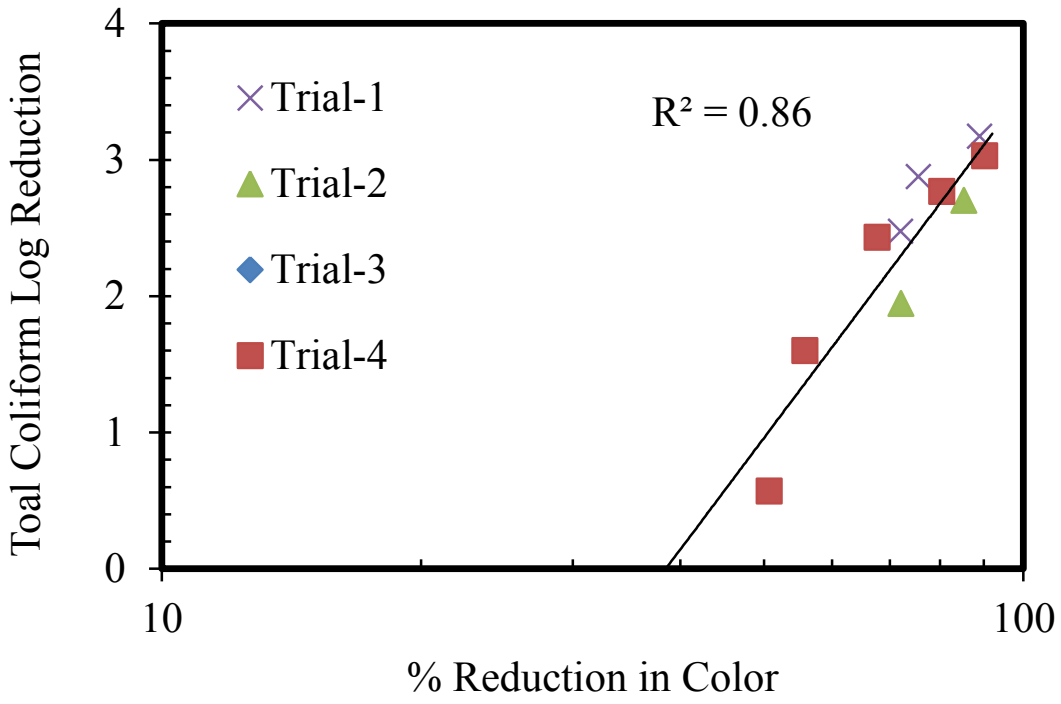


Figure 4.11 **Correlation between reduction in color and Total Coliform inactivation**

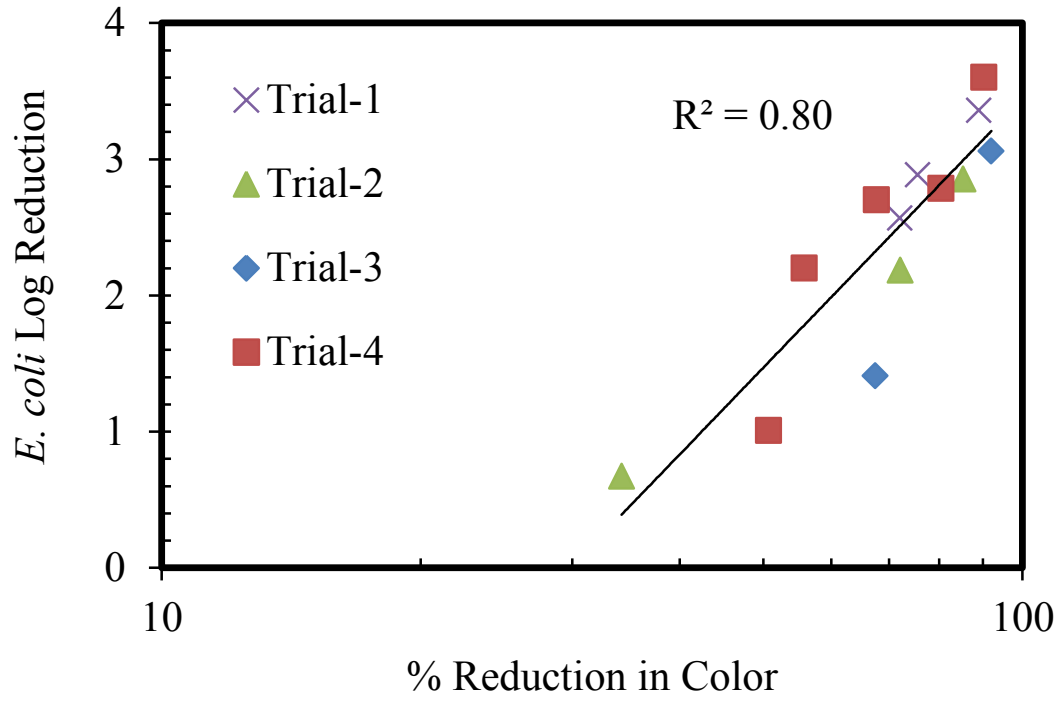


Figure 4.12 **Correlation between reduction in color and *E. coli* inactivation**

4.4 OTHER OBSERVATIONS

The relationship between TOD and reduction in UVA, and TOD and reduction in color was non-linear. Figure 4.13 and Figure 4.14 show the respective plots for both the cases. At TOD of 1.4 to 7.3 mg/L, the reduction in UVA was in the range of 4 to 50%, while reduction in color was in the range of 34 to 92%. The color was reduced by 34% even at the lowest transferred ozone dose, while there was almost zero reduction in the UVA if the ozone dose did not fulfill the initial ozone demand. From the plots, the correlation between TOD and reduction in UVA (R^2 = 0.85) is stronger than the correlation between TOD and color reduction (R^2 = 0.69). If the results of each experiment are plotted separately as shown in Appendix B and C, then excellent correlation ($R^2 > 0.94$) is observed in all cases. For individual experiments, Wert et al. (2009b) have also found a strong correlation ($R^2 > 0.95$) between the ozone dose and reduction in UVA as well as color measured at 455 nm. As shown in Table 4.8, the reduction in UVA and color observed in the current study is in line with the results reported from other studies.

Table 4.8 Reduction in UVA and color of secondary treated MWWE on ozone treatment

TOC/DOC	UV254A	Color*	Ozone dose	% Reduction post ozonation		Reference
mg/L	cm^{-1}	Color units	mg/L	UV254A	Color	
5.04 – 6.04	0.1065 to 0.1160	11.9 to 17.3 (456 nm)	1.4 to 7.3	4 to 50	34 to 92	Current study
< 10 – 14	0.174 to 0.208	NA (400 nm)	2 – 13	24 to 56	62 to 92	Xu et al. (2002)
< 11 – 30	0.260 to 0.509	NA (400 nm)	4 – 30	14 to 52	NA	Xu et al. (2002)
11.4 ± 0.9	0.278 ± 0.027	NA (436 nm)	~ 2 to 11.5	20 to 55	60 to 92	Bahr et al. (2007)
6.6	0.14	Not analyzed	1.7 to 6.6	27 to 55	-	Wert et al. (2009)
10.3	0.26	42 (455 nm)	2.5 to 11.6	15 to 61	21 to 91	Wert et al. (2009)
10.3	0.171	33 (455 nm)	2.5 to 10.6	16 to 58	51 to 96	Wert et al. (2009)

* The values in bracket are the wavelengths at which the absorbance was measured.

Legends: NA: Not available

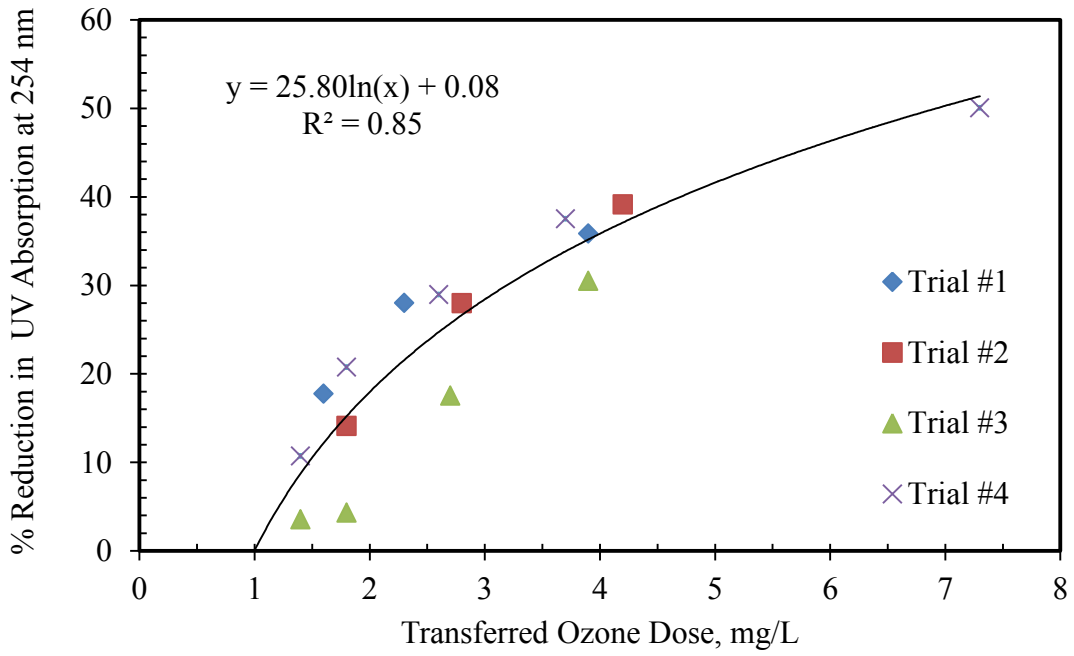


Figure 4.13 **Correlation between TOD and reduction in UVA**

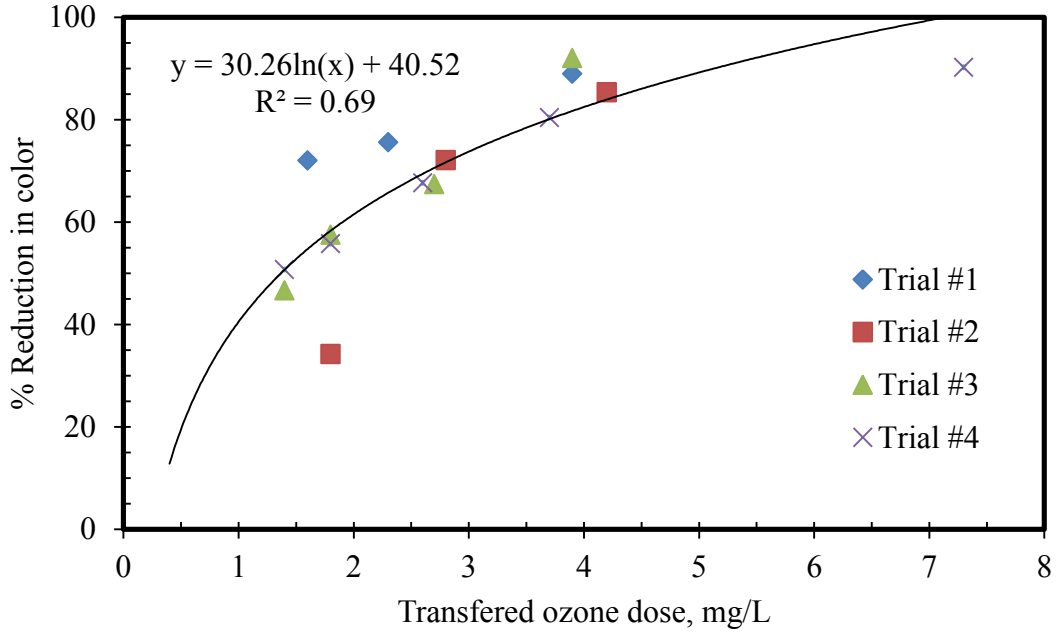


Figure 4.14 **Correlation between TOD and reduction in color**

The SUVA values of MWWE before ozonation were in the range of 1.76 to 2.3 (L/mg.m). After ozonation with TOD of around 0.72 mg O_3/mg DOC, the SUVA values decreased and were in the range of 1.16 to 1.35 (L/mg.m). The reduction was in the range of 34 to 42%. Since the SUVA values decreased and were < 2 (L/mg.m) after ozonation, this indicates that the biodegradability of the organics present in MWWE increased.

4.5 DISCUSSION

There is a disagreement between researchers on the mechanism responsible for inactivation of disinfection indicator microorganisms by ozone. The researchers either support the direct pathway (attack by ozone on the microorganisms) or the indirect pathway (the hydroxyl radicals formed on decomposition of ozone are responsible for inactivation of the disinfection indicator microorganisms) mechanism. If direct pathway is the main mechanism for disinfection, then the level of disinfection should keep on increasing until there is sufficient residual ozone in the effluent. In the current study, at TOD of 0.8 mg O_3/ mg C or less, the residual ozone concentration dropped to below 0.2 mg/L at the outlet of the first reaction chamber (3.4 minute contact time including the contact time in dissolution chamber). Comparing disinfection data from the end of the first and the subsequent three reaction chambers, i.e. between 3.4 minutes and 17 minutes of contact time, no further reduction in disinfection parameters was observed, even in cases where some residual ozone was observed at the end of the first reaction chamber. Tyrrell et al. (1995) and Zimmermann et al. (2011) have also made similar observations. In experiments by Tyrrell et al. (1995), even when 0.22 to 0.45 mg/L of residual ozone

was present at the end of two minutes of ozonation, they did not observe further major reduction in the count of the microorganisms. Hence, the low concentrations of residual ozone are not adequate for further major inactivation of microorganisms. This can be explained by the hypothesis by Xu et al. (2002) and Huber et al. (2005) that the microorganisms in the activated sludge flocs may be shielded from the oxidants and the low ozone residual is not sufficient for their inactivation. From this, it can be concluded that the major portion of the disinfection occurs before the residual ozone in the effluent reduces to low concentration, approximately 0.5 mg/L. In this experiment, at an ozone dose of 0.8 mg O_3/mg DOC or lower, the residual ozone concentration decreased to less than 0.2 mg/L in approximately 3.4 minutes of total contact time (1.7 minute in dissolution chamber and 1.7 minutes in the first contact chamber).

Buffle et al. (2006b) have observed that the concentration of hydroxyl radical decreases by more than two orders of magnitude during the first few seconds of ozonation. Hence, even if indirect pathway were mainly responsible for disinfection, the majority of disinfection would occur during the initial few seconds of the effluent coming in contact with oxidants.

From the results of this study and above discussion, it can be concluded that irrespective of the main mechanism responsible for inactivation of the microorganisms, disinfection with ozone is a fast process. At a typical disinfection dose applied in this study, an increase in disinfection level was not observed after the initial 200 seconds of MWWE being exposed to ozone. Since significant decrease in the count of disinfection indicator microorganism does not occur with an increase in the contact time, ozone contactors with long contact time do not provide any benefit. However, as aqueous ozone

is harmful to some aquatic animals even at low ozone dose (Arthur et al., 1975; Ward and DeGraeve, 1978; Summerfelt, 2003), the contact time should be sufficient to ensure that there is no residual ozone in the effluent before it is discharged to the receiving water body. In the current study, at TOD close to 0.8 mg O_3/mg C, the residual ozone in MWWE at the outlet of the pilot unit having 17 minutes of total contact time was always below quantification level.

Of the probable disinfection control parameters discussed, i.e. transferred ozone dose, residual ozone, UVA, SUVA, and color, correlation was not strong between TOD and disinfection, and residual ozone and disinfection. Nevertheless, TOD is an important parameter for disinfection. The TOD should be sufficient to fulfill the immediate ozone demand of the MWWE. The residual ozone concentration in the effluent leaving the dissolution chamber or first reaction chamber can be monitored as a surrogate parameter to ensure that the minimum level of disinfection is achieved. The correlation of inactivation of disinfection indicator microorganisms with UVA and color was strong, while it was not as strong with SUVA. Besides, to calculate SUVA, online monitoring of DOC is also required, which can be challenging. Hence, UVA and color can be used as a process control parameter to monitor and control disinfection process. The UVA of effluent can be continuously monitored due to the advancements in instrumentation technology (Ried et al., 2009). In addition, recent studies have proposed UVA and color as possible process control parameters for monitoring the transformation of PhACs and EDCs (Bahr et al., 2007; Dickenson et al., 2009; Wert et al., 2009b; Hansen et al., 2010; Nanaboina and Korshin, 2010).

The results indicate that TOD of around 4 mg/L (0.72 mg O_3/mg DOC) was sufficient to achieve consistently the disinfection target of < 200 MPN *E. coli*/100mL for the secondary treated effluent of LRPCP. This ozone dose was selected to study the transformation of the CECs in the secondary treated effluent by ozonation.

PART – II OCCURRENCE OF CECs IN MWWE AND THEIR TRANSFORMATION BY OZONATION

4.6 OCCURRENCE OF CECs IN SECONDARY TREATED MWWE

In this study, eight sets of MWWE samples were analyzed to determine the occurrence of target CECs in MWWE. These CECs consisted of 35 pharmaceutically active compounds (PhACs) and 9 endocrine disruptive chemicals (EDCs).

For reporting the results, the PhACs were categorized into groups such as Antibiotics, Antiphlogistics, Antiepileptic/Antidepressant, Ionophore, and Lipid Regulators. Out of the 35 PhACs targeted, six were not detected in any of the MWWE samples. Table 4.9 contains the list of these PhACs and their detection limits. Table 4.10 represents the results related to the occurrence of the remaining PhACs.

Table 4.9 List of PhACs not detected during the study

Pharmaceutical	Group	DL (ng/L)
Carbadox	Antibiotics	10
Chloramphenicol	Antibiotics	2
Lasalocid A	Antibiotics	10
Monensin sodium	Ionophore	10
Sulfachloropyridazine	Antibiotics	5
Warfarin	Anticoagulant	5

Legend: DL Detection limit

Table 4.10 Occurrence of PhACs in MWWE (LRPCP)

Compound	Detection Frequency	DL ng/L	Concentration, ng/L			
			Minimum	Maximum	Median	Mean ± SD
Antibiotics - Tetracyclines						
Chlortetracycline	4/8	10	33	188	52	81 ± 70
Doxycycline	7/8	5	20	304	57	91 ± 96
Meclocycline	5/8	10	28	319	63	130 ± 120
Oxytetracycline	7/8	5	8	78	32	37 ± 27
Tetracycline	6/8	10	23	402	103	145 ± 141
Antibiotics – Macrolides						
Erythromycin	8/8	10	11	87	29	36 ± 25
Lincomycin	4/8	0.5	4	89	72	60 ± 42
Roxithromycin	8/8	2	3	32	10	12 ± 10
Antibiotics – Sulfonamides						
Sulfadiazine sodium	3/8	5	13	22	14	16 ± 7
Sulfadimethoxine	2/8	1	1	3		
Sulfamerazine	3/8	1	1	5	3	3 ± 2
Sulfamethazine	4/8	1	6	69	46	42 ± 30
Sulfamethizole	4/8	2	3	7	3	4 ± 2
Sulfamethoxazole	8/8	2	3	2554	107	470 ± 826
Sulfathiazole	3/8	2	2	8	7	6 ± 3
Antibiotics – Fluoroquinolones						
Ciprofloxacin	6/8	0.5	52	2652	777	1082 ± 1119
Enrofloxacin	7/8	5	6	127	57	58 ± 45
Norfloxacin	7/8	10	15	11581	154	2601 ± 4014
Antibiotics – Miscellaneous						
Trimethoprim	5/8	1	4	435	59	132 ± 169
Antiphlogistics						
Acetaminophen	5/8	2	10	416	293	219 ± 193
Diclofenac	7/8	1	17	1198	156	323 ± 399
Ibuprofen	1/8	0.5		15638		
Indomethacin	3/8	5	11	43	13	22 ± 17
Ketoprofen	7/8	2	2	51	15	20 ± 18
Naproxen	8/8	2	9	261	109	119 ± 93
Antiepileptic/antidepressant						
Carbamazepine	3/8	1	85	381	303	256 ± 179
Lipid Regulators						
Bezafibrate	8/8	0.5	6	154	23	48 ± 52
Clofibric Acid	4/8	1	1	64	30	31 ± 33
Gemfibrozil	7/8	1	3	717	34	227 ± 273

Note: Values below DL were not included in calculating median and mean concentration.

Legends: DL Detection Limit SD Standard Deviation

4.6.1 Antibiotics

Out of the 23 antibiotics targeted, four were not detected in any of the eight sampling events. Four antibiotics had less than 50 % occurrence and the remaining had 50 % or greater occurrence. Table 4.10 includes the results related to the occurrence of the antibiotics.

The concentrations of tetracyclines group PhACs were in the range of 8 ng/L to 402 ng/L. Tetracycline had the highest median concentration of 103 ng/L, and the highest maximum concentration of 402 ng/L. The occurrence was 75%. The detection frequency and concentration of this compound is in line with previous studies by Miao et al. (2004), Sosiak et al. (2005), and Tabe et al. (2009). The median concentrations of the chlortetracycline, doxycycline, meclocycline, and oxytetracycline in the current study were less than 100 ng/L. The occurrence of these four drugs was at least 50%. In earlier studies conducted in Canada and abroad (Miao et al., 2004; Sosiak et al., 2005; Karthikeyan and Meyer, 2006; Tabe et al., 2009; Barber et al., 2011; Reungoat et al., 2011), most of these drugs were not detected in MWWE or their detection frequency were less than 25%.

Out of the three drugs in the macrolides group, erythromycin and roxithromycin were detected in all eight samples. The occurrence of lincomycin was 50%. It had the highest median and maximum concentration of 72 ng/L, and 89 ng/L, respectively.

Sulfachloropyridazine was the only drug of the sulfonamides group PhACs that was not detected in any of the samples. The frequency of detection of sulfamethoxazole in MWWE was 100%. In its group, it had the highest maximum concentration of 2554 ng/L. The concentrations of sulfadimethoxine, sulfamerazine, sulfamethizole, and sulfathiazole were less than 10 ng/L. The occurrence as well as concentration of

sulfonamides in the current study is in line with the results from previous studies by Miao et al. (2004), Sosiak et al. (2005), and Tabe et al. (2009).

In the fluoroquinolones group PhACs consisting of ciprofloxacin, enrofloxacin, and norfloxacin, the average concentration of ciprofloxacin and norfloxacin was greater than 1000 ng/L. Ciprofloxacin was detected twice in concentrations exceeding 2000 ng/L, the highest being 2652 ng/L. In Canada, the highest reported concentration of this drug in effluent until now is 888 ng/L by Sosiak et al. (2005). Rosal et al. (2010) from Spain have reported up to 5692 ng/L concentration of this drug. The concentration of norfloxacin exceeded 3000 ng/L in three samples. Its average and maximum concentration was 2601 ng/L and 11581 ng/L, respectively. This concentration is high when compared to the literature. Sosiak et al. (2005) have reported a maximum concentration of 821 ng/L in a Canadian MWWE. Hence, concentrations of ciprofloxacin and norfloxacin detected in the current study are high when compared to results reported from other studies from Canada.

4.6.2 Antiphlogistics

This study targeted six PhACs of this group. Ibuprofen was detected in only one MWWE sample, but in a high concentration of 15638 ng/L. Metcalfe et al. (2003a) and Brun et al. (2006) have detected ibuprofen in concentrations exceeding 20,000 ng/L. In the current study, the maximum concentration of diclofenac was 1198 ng/L. The concentrations of the remaining four PhACs were in range of 2 to 416 ng/L. This is in the range of values reported by other studies from Canada and abroad.

4.6.3 Antiepileptic/anti-depressant

Carbamazepine was the only compound targeted in this category. It was detected in three of the eight sampling events. The concentrations were between 85 and 381 ng/L, and the median concentration was 303 ng/L. These concentrations are in the range reported by studies from Canada (Metcalfe et al., 2003a; Metcalfe et al., 2003b; Sosiak et al., 2005; Tabe et al., 2009).

4.6.4 Lipid Regulators

The PhACs covered in this group were bezafibrate, clofibric acid, and gemfibrozil. The occurrence of bezafibrate was 100%. Its concentration was in the range of 6 to 154 ng/L. Clofibric acid was detected in 50% while its concentration was in the range of 1 to 64 ng/L. Occurrence of gemfibrozil was close to 90% and its concentrations were up to717 ng/L. The concentrations of these PhACs are in the range reported by studies from Canada (Metcalfe et al., 2003a; Metcalfe et al., 2003b; Sosiak et al., 2005; Brun et al., 2006; Tabe et al., 2009).

4.6.5 Endocrine Disrupting Chemicals

Table 4.11 compiles the results related to the occurrence of the nine EDCs targeted. The occurrence of diethylstilbestrol and equilin was less than 25% while their concentrations were up to 14 ng/L. Bisphenol-A was detected in five out of eight samples in the concentration range of 9 ng/L to 15341 ng/L. In two samples, its concentration exceeded 9000 ng/L. When compared to the published literature, the concentrations of bisphenol-A observed in current study are high.

Table 4.11 Occurrence of EDCs in MWWE (LRPCP)

Compound	Detection Frequency	Detection Limit, ng/L	Concentration, ng/L			
			Min	Max	Median	Mean ± SD
Estrogen Replacement Agents						
Bisphenol-A (BPA)	5/8	2	9	15341	144	4943 ± 6578
Diethylstilbestrol	1/8	10		14	14	14
Equilin	2/8	2	7	7	7	7
Reproductive Hormones						
17-α-Estradiol	4/8	5	9	4167	20	1054 ± 1858
17-β-Estradiol (E2)	5/8	2	5	52	12	22 ± 19
Estrone (E1)	6/8	2	3	24	13	12 ± 9
Estriol (E3)	4/8	5	27	541	79	181 ± 223
Progesterone	2/8	20	60	121	90	90 ± 51
Ovulation Inhibitors						
19-Norethisterone	3/8	5	5	41	23	23 ± 17

The occurrence of 17-α-estradiol was 50%. While its median concentration was 20 ng/L, in one sample it was detected in high concentration of 4167 ng/L. The highest concentration of eight other PhACs and EDCs also occurred during the same sampling event. This can indicate release of highly concentrated waste from source(s) other than households. The concentrations of E1 and E2 were in the ranges of 3 to 24 ng/L and 5 to 52 ng/L, respectively. These concentrations are in line with values reported by earlier studies. The maximum concentration of E3 detected during the study was 541 ng/L. This concentration is high when compared to results from other studies from Canada. However, E3 has been detected in MWWE in concentrations up to 275 ng/L in Austria (Clara et al., 2005a). In the current study, progesterone was detected in only two of the eight sampling events in concentrations of 60 ng/L and 121 ng/L. The ovulation inhibitor 19-norethisterone was detected in nearly 40% of the samples in the concentration range

of 5 to 41 ng/L. Fernandez et al. (2007) have detected this compound in concentrations up to 159 ng/L in Canadian MWWE.

4.7 TRANSFORMATION OF CECs IN MWWE BY OZONATION

The MWWE samples before and after ozone treatment from two sets of experiment were analyzed to study the transformation of the CECs. The results are presented in this section.

4.7.1 Data Processing

To get a better understanding of the actual transformation taking place, the transformation efficiencies of CECs having concentration below their detection limit (DL) in ozone treated MWWE were calculated only if their concentrations in MWWE before ozone treatment were equal to or greater than five times their DL. In addition, for CECs having concentration below their DL in the ozonated MWWE, a value equal to half their DL was used to calculate their transformation efficiencies.

4.7.2 Transformation of CECs at TOD of 4.4 mg/L (0.72 mg O_3/mg DOC)

In two experiments, the average initial dissolved organic carbon (DOC) of water was 6.1 mg/L. The average applied ozone dose was 8.8 mg/L that resulted in transferred ozone dose (TOD) of 4.4 mg/L or 0.72 mg O_3/mg DOC. The specific ozone consumption (Z_{spec}), i.e. the ratio of ozone consumption to the initial DOC was calculated to be 0.6 mg O_3/mg DOC. The pH of the water was in the range of 6.9 to 7.1, temperature was in the range of 18 to 21 ^{o}C, while alkalinity was in the range of 95 to 180 mg/L as

$CaCO_3$. Out of the 41 CECs targeted, the following eight CECs were not detected in both the experiments: carbadox, chloramphenicol, diethylstilbestrol, lasalocid A, monensin sodium, sulfachloropyridazine, sulfadimethoxine, and warfarin. Table 4.12 presents the data related to the concentration of the detected CECs, and their transformation on reaction with ozone.

Table 4.12 Transformation of CECs at TOD of 0.72 mg O_3/mg DOC

Compound	DL, ng/L	Concentration Pre Ozonation, ng/L		Concentration Post Ozonation, ng/L		Transformation %	
		Exp 1	Exp 2	Exp 1	Exp 2	Exp 1	Exp 2
Antiphlogistics							
Acetaminophen	2	293	9.7	ND	ND	99.7	
Diclofenac	1	17.4	302	ND	21.6	97.1	92.8
Ibuprofen	0.5	15638	ND	7.5	ND	99.9	
Indomethacin	5	ND	43.3	ND	ND		94.2
Ketoprofen	2	51.2	15	7.4	3.2	85.6	79
Naproxen	2	261	113	ND	2.2	99.6	98.1
Antibiotic - Fluoroquinolones							
Ciprofloxacin	0.5	1398	156	ND	33.1	99.9	78.8
Enrofloxacin	5	5.9	101	ND	77.6		22.8
Norfloxacin	10	3248	154	ND	45	99.8	70.7
Antibiotic - Macrolides							
Erythromycin	10	12	86.5	ND	42.9		50.4
Lincomycin	0.5	79.2	4.3	1.3	ND	98.3	94.1
Roxithromycin	2	2.5	31.5	ND	30.4		3.5
Antibiotic - Tetracyclines							
Chlortetracycline	10	ND	56.2	ND	45.9		18.4
Doxycycline	5	304	54.7	ND	28	99.2	48.8
Meclocycline	10	319	ND	ND	ND	98.4	
Oxytetracycline	5	64.6	32.2	40.1	29.3	38	8.8
Tetracycline	10	402	104	42	30.8	89.6	70.2
Antibiotic - Sulfonamides							
Sulfamerazine	1	5	ND	1.6	ND	68.5	
Sulfamethazine	1	69	ND	ND	ND	99.3	
Sulfamethoxazole	2	2554	581	8.8	ND	99.7	99.8
Antibiotic - Miscellaneous							
Trimethoprim	1	12.7	435	ND	ND	96.1	99.9
Antiepileptic, antidepressant							
Carbamazepine	1	ND	381	ND	ND		99.9
Lipid regulators							
Bezafibrate	0.5	11.5	154	2.1	ND	81.9	99.8
Clofibric acid	1	1.9	57.3	ND	ND		99.1
Gemfibrozil	1	386	3.4	ND	1.1	99.9	67.3
Estrogen replacement agents							
Bisphenol-A (BPA)	2	ND	122	3.8	ND		99
Equilin	2	6.6	ND	3.7	ND	43.9%	
Ovulation Inhibitors							
19-Norethersterone	5	23.2	ND	2.5	ND	89	
Reproductive Hormones							
17-α-Estradiol	5	9.5	20.6	ND	13.8		33
17-β-Estradiol (E2)	2	11.6	11.5	4.3	10	63	14
Estrone (E1)	2	14.3	2.7	ND	ND	93	
Estriol(E3)	5	83.1	ND	ND	ND	97	
Progesterone	20	59.9	ND	ND	ND		

Legends: DL Detection Limit Exp Experiment ND Not detected

The results show that ozonation is effective in transforming the majority of the investigated compounds. The sum of the concentration of all the targeted CECs in the pre ozonated MWWE in the experiment #1 and #2 was 25,346 ng/L and 3,033 ng/L, which decreased to 173 ng/L and 423 ng/L in the ozonated MWWE, respectively. The concentrations of the individual CECs in the pre ozonated MWWE were up to 15,638 ng/L, while their concentrations in the ozone treated MWWE were below 78 ng/L.

The transformations of the drugs in the antiphlogistics group were above 90% except for ketoprofen. Transformation of ketoprofen was still high but comparatively lower at 79 and 86%. Studies have reported above 90% reduction of acetaminophen, diclofenac, indomethacin, and naproxen at ozone doses up to 0.5 mg O_3/mg DOC (Bahr et al., 2005; Reungoat et al., 2010; Rosal et al., 2010; Reungoat et al., 2012). For ibuprofen, studies have reported less than 50% removal up to an ozone dose of 0.5 mg O_3/mg DOC and above 90% transformation at an ozone dose of 0.8 mg O_3/mg DOC or higher (Ternes et al., 2003; Bahr et al., 2005; Snyder et al., 2006; Wert et al., 2009a). For ketoprofen, the data vary in the literature. In experiments conducted with TOD/DOC ratios ranging between 0.2 and 1.2, Bahr et al. (2005) have reported transformation efficiencies ranging between 7 and 98%. At TOD/DOC ratio of 0.8, ketoprofen transformation was reported to be 82%, which is similar to the current study. Kim and Tanaka (2011) have reported 31 to 71% transformation of this drug at TOD/DOC ratio of 0.6 to 0.75.

In the fluoroquinolones subgroup of antibiotics, transformations of ciprofloxacin and norfloxacin were in the range of 71 to >99%. Rosal et al. (2010) and Kim and

Tanaka (2011) have reported 67 to >99% transformation of these drugs at ozone doses of 0.6 to 0.9 mg O_3/mg C. The transformation of enrofloxacin in the present study was only 23%. In the only study found that has reported the transformation of this chemical on ozonation of MWWE, Dodd et al. (2006) have reported >99% transformation at TOD/DOC ratio of around 0.6.

In the macrolides subgroup, the transformation efficiency of the antibiotic lincomycin was close to 99%. This is consistent with the finding by Rosal et al. (2010) and Kim and Tanaka (2011). However, the transformation of erythromycin and roxithromycin was only 50% and 3.5%. Transformations > 90 % has been previously reported for these two compounds at similar ozone doses (Reungoat et al., 2010; Rosal et al., 2010; Schaar et al., 2010; Reungoat et al., 2012).

The removal of chlortetracycline and oxytetracycline of the tetracyclines group of antibiotics was between 9 and 38%. Mean transformation of doxycycline, meclocycline, and tetracycline was in the range of 75 to 98%. Dodd et al. (2006) have reported >99% reduction of tetracycline from wastewater at a TOD/TOC ratio of around 0.3. No data regarding transformation of doxycycline and meclocycline on ozonation of MWWE was available in the published literature.

Ozonation reduced the concentration of sulfamethazine and sulfamethoxazole drugs of the sulfonamide group of antibiotics by over 99% and their concentrations decreased to below detection limit or close to the detection limit after ozone treatment. These results are consistent with the findings of other studies (Huber et al., 2005; Snyder et al., 2006; Hollender et al., 2009; Reungoat et al., 2012). Studies have reported over 90% transformation of sulfamethoxazole even at low ozone doses of around 0.2 mg

O_3/mg DOC (Ternes et al., 2003; Dickenson et al., 2009; Reungoat et al., 2012). Hence, this compound seems to transform readily on reaction with ozone.

The transformation of antidepressant and lipid regulator drugs such as carbamazepine, bezafibrate, clofibric acid, and gemfibrozil was above 90%. Bahr et al. (2005) have reported low removal of these drugs up to an ozone dose of 0.4 mg O_3/mg DOC. They observed 74 to 98% reduction at a comparatively higher ozone dose of 0.8 mg O_3/mg DOC. Hollender et al. (2009) have also reported average 88% and 66% removal of bezafibrate and clofibric acid at ozone doses of 0.6 to 0.67 mg O_3/mg DOC.

The data in Table 4.12 indicate that ozone was effective in transforming potential EDCs such as 19-norethisterone, estrone (E1), estriol (E3), and bisphenol A (BPA). Their transformation was in the range of 89 to 97%. The transformation of E2 was 14 and 63%. Equilin and 17-α-estradiol were detected at low concentrations and their transformation was 44% and 33%. Progesterone was detected at a concentration of 60 ng/L in the pre ozonated MWWE and below its detection limit in the ozonated MWWE in one experiment. Its transformation efficiency was not calculated because of the data processing rules described earlier.

Few studies have probed the effect of ozonation of MWWE on transformation of 19-norethisterone and progesterone. Snyder et al. (2006) have observed more than 80% reduction of progesterone present in surface water by ozonation at an ozone dose of 2.4 mg/L. Baig et al. (2008) have treated MWWE spiked with EDCs with ozone, and have reported 56% and > 84% reduction in concentration of norethisterone at ozone doses of ~ 0.3 and ~ 0.5 mg O_3/mg DOC. Studies have reported high removal of E1, E3

and BPA at ozone doses similar to or less than that of current study (Ternes et al., 2003; Huber et al., 2005; Nakada et al., 2007; Wert et al., 2009a). The structures of E1, E2, E3, equilin and BPA consist of phenolic moieties (Deborde et al., 2005; Westerhoff et al., 2005; Nakada et al., 2007) and the reaction between ozone and phenols is faster at neutral or basic pH (Deborde et al., 2005; Huber et al., 2005). The k_{O3} values of E1, E2, E3, and BPA are in the order of $10^5 – 10^6\ M^{-1} \cdot s^{-1}$ as per the published literature. Hence, high transformation of these compounds by ozonation is expected. The transformation efficiencies of E1, E3, and BPA in the current study were as per the expectation and in line with the earlier reported studies, but the transformation of E2 was contrary to the expectations and not consistent with its structural characteristics.

Figure 4.15 is a visual presentation of the data in Table 4.12. Out of 31 CECs for which transformation efficiencies could be calculated, average transformation efficiency of 21 CECs exceeded 80%. The average transformation of 17-α-estradiol, 17-β-estradiol, erythromycin, sulfamerazine, doxycycline, and tetracycline was between 30 – 80%. For the remaining four CECs (roxithromycin, chlortetracycline, enrofloxacin, and oxytetracycline; all antibiotics), the average transformation was less than 30%. Transformation of enrofloxacin, erythromycin, roxithromycin, and E2 was lower than expected. One of the reasons for the low transformation efficiency can be the analytical uncertainties and challenges while analyzing compounds in low ng/L concentrations.

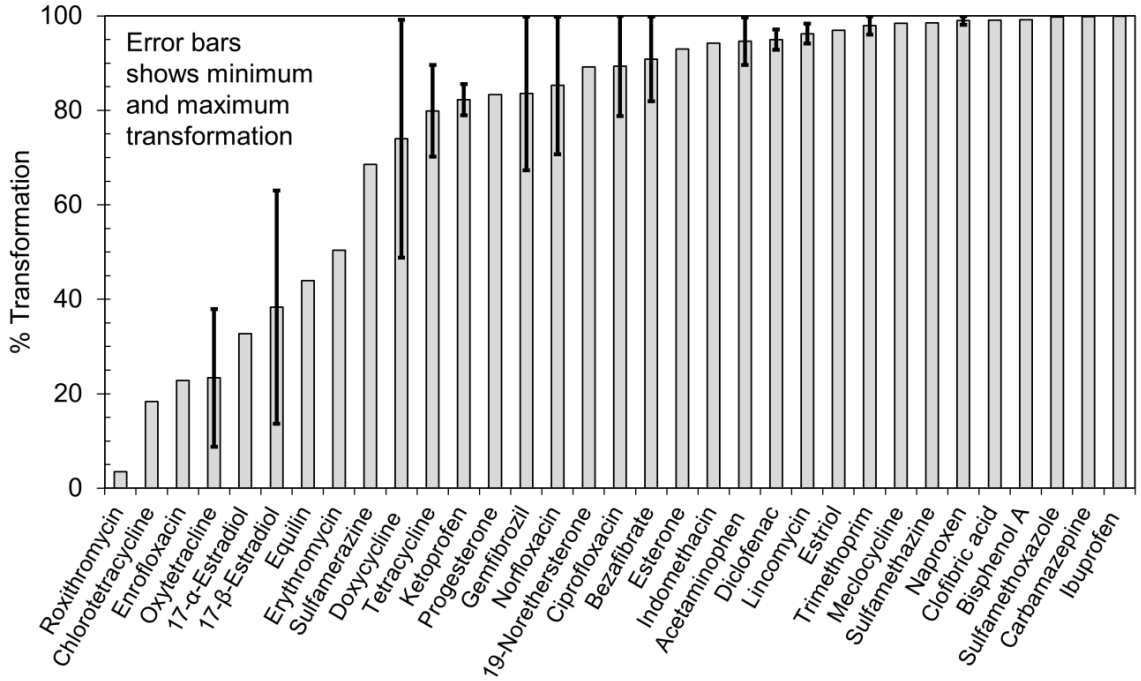


Figure 4.15 Transformation of CECs at TOD of 4.4 mg/L (0.72 mg O_3/mg DOC)

4.7.3 Comparison of transformation of CECs at TOD of 2.8 mg/L (0.46 mg O_3/mg DOC) and TOD of 4.4 mg/L (0.72 mg O_3/mg DOC)

In order to study the effect of different ozone doses on the transformation of the CECs, in one experiment the MWWE was treated with two different ozone doses. Table 4.13 shows the characteristics of the MWWE before ozone treatment. At transferred ozone doses of 2.8 mg/L and 4.4 mg/L, the UVA of the effluent reduced to 0.0817 and 0.0747 cm^{-1}, i.e. a reduction of 29 and 35% compared to the UVA value of the pre-ozonated effluent. The Z_{spec} was calculated to be 0.43 and 0.6 mg O_3/mg DOC. Table 4.14 and Figure 4.16 summarize the transformations of detected CECs at the two ozone doses.

Table 4.13 Characteristics of MWWE before ozone treatment

Parameter	Value	
DOC	6.12	mg/L
pH	6.92	
Temperature	20.5 – 20.8	^oC
Alkalinity	95	mg/L as $CaCO_3$
UV absorption at 254 nm (UVA)	0.1152	cm^{-1}

Table 4.14 Transformation of CECs at TOD of 2.8 and 4.4 mg/L

Compound	DL, ng/L	Concentration pre ozonation, ng/L	Concentration post ozonation, ng/L		Transformation, %	
			TOD 2.8 mg/L	TOD 4.4 mg/L	TOD 2.8 mg/L	TOD 4.4 mg/L
Antiphlogistics						
Diclofenac	1	302.4	22.5	21.6	92.6	92.8
Indomethacin	5	43.3	< 5	< 5	94.2	94.2
Ketoprofen	2	15	5.0	3.2	66.7	79.0
Naproxen	2	113	81.9	2.2	27.5	98.1
Antibiotics – Fluoroquinolones						
Ciprofloxacin	0.5	156.2	78.9	33.1	49.5	78.8
Enrofloxacin	5	100.6	107.1	77.6	-6.5	22.8
Norfloxacin	10	153.6	73.8	45.0	52.0	70.7
Antibiotics – Macrolides						
Erythromycin	10	86.5	52	42.9	39.9	50.4
Lincomycin	0.5	4.3	< 0.5	< 0.5	94.1	94.1
Roxithromycin	2	31.5	31.4	30.4	0.4	3.5
Antibiotics - Tetracyclines						
Chlortetracycline	10	56.2	49.4	45.9	12.2	18.4
Doxycycline	5	54.7	32.4	28.0	40.8	48.8
Oxytetracycline	5	32.2	31.8	29.3	1.0	8.8
Tetracycline	10	103.5	44.1	30.8	57.4	70.2
Antibiotics – Sulfonamides						
Sulfamethoxazole	2	580.6	109	1.0	81.2	99.8
Antibiotics - Miscellaneous						
Trimethoprim	1	435.2	3.6	<1	99.2	99.9
Antiepileptic/antidepressant						
Carbamazepine	1	381.2	24.7	< 1	93.5	99.9
Lipid Regulators						
Bezafibrate	0.5	153.7	48.2	< 0.5	68.6	99.8
Clofibric Acid	1	57.3	34.9	< 1	39.0	99.1
Gemfibrozil	1	3.4	1.2	1.1	64.9	67.3
EDCs						
17-α-Estradiol	5	20.6	12.4	13.8	39.7	32.7
17-β-Estradiol (E2)	2	11.5	16.2	10	-40.6	13.6
Bisphenol-A (BPA)	2	122.4	< 2	< 2	99.2	99.2

Legends: DL Detection limit TOD Transferred ozone dose

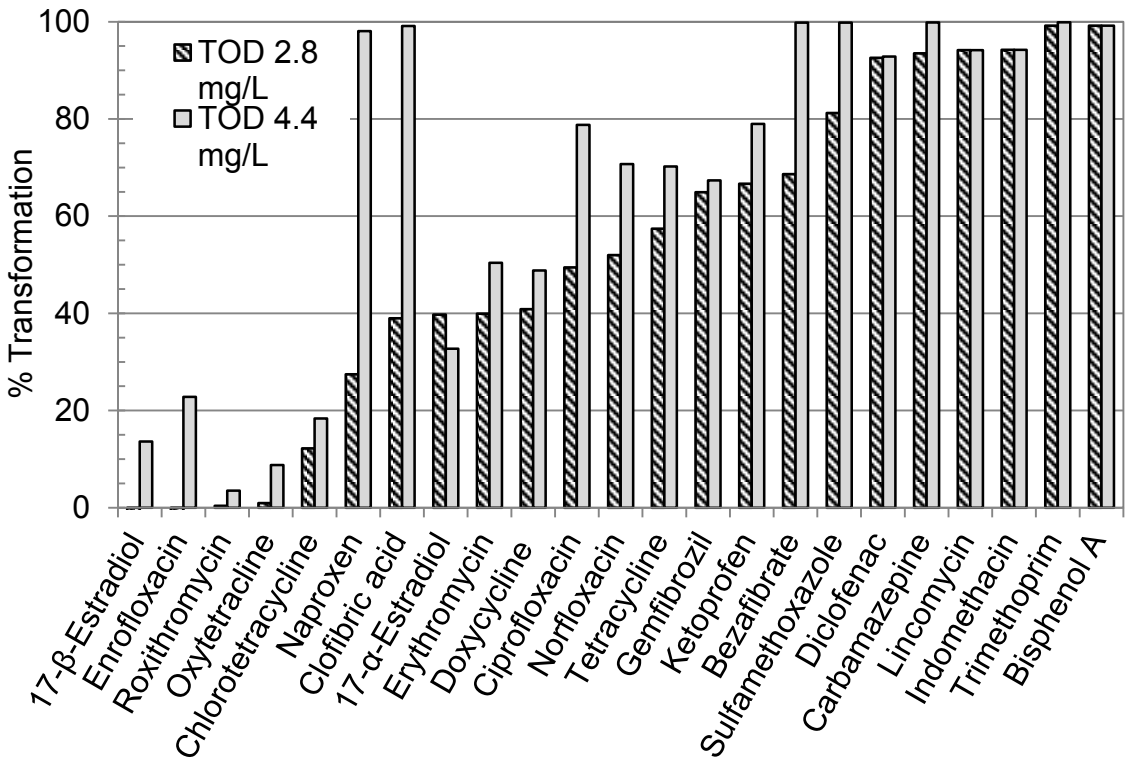


Figure 4.16 Transformation of CECs at TOD of 2.8 and 4.4 mg/L

Result shows that the number of CECs detected in the pre-ozonated MWWE but not in the ozone treated MWWE increased from three at the lower TOD of 2.8 mg/L to seven at the higher TOD of 4.4 mg/L. In general, the transformation of CECs was higher at the higher ozone dose. There was a noticeable increase in the transformation of naproxen, ciprofloxacin, bezafibrate, and clofibric acid from 27 - 67% at lower ozone dose to 79 - >99% at higher ozone dose. The transformation of BPA, carbamazepine, diclofenac, indomethacin, lincomycin, sulfamethoxazole, and trimethoprim was more than 80% at both ozone doses. For these drugs, the percentage transformation at both ozone doses was almost identical. Transformations of enrofloxacin, roxithromycin, oxytetracycline, and chlortetracycline were below 30% at both ozone doses.

4.7.4 Oxidation pathway and transformation

The oxidation pathway can dictate the type of by-products formed, and hence knowledge of it is important. On ozonation, transformation of a compound can be through the direct pathway (oxidation by molecular ozone) or indirect pathway (oxidation by hydroxyl radicals). The fraction of compound transformed by hydroxyl radical $\left(f_{OH,C}\right)$ and molecular ozone (f_{O3}) can be calculated with Equation 2.14, 2.15, and 2.16, repeated as follows:

$$\ln\left(\frac{C}{C_O}\right) = -(k_{O3} + k_{OH}\, R_{CT}) \int [O_3]\, dt \qquad (2.14)$$

$$f_{OH,C} = \frac{k_{OH}\, R_{CT}}{(k_{O3} + k_{OH}\, R_{CT})} \qquad (2.15)$$

$$f_{O3} = 1 - f_{OH,C} \qquad (2.16)$$

The ozone exposure value is required to calculate the R_{CT} value as per the Equation 2.14. The Extended Integrated CT_{10} method used to calculate ozone exposure for microorganism-inactivation credit calculations does not include the considerable ozone exposure in the dissolution chamber. While this is desirable for inactivation credit calculations as a safety factor, it will give lower than actual ozone exposure value for micropollutant kinetic calculations and hence the calculations will not be accurate. For micropollutant kinetic calculations in this study, the ozone exposure in the dissolution chamber was also included. Considering the dissolution chamber as a continuously stirred tank reactor (CSTR), the ozone exposure in it was considered equal to the product of residual ozone concentration measured in MWWE at its outlet and hydraulic retention

time of MWWE in the chamber. Total ozone exposure was the sum of the ozone exposure as per the Extended Integrated CT_{10} method and ozone exposure in the dissolution chamber.

If the ozone exposure is known, the R_{CT} value can be calculated from the transformation measured of a compound that has low reactivity with molecular ozone and high reactivity with hydroxyl radicals. The second-order reaction rate constant of ketoprofen with ozone is 0.4 $M^{-1} \cdot s^{-1}$ and with hydroxyl radicals is 8.4 x 10^9 $M^{-1} \cdot s^{-1}$ (Table 4.15). Hence, transformation measured of this compound was used to calculate R_{CT} value.

At experiment conducted with ozone doses of around 0.72 mg O_3/mg DOC, the total ozone exposure was 2.04 mg-min/L (2.55 x 10^{-3} M.s). Using this value, and transformation measured of ketoprofen, an average R_{CT} value of 8.12 x 10^{-8} was calculated. This value is in agreement with the R_{CT} values of 0.6-4.1 x 10^{-8} reported by Hollender et al. (2009) , 4.78-6.31 x 10^{-8} reported by Gonzales et al. (2012), and 4.94 x 10^{-8} reported by Launer et al. (2012).

Table 4.16 presents the results of the theoretical transformation calculations of CECs and their fraction transformation by hydroxyl radical and molecular ozone

Table 4.15 Rate constants for reaction of target compounds with ozone and hydroxyl radicals

Compound	k_{O3} $M^{-1} s^{-1}$	k_{OH} $M^{-1} s^{-1}$	References	
			k_{O3}	k_{OH}
Antiphlogistics				
Acetaminophen	2.7×10^5	1.7×10^9	Rivas et al. (2011)	Yang et al. (2009)
Diclofenac	$\sim 1 \times 10^6$	7.5×10^9	Huber et al. (2003)	
Ibuprofen	9.1	7.4×10^9	Huber et al. (2005)	
Indomethacin				
Ketoprofen	0.4	8.4×10^9	Real et al. (2009)	
Naproxen	2×10^5	9.6×10^9	Huber et al. (2005)	
Antibiotic - Fluoroquinolones				
Ciprofloxacin	1.9×10^4	4.1×10^9	Dodd et al. (2006)	
Enrofloxacin	1.5×10^5	4.5×10^9	Dodd et al. (2006)	
Norfloxacin	1.1×10^4	1×10^9	Rivas et al. (2011)	Rivas et al. (2010)
Antibiotic - Macrolides				
Erythromycin	6.93×10^4		Huang (2011)	
Lincomycin	6.7×10^5	8.5×10^9	Dodd et al. (2006)	
Roxithromycin	6.3×10^4	5.4×10^9	Dodd et al. (2006)	
Antibiotic - Tetracyclines				
Chlortetracycline	1.7×10^7	5.2×10^9	Ben et al. (2012)	Jeong et al. (2010)
Doxycycline	8×10^5	7.6×10^9	Rivas et al. (2011)	Jeong et al. (2010)
Meclocycline				
Oxytetracycline	6.9×10^6	5.6×10^9	Ben et al. (2012)	Jeong et al. (2010)
Tetracycline	1.9×10^6	7.7×10^9	Dodd et al. (2006)	
Antibiotic - Sulfonamides				
Sulfamerazine		7.8×10^9		Mezyk et al. (2007)
Sulfamethazine	2.9×10^6	8.3×10^9	Ben et al. (2012)	Mezyk et al. (2007)
Sulfamethoxazole	2.5×10^6	5.5×10^9	Huber et al. (2005)	
Antibiotic - Miscellaneous				
Trimethoprim	2.7×10^5	6.9×10^9	Dodd et al. (2006)	
Antiepileptic, antidepressant				
Carbamazepine	3×10^5	8.8×10^9	Huber et al. (2005)	
Lipid regulators				
Bezafibrate	590	7.4×10^9	Huber et al. (2003)	
Clofibric acid	< 20	4.7×10^9	Huber et al. (2005)	
Gemfibrozil	2×10^4	8.0×10^9	Wert et al. (2011)	Razavi et al. (2009)
Estrogen replacement agents				
Bisphenol-A (BPA)	1.7×10^4	1×10^{10}	Deborde et al. (2005)	Rosenfeldt et al. (2004)
Equilin				
Ovulation Inhibitors				
19-Norethersterone	2215		Brosèus et al. (2009)	
Reproductive Hormones				
17-α-Estradiol				
17-β-Estradiol (E2)	2.2×10^5	1.4×10^{10}	Deborde et al. (2005)	Rosenfeldt et al. (2004)
Estrone (E1)	9.4×10^5	2.6×10^{10}	Nakonechny et al. (2008)	
Estriol (E3)	1.0×10^5		Deborde et al. (2005)	
Progesterone	480	8.5×10^8	Barron et al. (2006)	Mezyk et al. (2010)

Note: Reaction rate constant are for pH ~7 and temperature ~ 20 °C. Check references for exact pH, temp.

Legends: k_{O3} Second-order reaction rate constant of compound with ozone

k_{OH} Second-order reaction rate constant of compound with hydroxyl radical

Table 4.16 Dominant oxidation pathway, and comparison of theoretical and actual transformation of CECs

Compound	k_{OH} M^{-1} s^{-1}	k_{O3} M^{-1} s^{-1}	Theoretical Calculations			Measured % transf.
			$f_{OH,C}$	f_{O3}	% transf.	
Antiphlogistics						
Acetaminophen	1.7×10^9	2.7×10^5	<0.01	>0.99	> 99.9	99.7
Diclofenac	7.5×10^9	$\sim 1 \times 10^6$	<0.01	>0.99	> 99.9	95
Ibuprofen	7.4×10^9	9.1	0.99	0.01	78.9	99.9
Ketoprofen	8.4×10^9	0.4	>0.99	<0.01	82.4	82.3
Naproxen	9.6×10^9	2×10^5	<0.01	>0.99	> 99.9	98.9
Antibiotic - Fluoroquinolones						
Ciprofloxacin	4.1×10^9	1.9×10^4	0.02	0.98	> 99.9	89.4
Enrofloxacin	4.5×10^9	1.5×10^5	<0.01	>0.99	> 99.9	22.8
Norfloxacin	1×10^9	1.1×10^4	0.01	0.99	> 99.9	85.3
Antibiotic - Macrolides						
Erythromycin		6.93×10^4			> 99.9*	50.4
Lincomycin	8.5×10^9	6.7×10^5	<0.01	>0.99	> 99.9	96.2
Roxithromycin	5.4×10^9	6.3×10^4	0.01	0.99	> 99.9	3.5
Antibiotic – Tetracyclines						
Chlortetracycline	5.2×10^9	1.7×10^7	<0.01	>0.99	> 99.9	18.4
Doxycycline	7.6×10^9	8×10^5	<0.01	>0.99	> 99.9	48.8
Oxytetracycline	5.6×10^9	6.9×10^6	<0.01	>0.99	> 99.9	98.4
Tetracycline	7.7×10^9	1.9×10^6	<0.01	>0.99	> 99.9	23.4
Antibiotic - Sulfonamides						
Sulfamerazine	7.8×10^9				80.1**	68.5
Sulfamethazine	8.3×10^9	2.9×10^6	<0.01	>0.99	> 99.9	99.3
Sulfamethoxazole	5.5×10^9	2.5×10^6	<0.01	>0.99	> 99.9	99.8
Antibiotic - Miscellaneous						
Trimethoprim	6.9×10^9	2.7×10^5	<0.01	>0.99	> 99.9	98
Antiepileptic, antidepressant						
Carbamazepine	8.8×10^9	3×10^5	<0.01	>99.99	> 99.9	99.9
Lipid regulators						
Bezafibrate	7.4×10^9	590	0.50	0.50	95.2	90.9
Clofibric acid	4.7×10^9	< 20	0.95	0.05	64.1	99.1
Gemfibrozil	8.0×10^9	2×10^4	0.03	0.97	> 99.9	83.6
Estrogen replacement agents						
Bisphenol-A (BPA)	1×10^{10}	1.7×10^4	0.05	0.95	> 99.9	99
Ovulation Inhibitors						
19-Norethersterone		2215			99.7*	89
Reproductive Hormones						
17-β-Estradiol (E2)	1.4×10^{10}	2.2×10^5	0.01	0.99	> 99.9	39
Estrone (E1)	2.6×10^{10}	9.4×10^5	<0.01	>99.99	> 99.9	93
Estriol (E3)		1.0×10^5			> 99.9*	97
Progesterone	8.5×10^8	480	0.13	0.87	75.3	> 67

Notes: * Theoretical percentage transformation is based on transformation with molecular ozone only.
** Theoretical percentage transformation is based on transformation with hydroxyl radicals only.

Legends:
- k_{O3} Second-order reaction rate constant of compound with ozone
- k_{OH} Second-order reaction rate constant of compound with hydroxyl radicals
- $f_{OH,C}$ fraction transformation of compound with hydroxyl radicals
- f_{O3} fraction transformation of compound with molecular ozone
- transf. transformation

The second-order reaction rate constant of most of the CECs with hydroxyl radical is > 10^9 $M^{-1} \cdot s^{-1}$ (Table 4.15). However, the results in Table 4.16 indicate that the oxidation pathway with hydroxyl radicals only dominates the transformation of compounds that are ozone recalcitrant and have low reactivity with ozone (less than ~ 600 $M^{-1} \cdot s^{-1}$). Bezafibrate has low reactivity with ozone (k_{O3} value 590 $M^{-1} \cdot s^{-1}$) and high reactivity with hydroxyl radicals (k_{OH} value of 7.4×10^9 $M^{-1} \cdot s^{-1}$). As per the calculations, its fraction of transformation is 0.50 by hydroxyl radicals and 0.50 by ozone. Progesterone also has low reactivity with ozone. Its reactivity with hydroxyl radicals is one to two magnitudes lower compared to most of the other CECs. In this case, the fraction of removal by ozone is 0.87 while that due to hydroxyl radicals is 0.13. For CECs with k_{O3} value > 10^4 $M^{-1} \cdot s^{-1}$, their fraction transformation due to reaction with ozone is > 0.99. At the operating conditions in this study, the direct pathway dictates the transformation of more than 80% of the CECs targeted.

Acero and von Gunten (2001) have shown that ozone-based AOPs, such as ozone + hydrogen peroxide, can increase the R_{CT} value by three to ten times. If the R_{CT} value determined in the current study is increased by 10 times and the new value is applied to the oxidation kinetic study, there is significant increase in the transformation of ozone-recalcitrant CECs by hydroxyl radicals. However, the direct pathway still dominates the transformation of majority of the CECs. Studies have shown that ozone-based AOP process that increase the hydroxyl radical concentration by decreasing the residual ozone concentration are not as effective as ozonation alone in disinfection of MWWE. Hence, ozone-based AOP processes for treatment of MWWE may adversely affect disinfection and might not improve significantly the transformation of CECs.

Results from Table 4.16 indicate that, in general, the actual average transformation values as in Table 4.12 are close to the calculated theoretical transformation values. For some CECs such as ibuprofen and clofibric acid, the actual transformation is higher than that theoretically calculated. On the other side, actual transformations of CECs such as enrofloxacin, erythromycin, roxithromycin, doxycycline, chlortetracycline, and tetracycline, were less than 60% while their theoretically calculated transformation were close to 100%. These CECs have high reactivity with ozone (k_{O3} value 10^4 to 10^5 $M^{-1} \cdot s^{-1}$) as well as hydroxyl radicals (k_{OH} value around 10^9 $M^{-1} \cdot s^{-1}$). Hence, their low transformation was contrary to the expectation. Similarly, the transformation of E2 was lower than expected. The analytical difficulties and challenges related to analysis of CECs in MWWE matrix that have concentrations less than 100 ng/L can be a reason for the low measured transformation.

4.8 Mutagenicity of secondary and tertiary treated effluent

Table 4.17 summarizes the results from the modified Ames fluctuation test conducted to determine mutagenicity of MWWE pre-ozonation (FE), MWWE post-ozonation (OZ), and MWWE post ozonation + GAC filtration (OZGAC). Four of the eighteen samples (i.e. 22% of samples) tested positive for mutagenic activity. Based on the test results, the FE and the OZ samples exhibited mutagenic effect. The FE and OZ samples with 50% dilution tested positive in two of the three trials. Their 10% concentration samples always tested negative. As per the classification suggested by Jolibois and Guerbet (2005) and reproduced in Table 4.18, the FE and OZ samples were moderately mutagenic. As their mutagenicity response intensities were similar, it shows

that ozone treatment did not increase the mutagenicity of ozonated MWWE. None of the GAC filtered MWWE samples tested positive. This indicates that ozonation plus GAC filtration reduced the mutagenic activity of the effluent.

Table 4.17 Mutagenicity of secondary and tertiary treated MWWE samples

Sample	Mutagenicity ratio (average ± standard error)		
	Trial #1	Trial #2	Trial #3
Background	1.00 ± 0.15	1.00 ± 0.10	1.00 ± 0.04
50% FE	1.44 ± 0.48	**2.57^{c} ± 0.27**	**5.96^{c} ± 0.24**
10% FE	0.85 ± 0.24	0.34 ± 0.06	0.62 ± 0.06
50% OZ	0.85 ± 0.15	**2.32^{c} ± 0.26**	**4.62^{c} ± 0.37**
10% OZ	0.97 ± 0.20	0.27 ± 0.06	0.84 ± 0.12
50% OZGAC	0.91 ± 0.18	0.40 ± 0.04	1.02 ± 0.37
10% OZGAC	0.74 ± 0.12	0.38 ± 0.05	0.67 ± 0.17

Notes:
1) The statistically significant positive results are highlighted in bold.
2) Prefix: 10%, 50% indicates the sample concentration in sterile distilled water.

Legends:

a	$p < 0.05$	(statistical significance)
b	$p < 0.01$	
c	$p < 0.001$	
FE:	MWWE pre ozonation	
OZ:	MWWE post ozonation	
OZGAC:	MWWE post ozonation + GAC filtration	

Table 4.18 Mutagenic intensity

Sample concentration	Statistical significance level		
	$p < 0.05$	$p < 0.01$	$p < 0.001$
10%	Slight	Moderate	Strong
50%	Slight	Slight	Moderate

Note: Table is adapted from Jolibois and Guerbet (2005).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In this study, a pilot-scale ozonation plant was installed at Little River Pollution Control Plant, Canada, and experiments were conducted to determine the efficacy of ozonation of secondary treated municipal wastewater effluent (MWWE) for disinfection and transformation of contaminants of concern. The results of experiments conducted to study disinfection reveal the following:

- The disinfection target of < 200 MPN *E. coli*/100 mL was consistently achieved at transferred ozone dose (TOD) of around 0.72 mg O_3/mg DOC and sometimes but not always at TOD of 0.46 mg O_3/mg DOC.
- Contact time of 2 minutes at TOD of around 0.72 mg O_3/mg DOC was sufficient to meet the disinfection target.
- Residual ozone concentration reduced to less than quantifiable concentration of 0.01 mg/L within a contact time of 8 minutes or less.
- Disinfection efficiency (measured as reduction in *E. coli* count) showed correlation with TOD, residual ozone, UV absorption at 254 nm (UVA), SUVA, and color. The correlation coefficient (R^2 value) was in the range of 0.53 to 0.80. A strong correlation was observed between disinfection efficiency and reduction in the UVA as well as color (R^2 value of 0.80 in both cases).

- There was a positive change in the physicochemical properties of MWWE after ozonation. Ozonation improved the aesthetics of MWWE by removing color, increasing the dissolved oxygen (DO) concentration, and decreasing the aromaticity (measured as UVA). At TOD of around 0.72 mg O_3/mg DOC, the DO increased from < 2.5 mg/L to around 8 mg/L. UVA reduction was between 31 and 39% while color reduction was between 80 and 92%.
- Mineralization of the organics did not occur at TOD of around 0.72 mg O_3/mg DOC since no change was observed in bulk organic concentration (TOC) after ozonation. However, SUVA decreased by 34 to 42% and its value after ozonation was in the range of 1.16 to 1.35 (L/mg.m). This indicates that ozonation of MWWE resulted in breaking of organic molecules into molecules with lower molecular weight, and there was an increase in the biodegradability of the organics.

The result of experiments conducted to study the occurrence of CECs in MWWE and their transformation on ozonation reveal the following:

- CECs were present in the MWWE in ng/L to μg/L concentrations.
- At TOD of 0.72 mg O_3/mg DOC, the sum of concentration of all the CECs targeted reduced by 86 to 99%. Out of 31 CECs for which the transformation efficiency could be calculated, transformation of 21 CECs exceeded 80%. The concentrations of 11 CECs were reduced to less than their detection limit.

- The transformation of the CECs was lower at TOD of 0.46 mg O_3/mg DOC than at TOD of 0.72 mg O_3/mg DOC. The difference between transformation at the two ozone doses was significantly higher for compounds having low reactivity with ozone, example: bezafibrate and clofibric acid. The transformation of CECs such as BPA, carbamazepine, diclofenac, indomethacin, lincomycin, sulfamethoxazole, and trimethoprim was more than 80% at both ozone doses.
- The direct pathway dominated transformation of more than 80% of the CECs targeted. The indirect pathway dictated the transformation of CECs that are less reactive with ozone (second-order reaction rate constant with ozone less than ~ 600 $M^{-1} \cdot s^{-1}$).
- The mutagenicity of MWWE did not increase after ozonation.

The results indicate that for a properly treated secondary or tertiary MWWE, a transferred ozone dose of < 1 mg O_3/mg DOC should suffice to achieve the dual purpose of disinfection as well as transformation of CECs.

5.2 RECOMMENDATIONS

- Testing methods should be developed for inline measurement of disinfection of MWWE.
- Results of current study indicate that UV absorption at 254 nm and color has strong correlation with inactivation of disinfection indicator microorganism.

More studies should be conducted with MWWE of different municipal wastewater treatment plants to confirm the finding.

- Surrogate parameters to indirectly measure transformation of CECs on ozonation should be developed.
- By-products formed on ozonation of MWWE can be more mutagenic than their parent compound. Test results of current study with modified Ames test indicate that the mutagenicity of the effluent did not increase after ozonation at the operating conditions. The finding should be confirmed with a battery of genotoxicity tests.
- The MWWE before ozonation and after ozonation tested positive for mutagenicity in the current study. The effect of biofiltration of ozonated MWWE on reduction of genotoxicity and mutagenicity of the MWWE should be investigated.

APPENDICES

APPENDIX A

Effect of ozonation of MWWE spiked with PhACs and EDCs

Compound	No. of sample	TOC or DOC mg/L	O_3 dose mg/L	O_3 dose mg O_3/ mgC	RL O_3 samples ng/L	Pre Ozonated effluent ng/L	Post Ozonated Effluent ng/L	% Reduction Range (Median)	Reference
Ciprofloxacin		5.3	1	~ 0.2		331,340		41	DD
		5.3	1.5	~ 0.3		331,340		66	DD
		5.3	3	~ 0.6		331,340		> 99	DD
Enrofloxacin		5.3	1	~ 0.2		359,390		62	DD
		5.3	1.5	~ 0.3		359,390		90	DD
		5.3	3	~ 0.6		359,390		> 99	DD
Lincomycin		5.3	1	~ 0.2		406,540		70	DD
Penicillin G		5.3	1	~ 0.2		334,390		20	DD
		5.3	1.5	~ 0.3		334,390		40 ± 15	DD
		5.3	3	~ 0.6		334,390		70	DD
		5.3	5	~ 1		334,390		> 99	DD
Roxithromycin		5.3	1	~ 0.2		837,050		55 ± 10	DD
Sulfamethoxazole		5.3	1	~ 0.2		253,280		66	DD
		5.3	1.5	~ 0.3		253,280		93	DD
		5.3	3	~ 0.6		253,280		> 99	DD
Tetracycline		5.3	1	~ 0.2		444,430		85	DD
		5.3	1.5	~ 0.3		444,430		> 99	DD

Appendix A cont'd (Effect of ozonation of MWWE spiked with PhACs and EDCs)

Compound	No. of sample	TOC or DOC	O_3 dose	O_3 dose	RL O_3 samples	Pre Ozonated effluent	Post Ozonated Effluent	% Reduction Range (Median)	Reference
		mg/L	mg/L	mg O_3/ mgC	ng/L	ng/L	ng/L		
Trimethoprim		5.3	1	~ 0.2		290,320		59	DD
		5.3	1.5	~ 0.3		290,320		87	DD
		5.3	3	~ 0.6		290,320		> 99	DD
17β-Estradiol		1.6	1			50,000		80	BL
		1.6	5			50,000		>99	BL
		1.6	10			50,000		99.6	BL
		COD: 59	4.3			40		90	HS
		COD: 44	1.9			40		90	HS
		BOD: 2.5-4	3		0.7	200		> 90	HM
Estrone		COD: 59	6.1			40		90	HS
		BOD: 2.5-4	1		0.7	200		> 90	HM
		BOD: 2.5-4	3		0.7	200	> RL	> 99	HM
17α-Ethinyl Estradiol		COD: 59	6.2			40		90	HS
		COD: 44	2.5			40		90	HS
		BOD: 2.5-4	1		0.7	200		> 90	HM
		BOD: 2.5-4	3		0.7	200	~ 10	~ 95	HM

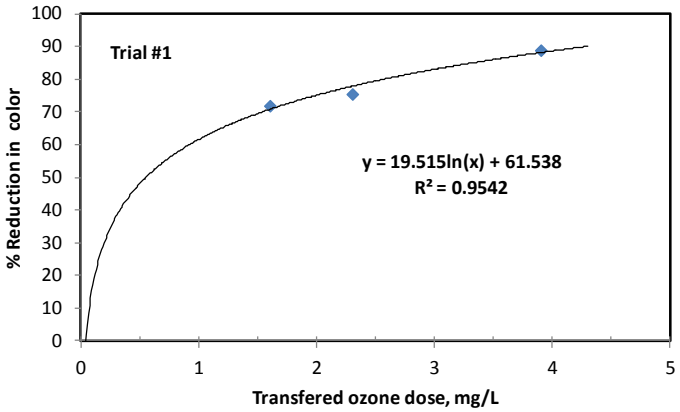
Legends: TOC: Total Organic Carbon DOC: Dissolved Organic Carbon O_3: Ozone RL: Reported Limit

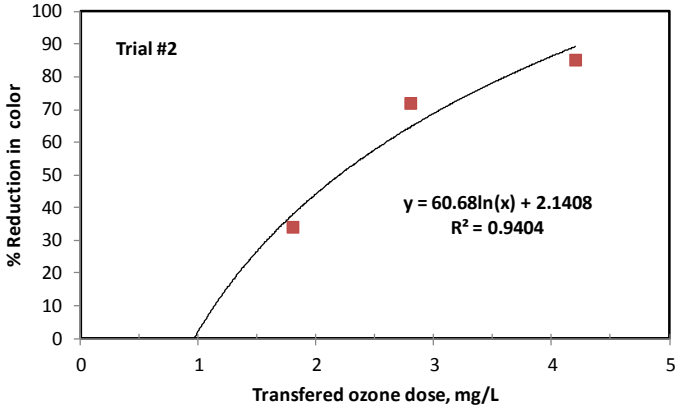
Reference Legends:

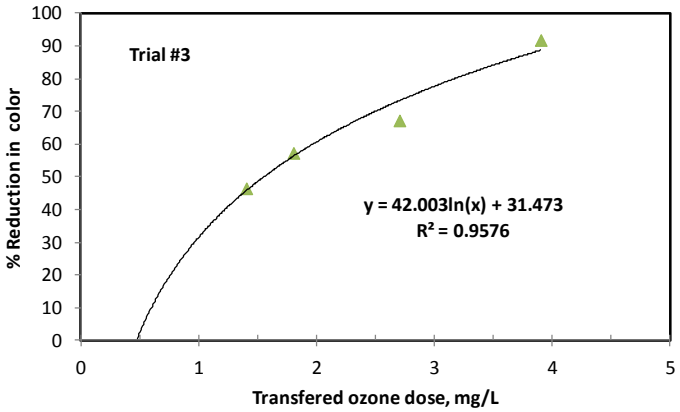
DD Dodd et al. (2006)
BL Bila et al. (2007)
HS Hansen et al. (2010)

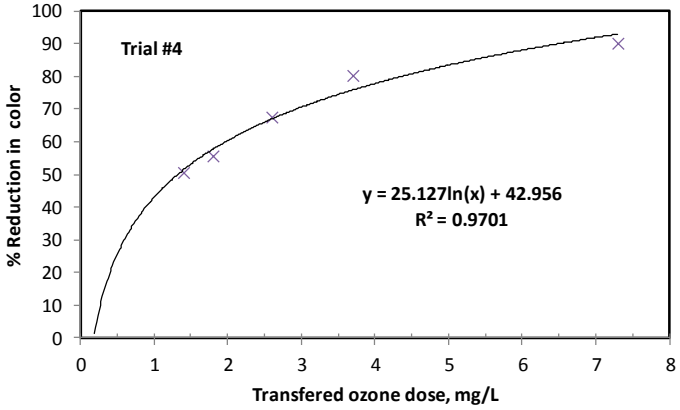
APPENDIX B

Correlation between TOD and reduction in color (for each trial)



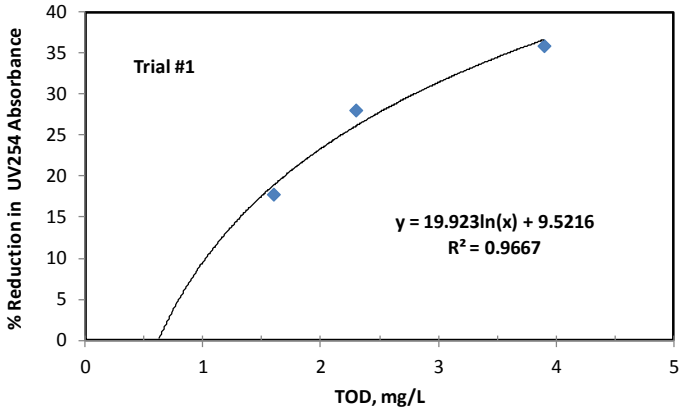


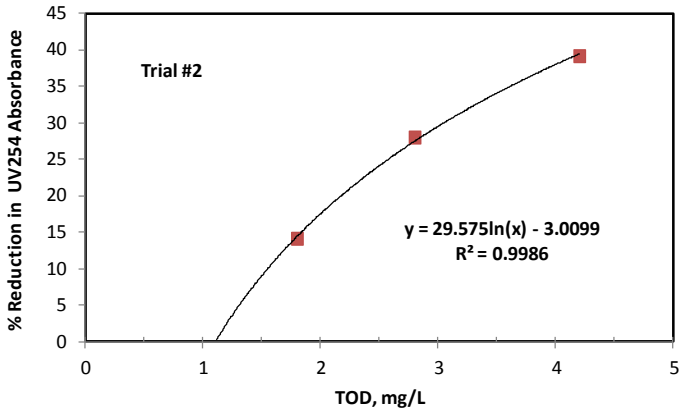


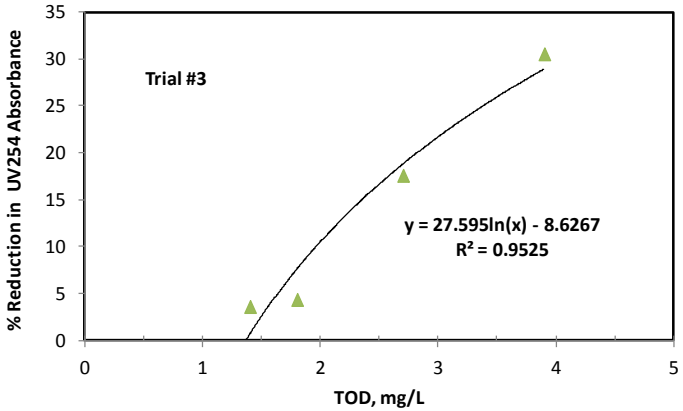


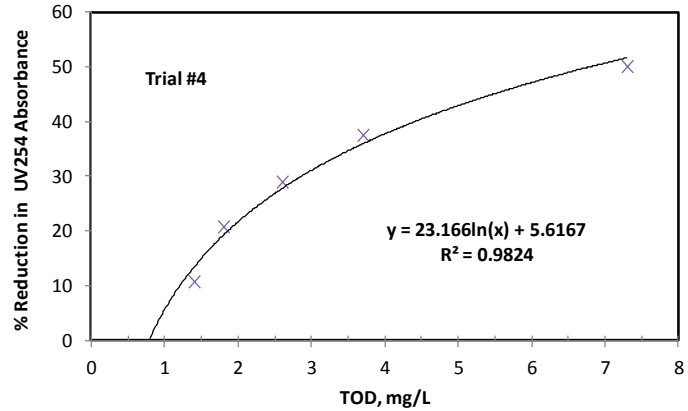
APPENDIX C

Correlation between TOD and reduction in UVA (for each trial)



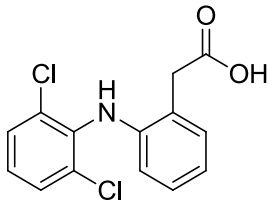
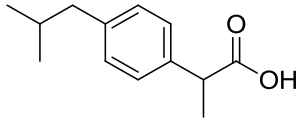




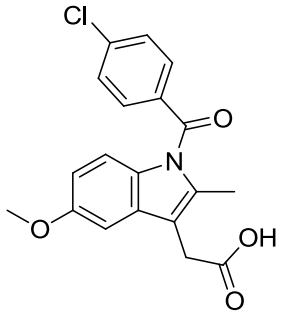
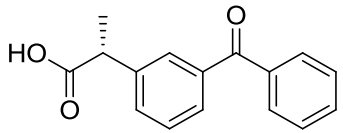
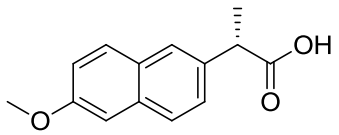
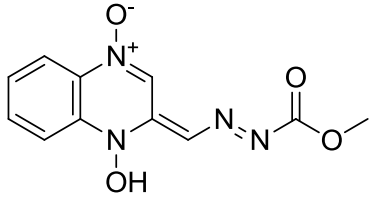


APPENDIX D

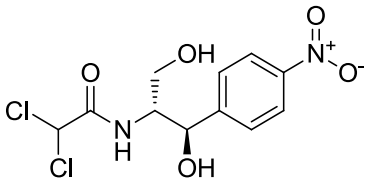
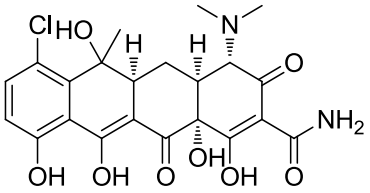
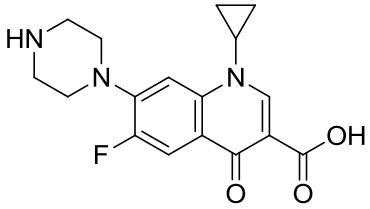
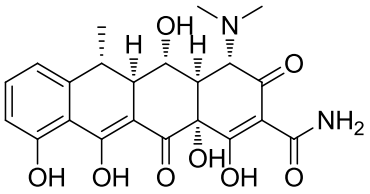
Details of the CECs targeted

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Analgesic/Anti-inflammatory Agents					
Diclofenac	15307-86-5	$C_{14}H_{11}Cl_2NO_2$	296.15	2-(2,6-dichloranilino) phenylacetic acid	
Ibuprofen	15687-27-1	$C_{13}H_{18}O_2$	206.28	2-[4-(2-methylpropyl)phenyl]propanoic acid	

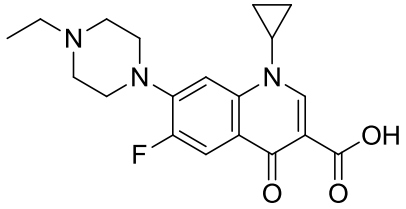
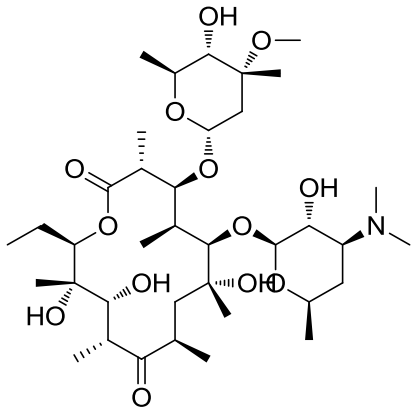
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Indomethacin (6259)	53-86-1	$C_{19}H_{16}ClNO_4$	357.79	2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetic acid	
Ketoprofen	22071-15-4	$C_{16}H_{14}O_3$	254.28	(2R)-2-(3-benzoylphenyl)propanoic acid	
Naproxen (7997)	22204-53-1	$C_{14}H_{14}O_3$	230.26	(2S)-2-(6-methoxynaphthalen-2-yl)propanoic acid	
Antibiotics					
Carbadox	6804-07-5	$C_{11}H_{10}N_4O_4$	262.22	methyl-N-[(1-hydroxy-4-oxidoquinoxalin-4-ium-2-ylidene)methylimino]carbamate	

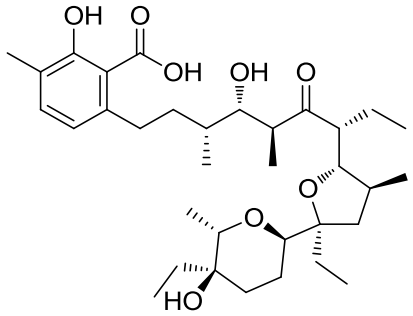
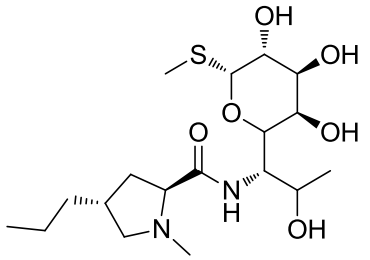
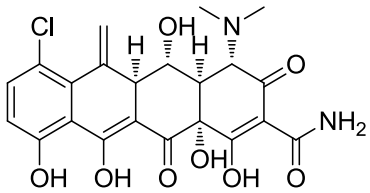
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Chloramphenicol	56-75-7	$C_{11}H_{12}Cl_2N_2O_5$	323.13	2,2-dichloro-N-((1R,2R)-1,3-dihydroxy-1-(4-nitrophenyl)propan-2-yl)acetamide	
Chlortetracycline	57-62-5	$C_{22}H_{23}ClN_2O_8$	478.88	(4S,4aS,5aS,12aR)-7-chloro-4-(dimethylamino)-1,6,10,11,12a-pentahydroxy-6-methyl-3,12-dioxo-4,4a,5,5a-tetrahydrotetracene-2-carboxamide	
Ciprofloxacin	85721-33-1	$C_{17}H_{18}FN_3O_3$	331.34	1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid	
Doxycycline	564-25-0	$C_{22}H_{24}N_2O_8$	444.43	(4S,4aR,5S,5aR,6R,12aR)-4-(dimethylamino)-1,5,10,11,12a-pentahydroxy-6-methyl-3,12-dioxo-4a,5,5a,6-tetrahydro-4H-tetracene-2-carboxamide	

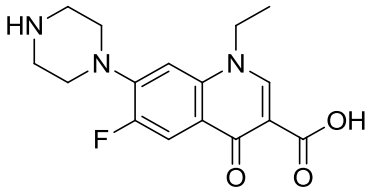
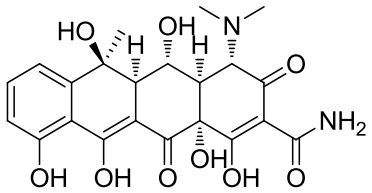
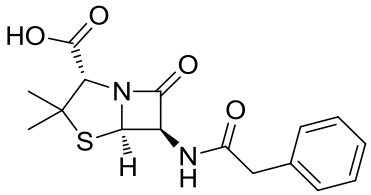
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Enrofloxacin	93106-60-6	$C_{19}H_{22}FN_3O_3$	359.39	1-cyclopropyl-7-(4-ethylpiperazin-1-yl)-6-fluoro-4-oxoquinoline-3-carboxylic acid	
Erythromycin	114-07-8	$C_{37}H_{67}NO_{13}$	733.93	(3R,4S,5S,6R,7R,9R,11R,12R,13S,14R)-6-[(2S,3R,4S,6R)-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy-14-ethyl-7,12,13-trihydroxy-4-[(2R,4R,5S,6S)-5-hydroxy-4-methoxy-4,6-dimethyloxan-2-yl]oxy-3,5,7,9,11,13-hexamethyl-oxacyclotetradecane-2,10-dione	

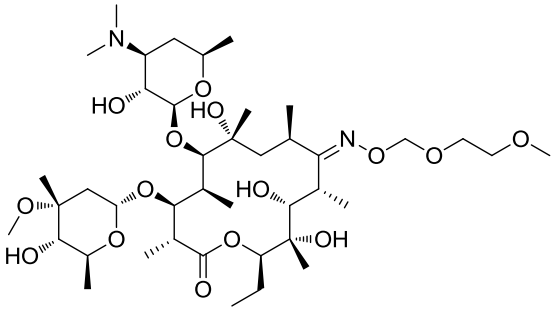
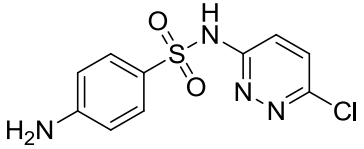
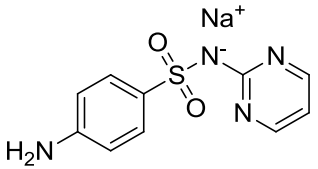
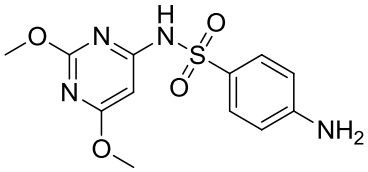
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Lasalocid A	25999-31-9	$C_{34}H_{54}O_8$	590.79	6-[(3R,4S,5S,7R)-7-[(2S,3S,5S)-5-ethyl-5-[(2R,5R,6S)-5-ethyl-5-hydroxy-6-methyloxan-2-yl]-3-methyloxolan-2-yl]-4-hydroxy-3,5-dimethyl-6-oxononyl]-2-hydroxy-3-methylbenzoic acid	
Lincomycin	154-21-2	$C_{18}H_{34}N_2O_6S$	406.54	(2S,4R)-N-[(1S)-2-hydroxy-1-[(3R,4S,5R,6R)-3,4,5-trihydroxy-6-methylsulfanyloxan-2-yl]propyl]-1-methyl-4-propylpyrrolidine-2-carboxamide	
Meclocycline	2013-58-3	$C_{22}H_{21}ClN_2O_8$	476.86	(4S,4aR,5S,5aR,12aR)-7-chloro-4-(dimethylamino)-1,5,10,11,12a-pentahydroxy-6-methylidene-3,12-dioxo-4,4a,5,5a-tetrahydrotetracene-2-carboxamide	

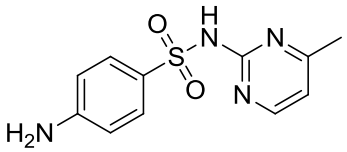
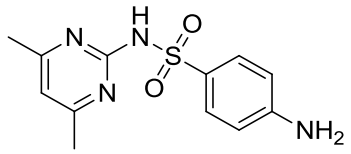
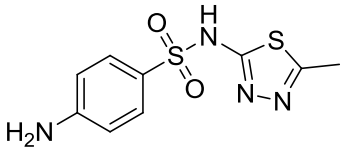
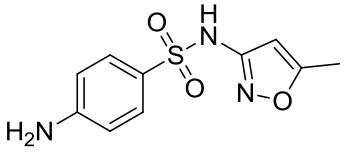
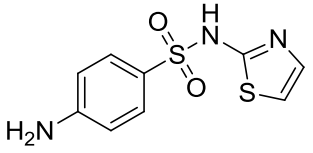
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Norfloxacin	70458-96-7	$C_{16}H_{18}FN_3O_3$	319.33	1-ethyl-6-fluoro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid	
Oxytetracycline	79-57-2	$C_{22}H_{24}N_2O_9$	460.43	(4S,4aR,5S,5aR,6S,12aR)-4-(dimethylamino)-1,5,6,10,11,12a-hexahydroxy-6-methyl-3,12-dioxo-4,4a,5,5a-tetrahydrotetracene-2-carboxamide	
Penicillin G	61-33-6	$C_{16}H_{18}N_2O_4S$	334.39	(2S,5R,6R)-3,3-dimethyl-7-oxo-6-[(2-phenylacetyl)amino]-4-thia-1-azabicyclo[3.2.0]heptane-2-carboxylic acid	

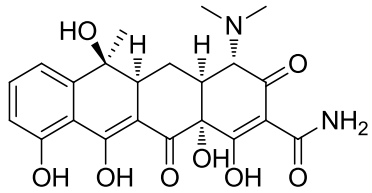
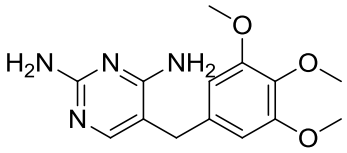
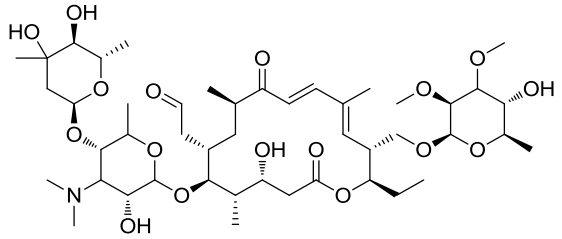
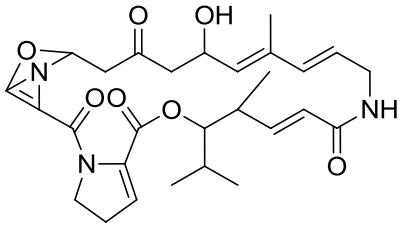
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Roxithromycin	80214-83-1	$C_{41}H_{76}N_2O_{15}$	837.05	(3R,4S,5S,6R,7R,9R,10Z,11S,12R,13S,14R)-6-[(2S,3R,4S,6R)-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy-14-ethyl-7,12,13-trihydroxy-4-[(2R,4R,5S,6S)-5-hydroxy-4-methoxy-4,6-dimethyloxan-2-yl]oxy-10-(2-methoxyethoxymethoxyimino)-3,5,7,9,11,13-hexamethyl-oxacyclotetradecan-2-one	
Sulfachloropyridazine	80-32-0	$C_{10}H_9ClN_4O_2S$	284.72	4-amino-N-(6-chloropyridazin-3-yl)benzenesulfonamide	
Sulfadiazine sodium	547-32-0	$C_{10}H_9N_4NaO_2S$	272.26	sodium (4-aminophenyl)sulfonyl-pyrimidin-2-ylazanide	
Sulfadimethoxine	122-11-2	$C_{12}H_{14}N_4O_4S$	310.33	4-amino-N-(2,6-dimethoxypyrimidin-4-yl)benzenesulfonamide	

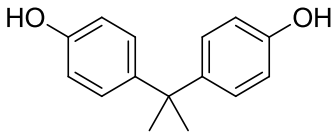
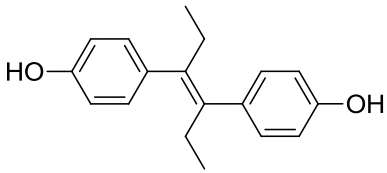
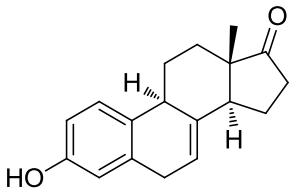
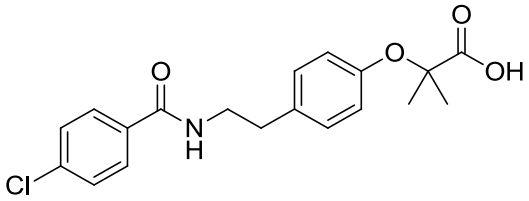
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Sulfamerazine	127-79-7	$C_{11}H_{12}N_4O_2S$	264.30	4-amino-N-(4-methylpyrimidin-2-yl)benzenesulfonamide	
Sulfamethazine	57-68-1	$C_{12}H_{14}N_4O_2S$	278.33	4-amino-N-(4,6-dimethylpyrimidin-2-yl)benzenesulfonamide	
Sulfamethizole	144-82-1	$C_9H_{10}N_4O_2S_2$	270.33	4-amino-N-(5-methyl-1,3,4-thiadiazol-2-yl)benzenesulfonamide	
Sulfamethoxazole	723-46-6	$C_{10}H_{11}N_3O_3S$	253.28	4-amino-N-(5-methyl-1,2-oxazol-3-yl)benzenesulfonamide	
Sulfathiazole	72-14-0	$C_9H_9N_3O_2S_2$	255.32	4-amino-N-(1,3-thiazol-2-yl)benzenesulfonamide	

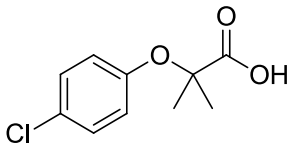
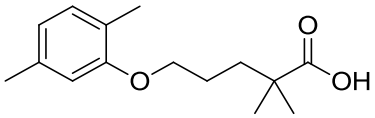
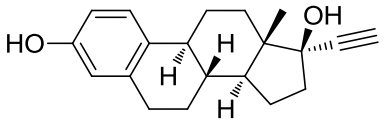
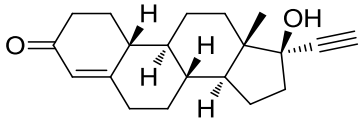
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Tetracycline	60-54-8	$C_{22}H_{24}N_2O_8$	444.43	(4S,4aS,5aS,6S,12aR)-4-(dimethylamino)-1,6,10,11,12a-pentahydroxy-6-methyl-3,12-dioxo-4,4a,5,5a-tetrahydrotetracene-2-carboxamide	
Trimethoprim	738-70-5	$C_{14}H_{18}N_4O_3$	290.32	5-[(3,4,5-trimethoxyphenyl)methyl]pyrimidine-2,4-diamine	
Tylosin	1401-69-0	$C_{46}H_{77}NO_{17}$	916.10	2-[(4R,5S,6S,7S,9R,11E,13E,15R,16R)-6-[(3R,5S)-5-[(2S,5S,6S)-4,5-dihydroxy-4,6-dimethyloxan-2-yl]oxy-4-(dimethylamino)-3-hydroxy-6-methyloxan-2-yl]oxy-16-ethyl-4-hydroxy-15-[[(2R,3S,5R,6R)-5-hydroxy-3,4-dimethoxy-6-methyloxan-2-yl]oxymethyl]-5,9,13-trimethyl-2,10-dioxo-1-oxacyclohexadeca-11,13-dien-7-yl]acetaldehyde	
Virginiamycin M1	21411-53-0	$C_{28}H_{35}N_3O_7$	525.59	8,9,14,15,24,25-Hexahydro-14-hydroxy-4,12-dimethyl-3-(1-methylethyl)-3H-21,18-nitrilo-1H,22H-pyrrolo[2,1-C][1,8,4,19]dioxadiazacyclotetracosine-1,7,16,22(4H,17H)-tetrone	

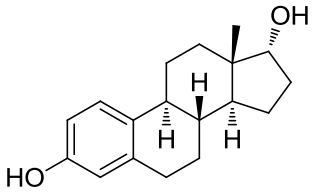
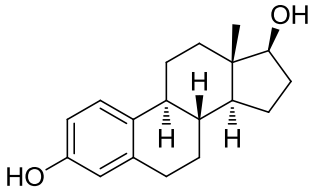
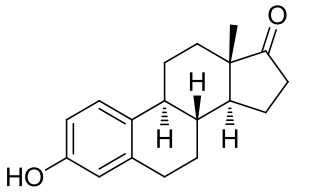
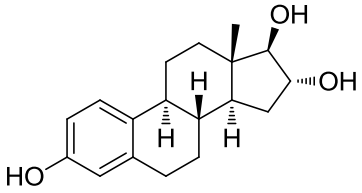
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Estrogen Replacement Agents					
Bisphenol A	80-05-7	$C_{15}H_{16}O_2$	228.29	4-[2-(4-hydroxyphenyl)propan-2-yl]phenol	
Diethylstilbestrol	56-53-1	$C_{18}H_{20}O_2$	268.35	4-[(E)-4-(4-hydroxyphenyl)hex-3-en-3-yl]phenol	
Equilin	474-86-2	$C_{18}H_{20}O_2$	268.35	(9S,13S,14S)-3-hydroxy-13-methyl-9,11,12,14,15,16-hexahydro-6H-cyclopenta[a]phenanthren-17-one	
Lipid regulators					
Bezafibrate	41859-67-0	$C_{19}H_{20}ClNO_4$	361.82	2-[4-[2-[(4-chlorobenzoyl)amino]ethyl]phenoxy]-2-methylpropanoic acid	

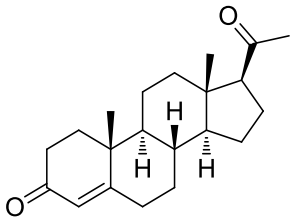
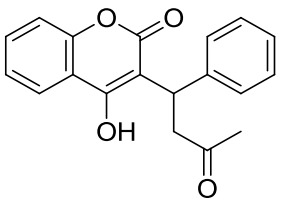
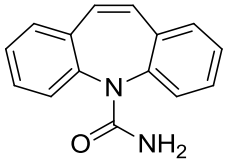
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Clofibric acid	882-09-7	$C_{10}H_{11}ClO_3$	214.65	2-(4-chlorophenoxy)-2-methylpropanoic acid	
Gemfibrozil	25812-30-0	$C_{15}H_{22}O_3$	250.33	5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoic acid	
Ovulation Inhibitors					
17-α-Ethynyl Estradiol	57-63-6	$C_{20}H_{24}O_2$	296.40	(8R,9S,13S,14S,17R)-17-ethynyl-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol	
19-Norethisterone	68-22-4	$C_{20}H_{26}O_2$	298.42	(8R,9S,10R,13S,14S,17R)-17-ethynyl-17-hydroxy-13-methyl-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one	
Reproductive Hormones					

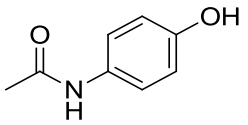
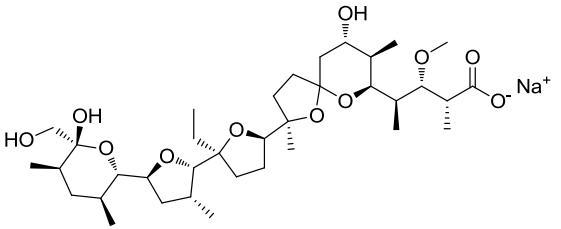
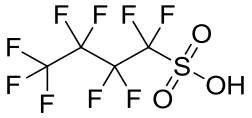
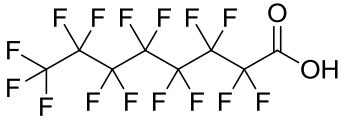
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
17-α-Estradiol	57-91-0	$C_{18}H_{24}O_2$	272.38	(8R,9S,13S,14S,17R)-13-methyl-6,7,8,9,11,12,14,15,16,17-decahydrocyclopenta[a]phenanthrene-3,17-diol	
17-β-Estradiol	57-91-0	$C_{18}H_{24}O_2$	272.38	(8R,9S,13S,14S,17S)-13-methyl-6,7,8,9,11,12,14,15,16,17-decahydrocyclopenta[a]phenanthrene-3,17-diol	
Estrone	53-16-7	$C_{18}H_{22}O_2$	270.37	(8R,9S,13S,14S)-3-hydroxy-13-methyl-7,8,9,11,12,14,15,16-octahydro-6H-cyclopenta[a]phenanthren-17-one	
Estriol	50-27-1	$C_{18}H_{24}O_3$	288.38	(8R,9S,13S,14S,16R,17R)-13-methyl-6,7,8,9,11,12,14,15,16,17-decahydrocyclopenta[a]phenanthrene-3,16,17-triol	

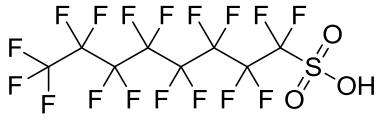
Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Progesterone	57-83-0	$C_{21}H_{30}O_2$	314.46	(8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-1,2,6,7,8,9,11,12,14,15,16,17-dodecahydrocyclopenta[a]phenanthren-3-one	
Anitcoagulant					
Warfarin	81-81-2	$C_{19}H_{16}O_4$	308.33	4-hydroxy-3-(3-oxo-1-phenylbutyl)chromen-2-one	
Antiepileptic, antidepressant					
Carbamazepine	298-46-4	$C_{15}H_{12}N_2O$	236.27	5H-Dibenzo[b,f]azepine-5-carboxamide	

Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Antipyretic					
Acetaminophen	103-90-2	$C_8H_9NO_2$	151.16	N-(4-hydroxyphenyl)acetamide	
Ionophore					
Monensin sodium	17090-79-8	$C_{36}H_{61}NaO_{11}$	692.85	sodium(2R,3S,4R)-4-[(2R,6R,7S,8R,9S)-2-[(2R,5S)-5-ethyl-5-[(2S,3R,5S)-5-[(2S,3S,5R,6R)-6-hydroxy-6-(hydroxymethyl)-3,5-dimethyloxan-2-yl]-3-methyloxolan-2-yl]oxolan-2-yl]-9-hydroxy-2,8-dimethyl-1,6-dioxaspiro[4.5]decan-7-yl]-3-methoxy-2-methylpentanoate	
Perfluorosurfactants					
Perfluorobutanesulfonic acid (PFBS)	375-73-5	$C_4HF_9O_3S$	300.10	1,1,2,2,3,3,4,4,4-nonafluorobutane-1-sulfonic acid	
Perfluorooctanoic acid (PFOA)	335-67-1	$C_8HF_{15}O_2$	414.07	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoic acid	

Appendix D cont'd (Details of the CECs targeted)

Compound	CAS-RN	Molecular formula	Mol Wt. g/mol	Chemical Name	Structure
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	$C_8HF_{17}O_3S$	500.13	1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-heptadecafluorooctane-1-sulfonic acid	

References:

(1) Chemical name: http://www.ncbi.nlm.nih.gov/pccompound, Accessed on: Jan 02, 2012

(2) CAS number: http://www.chemicalbook.com Accessed on: Jan 02, 2012

(3) Drawings: Chemdraw

REFERENCES

Absi, F., Gamache, F., Gehr, R., Liechti, P. and Nicell, J. (1993) Pilot plant investigation of ozone disinfection of a physico-chemically treated municipal wastewater, San Francisco, California.

Acero, J.L. and von Gunten, U. (2001) Characterization of oxidation processes: ozonation and the AOP O-3/H2O2. *Journal American Water Works Association* **93**(10), 90-100.

Aga, D.S. (2008) *Fate of pharmaceuticals in the environment and in water treatment systems*, CRC Press, Boca Raton.

Almeida, C. and Nogueira, J.M.F. (2006) Determination of steroid sex hormones in water and urine matrices by stir bar sorptive extraction and liquid chromatography with diode array detection. *Journal of Pharmaceutical and Biomedical Analysis* **41**(4), 1303-1311.

Alvares, A.B.C., Diaper, C. and Parsons, S.A. (2001) Partial oxidation by ozone to remove recalcitrance from wastewaters - A review. *Environmental Technology* **22**(4), 409-427.

Anderson, P.O., Knoben, J.E. and Troutman, W.G. (2002) *Handbook of clinical drug data*, McGraw-Hill Medical Pub. Division, New York.

Andreasen, F., Elsborg, L., Husted, S. and Thomsen, O. (1978) Pharmacokinetics of Sulfadiazine and Trimethoprim in Man. *European Journal of Clinical Pharmacology* **14**(1), 57-67.

Andreozzi, R., Marotta, R., Pinto, G. and Pollio, A. (2002) Carbamazepine in water: persistence in the environment, ozonation treatment and preliminary assessment on algal toxicity. *Water Research* **36**(11), 2869-2877.

APHA (1998) Standard methods for the examination of water and wastewater, 20th Edition. Clesceri, L.S., Greenberg, A.E. and Eaton, A.D. (eds), American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.

Arthur, J.W., Andrew, R.W., Mattson, V.R., Olson, D.T., Glass, G.E., Halligan, B.J. and Walbridge, C.T. (1975) *Comparative toxicity of sewage-effluent disinfection to freshwater aquatic life*, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Research Laboratory, Duluth.

Auriol, M., Filali-Meknassi, Y., Tyagi, R.D., Adams, C.D. and Surampalli, R.Y. (2006) Endocrine disrupting compounds removal from wastewater, a new challenge. *Process Biochemistry* **41**(3), 525-539.

Bahr, C., Ernst, M., Reemtsma, T., Heinzmann, B., Luck, F. and Jekel, M. (2005) Pilot scale ozonation of treated municipal effluents for removal of pharmaceutical compounds and pathogens – The Berlin study, IOA, Strasbourg.

Bahr, C., Schumacher, J., Ernst, M., Luck, F., Heinzmann, B. and Jekel, M. (2007) SUVA as control parameter for the effective ozonation of organic pollutants in secondary effluent. *Water Science and Technology* **55**(12), 267-274.

Baig, S., Hansmann, G. and Paolini, B. (2008) Ozone oxidation of oestrogenic active substances in wastewater and drinking water. *Water Science and Technology* **58**(2), 451-458.

Baker, J.C. (1925) Chlorine in Sewage and Waste Disposal. *Industrial & Engineering Chemistry* **17**(10), 1059-1060.
Baldwin, R.T. (1927) Chlorine research. *Journal of Chemical Education* **4**(5).
Bancroft, K., Chrostowski, P., Wright, R.L. and Suffet, I.H. (1984) Ozonation and Oxidation Competition Values - Relationship to Disinfection and Microorganisms Regrowth. *Water Research* **18**(4), 473-478.
Barber, L.B., Keefe, S.H., Kolpin, D.W., Schnoebelen, D.J., Flynn, J.L., Brown, G.K., Furlong, E.T., Glassmeyer, S.T., Gray, J.L., Meyer, M.T., Sandstrom, M.W., Taylor, H.E. and Zaugg, S.D. (2011) Lagrangian sampling of wastewater treatment plant effluent in Boulder Creek, Colorado, and Fourmile Creek, Iowa, during the summer of 2003 and spring of 2005—Hydrological and Water-Quality data, p. 84, U.S. Geological Survey, Reston, Virginia.
Barron, E., Deborde, M., Rabouan, S., Mazellier, P. and Legube, B. (2006) Kinetic and mechanistic investigations of progesterone reaction with ozone. *Water Research* **40**(11), 2181-2189.
Batt, A.L., Kim, S. and Aga, D.S. (2007) Comparison of the occurrence of antibiotics in four full-scale wastewater treatment plants with varying designs and operations. *Chemosphere* **68**(3), 428-435.
Behera, S.K., Kim, H.W., Oh, J.E. and Park, H.S. (2011) Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. *Science of the Total Environment* **409**(20), 4351-4360.
Ben, W., Qiang, Z., Pan, X. and Nie, Y. (2012) Degradation of Veterinary Antibiotics by Ozone in Swine Wastewater Pretreated with Sequencing Batch Reactor. *Journal of Environmental Engineering-Asce* **138**(3), 272-277.
Bennett, L.E. and Drikas, M. (1993) The Evaluation of Color in Natural-Waters. *Water Research* **27**(7), 1209-1218.
Bennink, H.J.T.C. (2004) Are all estrogens the same? *Maturitas* **47**(4), 269-275.
Benotti, M.J., Trenholm, R.A., Vanderford, B.J., Holady, J.C., Stanford, B.D. and Snyder, S.A. (2009) Pharmaceuticals and Endocrine Disrupting Compounds in US Drinking Water. *Environmental Science & Technology* **43**(3), 597-603.
Bertanza, G., Papa, M., Pedrazzani, R., Repice, C. and Dal Grande, M. (2012) Tertiary ozonation of industrial wastewater for the removal of estrogenic compounds (NP and BPA): a full scale case study, International Water Association, Goslar, Germany.
Besse, J.P. and Garric, J. (2009) Progestagens for human use, exposure and hazard assessment for the aquatic environment. *Environmental Pollution* **157**(12), 3485-3494.
Besse, J.P., Kausch-Barreto, C. and Garric, J. (2008) Exposure assessment of pharmaceuticals and their metabolites in the aquatic environment: Application to the French situation and preliminary prioritization. *Human and Ecological Risk Assessment* **14**(4), 665-695.
Bhandari, A., Environmental Council of the States (U.S.) Emerging Contaminants of Concern Task Committee and Environmental and Water Resources Institute (U.S.) (2009) *Contaminants of Emerging Environmental Concern*, American Society of Civil Engineers, Reston, Va.

Bila, D., Montalvao, A.F., Azevedo, D.D. and Dezotti, M. (2007) Estrogenic activity removal of 17 beta-estradiol by ozonation and identification of by-products. *Chemosphere* **69**(5), 736-746.

Black & Veatch, C. (2010) *White's Handbook of Chlorination and Alternative Disinfectants (5th Edition)*, John Wiley & Sons, Hoboken, NJ.

Bloetscher, F. and Plummer, J.D. (2011) Environmental Review & Case Study: Evaluating the Significance of Certain Pharmaceuticals and Emerging Pathogens in Raw Water Supplies. *Environmental Practice* **13**(03), 198-215.

Boyd, G.R., Reemtsma, H., Grimm, D.A. and Mitra, S. (2003) Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *Science of the Total Environment* **311**(1-3), 135-149.

Braga, O., Smythe, G.A., Schafer, A.I. and Feitz, A.J. (2005) Fate of steroid estrogens in Australian inland and coastal wastewater treatment plants. *Environmental Science & Technology* **39**(9), 3351-3358.

Bratby, J. (2006) *Coagulation and flocculation in water and wastewater treatment*, IWA Publishing, London; Seattle.

Brosèus, R., Vincent, S., Aboulfadl, K., Daneshvar, A., Sauvé, S., Barbeau, B. and Prévost, M. (2009) Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment. *Water Research* **43**(18), 4707-4717.

Brun, G.L., Bernier, M., Losier, R., Doe, K., Jackman, P. and Lee, H.B. (2006) Pharmaceutically active compounds in Atlantic Canadian sewage treatment plant effluents and receiving waters, and potential for environmental effects as measured by acute and chronic aquatic toxicity. *Environmental Toxicology and Chemistry* **25**(8), 2163-2176.

Buffle, M.O., Schumacher, J., Meylan, S., Jekel, M. and von Gunten, U. (2006a) Ozonation and advanced oxidation of wastewater: Effect of O_3 dose, pH, DOM and HO•-scavengers on ozone decomposition and HO• generation. *Ozone-Science & Engineering* **28**(4), 247-259.

Buffle, M.O., Schumacher, J., Salhi, E., Jekel, M. and von Gunten, U. (2006b) Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system: Application to disinfection and pharmaceutical oxidation. *Water Research* **40**(9), 1884-1894.

Buxton, G.V. and Elliot, A.J. (1986) Rate Constant for Reaction of Hydroxyl Radicals with Bicarbonate Ions. *Radiation Physics and Chemistry* **27**(3), 241-243.

Buxton, G.V., Greenstock, C.L., Helman, W.P. and Ross, A.B. (1988) Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (•Oh/•O^-) in Aqueous Solution. *Journal of Physical and Chemical Reference Data* **17**(2), 513-886.

Can, Z.S. and Çakir, E. (2010) Treatability of Organic Constituents in the Paşaköy Wastewater Treatment Plant Effluent by O_3 and O_3/H_2O_2. *Ozone-Science & Engineering* **32**(3), 209-214.

Carballa, M., Omil, F., Lema, J.M., Llompart, M., García-Jares, C., Rodríguez, I., Gómez, M. and Ternes, T. (2004) Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. *Water Research* **38**(12), 2918-2926.

Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D. and Zuccato, E. (2006) Removal of pharmaceuticals in sewage treatment plants in Italy. *Environmental Science & Technology* **40**(1), 357-363.

Çeçen, F. and Aktas, Ö. (2012) *Activated carbon for water and wastewater treatment : integration of adsorption and biological treatment*, Wiley-VCH, Weinheim, Germany.

Cermola, M., DellaGreca, M., Iesce, M.R., Previtera, L., Rubino, M., Temussi, F. and Brigante, M. (2005) Phototransformation of fibrate drugs in aqueous media. *Environmental Chemistry Letters* **3**(1), 43-47.

Chambers, P.A., Allard, M., Walker, S.L., Marsalek, J., Lawrence, J., Servos, M., Busnarda, J., Munger, K.S., Adare, K., Jefferson, C., Kent, R.A. and Wong, M.P. (1997) The Impacts of Municipal Wastewater Effluents on Canadian Waters: A Review. *Water Quality Research Journal of Canada* **32**(4), 659-713.

Cho, M., Kim, J., Kim, J.Y., Yoon, J. and Kim, J.H. (2010) Mechanisms of Escherichia coli inactivation by several disinfectants. *Water Research* **44**(11), 3410-3418.

Choi, K., Kim, Y., Park, J., Park, C.K., Kim, M., Kim, H.S. and Kim, P. (2008) Seasonal variations of several pharmaceutical residues in surface water and sewage treatment plants of Han River, Korea. *Science of the Total Environment* **405**(1-3), 120-128.

Christensen, F.M. (1998) Pharmaceuticals in the environment - A human risk? *Regulatory Toxicology and Pharmacology* **28**(3), 212-221.

Clara, M., Kreuzinger, N., Strenn, B., Gans, O. and Kroiss, H. (2005a) The solids retention time - a suitable design parameter to evaluate the capacity of wastewater treatment plants to remove micropollutants. *Water Research* **39**(1), 97-106.

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H. (2005b) Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. *Water Research* **39**(19), 4797-4807.

Comeau, F., Surette, C., Brun, G.L. and Losier, R. (2008) The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada. *Science of the Total Environment* **396**(2-3), 132-146.

Crouse, B.A., Ghoshdastidar, A.J. and Tong, A.Z. (2012) The presence of acidic and neutral drugs in treated sewage effluents and receiving waters in the Cornwallis and Annapolis River watersheds and the Mill CoveSewage Treatment Plant in Nova Scotia, Canada. *Environmental Research* **112**(0), 92-99.

D'Ascenzo, G., Di Corcia, A., Gentili, A., Mancini, R., Mastropasqua, R., Nazzari, M. and Samperi, R. (2003) Fate of natural estrogen conjugates in municipal sewage transport and treatment facilities. *Science of the Total Environment* **302**(1-3), 199-209.

Dahi, E. (1976) Physicochemical Aspects of Disinfection of Water by Means of Ultrasound and Ozone. *Water Research* **10**(8), 677-684.

Daughton, C.G. and Ternes, T.A. (1999) Pharmaceuticals and personal care products in the environment: Agents of subtle change? *Environmental Health Perspectives* **107**, 907-938.

Deborde, M., Rabouan, S., Duguet, J.P. and Legube, B. (2005) Kinetics of aqueous ozone-induced oxidation of some endocrine disruptors. *Environmental Science & Technology* **39**(16), 6086-6092.

Dhar, N.R. (1934) Formation of hydroxyl radical from the photolysis of water and the generation of formaldehyde. *Trans. Faraday Soc. Transactions of the Faraday Society* **30**.

Dickenson, E.R.V., Drewes, J.E., Sedlak, D.L., Wert, E.C. and Snyder, S.A. (2009) Applying Surrogates and Indicators to Assess Removal Efficiency of Trace Organic Chemicals during Chemical Oxidation of Wastewaters. *Environmental Science & Technology* **43**(16), 6242-6247.

Dodd, M.C., Buffle, M.O. and von Gunten, U. (2006) Oxidation of antibacterial molecules by aqueous ozone: Moiety-specific reaction kinetics and application to ozone-based wastewater treatment. *Environmental Science & Technology* **40**(6), 1969-1977.

Dong, M.M., Mezyk, S.P. and Rosario-Ortiz, F.L. (2010) Reactivity of Effluent Organic Matter (Ef0M) with Hydroxyl Radical as a Function of Molecular Weight. *Environmental Science & Technology* **44**(15), 5714-5720.

Drury, D.D., Snyder, S.A. and Wert, E.C. (2006) Using Ozone Disinfection for EDC Removal. *Proceedings of the Water Environment Federation* **2006**(12), 1249-1258.

Dufour, A.P. (1977) Bacterial Indicators / Health Hazards Associated With Water. Hoadley, A.W. and Dutka, B.J. (eds), pp. 48-58, American Society for Testing and Materials, Philadelphia, PA.

Ebadi, M.S. (2008) *Desk reference of clinical pharmacology*, CRC Press, Boca Raton.

Edzwald, J.K. and Tobiason, J.E. (1999) Enhanced coagulation: US requirements and a broader view. *Water Science and Technology* **40**(9), 63-70.

Elmund, G.K., Allen, M.J. and Rice, E.W. (1999) Comparison of *Escherichia coli*, total coliform, and fecal coliform populations as indicators of wastewater treatment efficiency. *Water Environment Research* **71**(3), 332-339.

Elovitz, M.S. and von Gunten, U. (1999) Hydroxyl radical/ozone ratios during ozonation processes. I.The R_{ct} concept. *Ozone-Science & Engineering* **21**(3), 239-260.

Elovitz, M.S., von Gunten, U. and Kaiser, H.P. (2000) Hydroxyl radical/ozone ratios during ozonation processes. II. The effect of temperature, pH, alkalinity, and DOM properties. *Ozone-Science & Engineering* **22**(2), 123-150.

Emblidge, J.P. and DeLorenzo, M.E. (2006) Preliminary risk assessment of the lipid-regulating pharmaceutical clofibric acid, for three estuarine species. *Environmental Research* **100**(2), 216-226.

EMEA (1998) Lincomycin - Summary Report (1), European Medicines Agency - Veterinary Medicines and Inspections, Committe for Veterinary Medicinal Products.

Environment Canada and Health Canada (2008) Screening Assessment for the Challenge Phenol, 4,4' -(1-methylethylidene) bis (Bisphenol A), Chemical Abstracts Service Registry Number 80-05-7, Environment Canada & Health Canada.

Fernandez, M.P., Ikonomou, M.G. and Buchanan, I. (2007) An assessment of estrogenic organic contaminants in Canadian wastewaters. *Science of the Total Environment* **373**(1), 250-269.

Ferrari, B., Paxéus, N., Lo Giudice, R., Pollio, A. and Garric, J. (2003) Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac. *Ecotoxicology and Environmental Safety* **55**(3), 359-370.

Finch, G.R. and Smith, D.W. (1987) Ozone disinfection of secondary effluent containing antibiotic-resistant *Escherichia coli*. *Canadian Journal of Civil Engineering* **14**(2), 234-238.

Finch, G.R. and Smith, D.W. (1989) Ozone Dose-Response of *Escherichia Coli* in Activated Sludge Effluent. *Water Research* **23**(8), 1017-1025.

Finch, G.R., Yuen, W.C. and Uibel, B.J. (1992) Inactivation of *Escherichia Coli* Using Ozone and Ozone - Hydrogen Peroxide. *Environmental Technology* **13**(6), 571-578.

Folmar, L.C., Denslow, N.D., Rao, V., Chow, M., Crain, D.A., Enblom, J., Marcino, J. and Guillette Jr., L.J. (1996) Vitellogenin induction and reduced serum testosterone concentrations in feral male carp (Cyprinus carpio) captured near a major metropolitan sewage treatment plant. *Environmental Health Perspectives* **104**(10), 1096-1101.

García-Galán, M.J., Díaz-Cruz, M.S. and Barceló, D. (2008) Identification and determination of metabolites and degradation products of sulfonamide antibiotics. *Trends in Analytical Chemistry* **27**(11), 1008-1022.

Gascoigne, G.B. (1931) Chlorination of Sewage and Sewage Effluents. *Sewage Works Journal* **3**(1), 38-49.

Gehr, R. and Nicell, J. (1996) Pilot Studies and Assessment of Downstream Effects of UV and Ozone Disinfection of a Physicochemical Wastewater. *Water Quality Research Journal of Canada* **31**(2), 263-282.

Gehr, R., Wagner, M., Veerasubramanian, P. and Payment, P. (2003) Disinfection efficiency of peracetic acid, UV and ozone after enhanced primary treatment of municipal wastewater. *Water Research* **37**(19), 4573-4586.

Gerrity, D., Gamage, S., Holady, J.C., Mawhinney, D.B., Quiñones, O., Trenholm, R.A. and Snyder, S.A. (2011) Pilot-scale evaluation of ozone and biological activated carbon for trace organic contaminant mitigation and disinfection. *Water Research* **45**(5), 2155-2165.

Ghosh, G.C., Okuda, T., Yamashita, N. and Tanaka, H. (2009) Occurrence and elimination of antibiotics at four sewage treatment plants in Japan and their effects on bacterial ammonia oxidation. *Water Science and Technology* **59**(4), 779-786.

Gilbert, R.I. (1980) The Analysis of Fluctuation Tests. *Mutation Research* **74**(4), 283-289.

Glaze, W.H. and Kang, J.W. (1989) Advanced Oxidation Processes. Test of a Kinetic Model for the Oxidation of Organic Compounds with Ozone and Hydrogen Peroxide in a Semibatch Reactor. *Industrial & Engineering Chemistry Research* **28**(11), 1580-1587.

Göbel, A., Thomsen, A., McArdell, C.S., Alder, A.C., Giger, W., Theiß, N., Löffler, D. and Ternes, T.A. (2005a) Extraction and determination of sulfonamides, macrolides, and trimethoprim in sewage sludge. *Journal of Chromatography A* **1085**(2), 179-189.

Göbel, A., Thomsen, A., McArdell, C.S., Joss, A. and Giger, W. (2005b) Occurrence and sorption behavior of sulfonamides, macrolides, and trimethoprim in activated sludge treatment. *Environmental Science & Technology* **39**(11), 3981-3989.

Gonzales, S., Peña, A. and Rosario-Ortiz, F.L. (2012) Examining the Role of Effluent Organic Matter Components on the Decomposition of Ozone and Formation of Hydroxyl Radicals in Wastewater. *Ozone: Science & Engineering* **34**(1), 42-48.

Gorman, J.A. (2010) Drugs in our Water: A Legal Proposal for Responsible Nationwide Pharmaceutical Consumption. *Journal of Land Use & Environmental Law* **26**(1), 147-178.

Gottschalk, C., Libra, J.A. and Saupe, A. (2000) *Ozonation of water and waste water : a practical guide to understanding ozone and its application*, Wiley-VCH, Weinheim; New York.

Grünebaum, T. (2011) Elimination von Arzneimittelrückständen in kommunalen Kläranlagen - Schlussbericht Phase 1, Germany.

Grung, M., Källqvist, T., Sakshaug, S., Skurtveit, S. and Thomas, K.V. (2008) Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline. *Ecotoxicology and Environmental Safety* **71**(2), 328-340.

Gulkowska, A., Leung, H.W., So, M.K., Taniyasu, S., Yamashita, N., Yeunq, L.W.Y., Richardson, B.J., Lei, A.P., Giesy, J.P. and Lam, P.K.S. (2008) Removal of antibiotics from wastewater by sewage treatment facilities in Hong Kong and Shenzhen, China. *Water Research* **42**(1-2), 395-403.

Haag, W.R. and Hoigné, J. (1983) Ozonation of Bromide-Containing Waters: Kinetics of Formation of Hypobromous Acid and Bromate. *Environmental Science & Technology* **17**(5), 261-267.

Haas, C.N. and Karra, S.B. (1984) Kinetics of Microbial Inactivation by Chlorine .1. Review of Results in Demand-Free Systems. *Water Research* **18**(11), 1443-1449.

Hannah, R., D'Aco, V.J., Anderson, P.D., Buzby, M.E., Caldwell, D.J., Cunningham, V.L., Ericson, J.F., Johnson, A.C., Parke, N.J., Samuelian, J.H. and Sumpter, J.P. (2009) Exposure Assessment of 17α-Ethinylestradiol in Surface Waters of the United States and Europe. *Environmental Toxicology and Chemistry* **28**(12), 2725-2732.

Hansen, K.M.S., Andersen, H.R. and Ledin, A. (2010) Ozonation of estrogenic chemicals in biologically treated sewage. *Water Science and Technology* **62**(3), 649-657.

Hao, C.Y., Zhao, X.M., Tabe, S. and Yang, P. (2008) Optimization of a multiresidual method for the determination of waterborne emerging organic pollutants using solid-phase extraction and liquid chromatography/tandem mass spectrometry and isotope dilution mass spectrometry. *Environmental Science & Technology* **42**(11), 4068-4075.

Harries, J.E., Sheahan, D.A., Jobling, S., Matthiessen, P., Neall, M., Sumpter, J.P., Tylor, T. and Zaman, N. (1997) Estrogenic activity in five United Kingdom rivers detected by measurement of vitellogenesis in caged male trout. *Environmental Toxicology and Chemistry* **16**(3), 534-542.

Hashimoto, T., Takahashi, K. and Murakami, T. (2006) Characteristics of estrogen decomposition by ozonation. *Water Science and Technology* **54**(10), 87-93.

Heberer, T. (2002) Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data. *Toxicology Letters* **131**(1-2), 5-17.

Hoigné, J. (1994) Characterization of Water Quality Criteria for Ozonation Processes. Part I: Minimal Set of Analytical Data. *Ozone-Science & Engineering* **16**(2), 113-120.

Hoigné, J. and Bader, H. (1983a) Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water - I. Non-Dissociating Organic Compounds. *Water Research* **17**(2), 173-183.

Hoigné, J. and Bader, H. (1983b) Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water - II. Dissociating Organic Compounds. *Water Research* **17**(2), 185-194.

Hoigné, J. and Bader, H. (1976) Role of Hydroxyl Radical Reactions in Ozonation Processes in Aqueous Solutions. *Water Research* **10**(5), 377-386.

Hoigné, J., Bader, H., Haag, W.R. and Staehelin, J. (1985) Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water - III. Inorganic Compounds and Radicals. *Water Research* **19**(8), 993-1004.

Hollender, J., Zimmermann, S.G., Koepke, S., Krauss, M., McArdell, C.S., Ort, C., Singer, H., von Gunten, U. and Siegrist, H. (2009) Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. *Environmental Science & Technology* **43**(20), 7862-7869.

Hope, B.K., Pillsbury, L. and Boling, B. (2012) A state-wide survey in Oregon (USA) of trace metals and organic chemicals in municipal effluent. *Science of the Total Environment* (0).

Hua, W.Y., Bennett, E.R., Maio, X.S., Metcalfe, C.D. and Letcher, R.J. (2006) Seasonality effects on pharmaceuticals and s-triazine herbicides in wastewater effluent and surface water from the Canadian side of the upper Detroit River. *Environmental Toxicology and Chemistry* **25**(9), 2356-2365.

Huang, C.H. and Sedlak, D.L. (2001) Analysis of estrogenic hormones in municipal wastewater effluent and surface water using enzyme-linked immunosorbent assay and gas chromatography/tandem mass spectrometry. *Environmental Toxicology and Chemistry* **20**(1), 133-139.

Huang, L. (2011) *Ozonation of Erythromycin and the Effects of pH, Carbonate and Phosphate Buffers, and Initial Ozone Dose*, The University of Texas at Austin, Austin.

Huber, M.M., Canonica, S., Park, G.Y. and von Gunten, U. (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. *Environmental Science & Technology* **37**(5), 1016-1024.

Huber, M.M., Göbel, A., Joss, A., Hermann, N., Löffler, D., McArdell, C.S., Ried, A., Siegrist, H., Ternes, T.A. and von Gunten, U. (2005) Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study. *Environmental Science & Technology* **39**(11), 4290-4299.

Hunt, N.K. and Mariñas, B.J. (1999) Inactivation of *Escherichia coli* with ozone: Chemical and inactivation kinetics. *Water Research* **33**(11), 2633-2641.

Hunt, N.K. and Mariñas, B.J. (1997) Kinetics of *Escherichia coli* inactivation with ozone. *Water Research* **31**(6), 1355-1362.
Ifelebuegu, A.O. (2011) The fate and behavior of selected endocrine disrupting chemicals in full scale wastewater and sludge treatment unit processes. *International Journal of Environmental Science and Technology* **8**(2), 245-254.
Ishizaki, T., Sasaki, T., Suganuma, T., Horai, Y., Chiba, K., Watanabe, M., Asuke, W. and Hoshi, H. (1980) Pharmacokinetics of Ketoprofen Following Single Oral, Intramuscular and Rectal Doses and After Repeated Oral Administration. *European Journal of Clinical Pharmacology* **18**(5), 407-414.
Jackevicius, C.A., Tu, J.V., Ross, J.S., Ko, D.T., Carreon, D. and Krumholz, H.M. (2011) Use of Fibrates in the United States and Canada. *Jama-Journal of the American Medical Association* **305**(12), 1217-1224.
Jeong, J., Song, W.H., Cooper, W.J., Jung, J. and Greaves, J. (2010) Degradation of tetracycline antibiotics: Mechanisms and kinetic studies for advanced oxidation/reduction processes. *Chemosphere* **78**(5), 533-540.
Jin, S., Yang, F., Liao, T., Hui, Y. and Xu, Y. (2008) Seasonal variations of estrogenic compounds and their estrogenicities in influent and effluent from a municipal sewage treatment plant in China. *Environmental Toxicology and Chemistry* **27**(1), 146-153.
Johnson, A.C. and Sumpter, J.P. (2001) Removal of endocrine-disrupting chemicals in activated sludge treatment works. *Environmental Science & Technology* **35**(24), 4697-4703.
Jolibois, B. and Guerbet, M. (2005) Efficacy of two wastewater treatment plants in removing genotoxins. *Archives of Environmental Contamination and Toxicology* **48**(3), 289-295.
Jones-Lepp, T.L. and Stevens, R. (2007) Pharmaceuticals and personal care products in biosolids/sewage sludge: the interface between analytical chemistry and regulation. *Analytical and Bioanalytical Chemistry* **387**(4), 1173-1183.
Joss, A., Keller, E., Alder, A.C., Göbel, A., McArdell, C.S., Ternes, T. and Siegrist, H. (2005) Removal of pharmaceuticals and fragrances in biological wastewater treatment. *Water Research* **39**(14), 3139-3152.
Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C.S., Ternes, T.A., Thomsen, A. and Siegrist, H. (2006) Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme. *Water Research* **40**(8), 1686-1696.
Karlowsky, J.A., Lagacé-Wiens, P.R.S., Low, D.E. and Zhanel, G.G. (2009) Annual macrolide prescription rates and the emergence of macrolide resistance among Streptococcus pneumoniae in Canada from 1995 to 2005. *International Journal of Antimicrobial Agents* **34**(4), 375-379.
Karthikeyan, K.G. and Meyer, M.T. (2006) Occurrence of antibiotics in wastewater treatment facilities in Wisconsin, USA. *Science of the Total Environment* **361**(1-3), 196-207.
Kavlock, R.J., Daston, G.P., DeRosa, C., Fenner-Crisp, P., Gray, L.E., Kaattari, S., Lucier, G., Luster, M., Mac, M.J., Maczka, C., Miller, R., Moore, J., Rolland, R., Scott, G., Sheehan, D.M., Sinks, T. and Tilson, H.A. (1996) Research needs for the risk assessment of health and environmental effects of endocrine disruptors: A

report of the US EPA-sponsored workshop. *Environmental Health Perspectives* **104**, 715-740.
Khan, S.J. and Ongerth, J.E. (2004) Modelling of pharmaceutical residues in Australian sewage by quantities of use and fugacity calculations. *Chemosphere* **54**(3), 355-367.
Kim, H.S., Yamada, H. and Tsuno, H. (2007a) The removal of estrogenic activity and control of brominated by-products during ozonation of secondary effluents. *Water Research* **41**(7), 1441-1446.
Kim, I. and Tanaka, H. (2011) Energy Consumption for PPCPs Removal by O_3 and O_3/UV. *Ozone-Science & Engineering* **33**(2), 150-157.
Kim, I., Yamashita, N. and Tanaka, H. (2009) Performance of UV and UV/H_2O_2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. *Journal of Hazardous Materials* **166**(2-3), 1134-1140.
Kim, S.D., Cho, J., Kim, I.S., Vanderford, B.J. and Snyder, S.A. (2007b) Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water Research* **41**(5), 1013-1021.
Koh, Y.K.K., Chiu, T.Y., Boobis, A., Cartmell, E., Scrimshaw, M.D. and Lester, J.N. (2008) Treatment and removal strategies for estrogens from wastewater. *Environmental Technology* **29**(3), 245-267.
Komori, K., Tanaka, H., Okayasu, Y., Yasojima, M. and Sato, C. (2004) Analysis and occurrence of estrogen in wastewater in Japan. *Water Science and Technology* **50**(5), 93-100.
Koutsouba, V., Heberer, T., Fuhrmann, B., Schmidt-Baumler, K., Tsipi, D. and Hiskia, A. (2003) Determination of polar pharmaceuticals in sewage water of Greece by gas chromatography-mass spectrometry. *Chemosphere* **51**(2), 69-75.
Kuspis, D.A. and Krenzelok, E.P. (1996) What happens to expired medications? A survey of community medication disposal. *Veterinary and Human Toxicology* **38**(1), 48-49.
Langford, K. and Jason, L. (2002) Endocrine Disrupters in Wastewater and Sludge Treatment Processes. Birkett, J.W. and Lester, J.N. (eds), CRC Press.
Larocque, R.L. (1999) Ozone applications in Canada - A state of the art review. *Ozone-Science & Engineering* **21**(2), 119-125.
Launer, M., Lyko, S., Fahlenkamp, H., Jagemann, P. and Ehrhard, P. (2012) Application of CFD simulation for process optimization at a full-scale ozonation plant for the removal of micropollutants from secondary effluent, International Water Association, Goslar, Germany.
Lazarova, V., Janex, M.L., Fiksdal, L., Oberg, C., Barcina, I. and Pommepuy, M. (1998) Advanced wastewater disinfection technologies: Short and long term efficiency. *Water Science and Technology* **38**(12), 109-117.
Le-Minh, N., Khan, S.J., Drewes, J.E. and Stuetz, R.M. (2010) Fate of antibiotics during municipal water recycling treatment processes. *Water Research* **44**(15), 4295-4323.
Lee, C.O. (2010) *Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and EDCs from wastewater*, The University of New Mexico, Albuquerque, New Mexico.

Lee, C.O., Howe, K.J. and Thomson, B.M. (2012) Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. *Water Research* (0).

Lee, R.B., Sarafin, K., Peart, T.E. and Svoboda, M.L. (2003) Acidic pharmaceuticals in sewage - Methodology, stability test, occurrence, and removal from Ontario samples. *Water Quality Research Journal of Canada* **38**(4), 667-682.

Leong, L.Y.C., Kuo, J., Tang, C.-C. and Water Environment Research Foundation (2008) *Disinfection of Wastewater Effluent - Comparison of Alternative Technologies*, IWA Publishing, London.

Lévesque, L.E., Brophy, J.M. and Zhang, B. (2005) The risk for myocardial infarction with cyclooxygenase-2 inhibitors: A population study of elderly adults. *Annals of Internal Medicine* **142**(7), 481-489.

Liberti, L., Notarnicola, M. and Lopez, A. (2000) Advanced treatment for municipal wastewater reuse in agriculture. III - Ozone disinfection. *Ozone-Science & Engineering* **22**(2), 151-166.

Lindberg, R.H., Wennberg, P., Johansson, M.I., Tysklind, M. and Andersson, B.A.V. (2005) Screening of human antibiotic substances and determination of weekly mass flows in five sewage treatment plants in Sweden. *Environmental Science & Technology* **39**(10), 3421-3429.

Lishman, L., Smyth, S.A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Beland, M. and Seto, P. (2006) Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada. *Science of the Total Environment* **367**(2-3), 544-558.

Liu, Z.H., Kanjo, Y. and Mizutani, S. (2009) Removal mechanisms for endocrine disrupting compounds (EDCs) in wastewater treatment - physical means, biodegradation, and chemical advanced oxidation: A review. *Science of the Total Environment* **407**(2), 731-748.

McArdell, C.S., Molnar, E., Suter, M.J.F. and Giger, W. (2003) Occurrence and fate of macrolide antibiotics in wastewater treatment plants and in the Glatt Valley Watershed, Switzerland. *Environmental Science & Technology* **37**(24), 5479-5486.

Mehinto, A.C. (2009) *Impacts of the human pharmaceutical diclofenac in the aquatic environment*, University of Exeter.

Metcalf & Eddy, I., Tchobanoglous, G., Burton, F.L. and Stensel, H.D. (2002) *Wastewater engineering : treatment and reuse*, McGraw-Hill.

Metcalfe, C.D., Koenig, B.G., Bennie, D.T., Servos, M., Ternes, T.A. and Hirsch, R. (2003a) Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environmental Toxicology and Chemistry* **22**(12), 2872-2880.

Metcalfe, C.D., Miao, X.S., Hua, W., Letcher, R. and Servos, M. (2004) Pharmaceuticals in the Environment: Sources, Fate, Effects and Risks. Kümmerer, K. (ed), pp. 67-87, Springer-Verlag, Heidelberg Berlin.

Metcalfe, C.D., Miao, X.S., Koenig, B.G. and Struger, J. (2003b) Distribution of acidic and neutral drugs in surface waters near sewage treatment plants in the lower Great Lakes, Canada. *Environmental Toxicology and Chemistry* **22**(12), 2881-2889.

Mezyk, S.P., Abud, E.M., Swancutt, K.L., McKay, G. and Dionysiou, D.D. (2010) Contaminants of Emerging Concern in the Environment: Ecological and Human Health Considerations. Halden, R.U. (ed), pp. 213-225, American Chemical Society.

Mezyk, S.P., Neubauer, T.J., Cooper, W.J. and Peller, J.R. (2007) Free-radical-induced oxidative and reductive degradation of sulfa drugs in water: Absolute kinetics and efficiencies of hydroxyl radical and hydrated electron reactions. *Journal of Physical Chemistry A* **111**(37), 9019-9024.

Miao, X.S., Bishay, F., Chen, M. and Metcalfe, C.D. (2004) Occurrence of antimicrobials in the final effluents of wastewater treatment plants in Canada. *Environmental Science & Technology* **38**(13), 3533-3541.

Miao, X.S., Yang, J.J. and Metcalfe, C.D. (2005) Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant. *Environmental Science & Technology* **39**(19), 7469-7475.

Minnow Environmental, I. and CCME, C.C.o.M.o.t.E. (2005) Environmental risk-based approaches for managing municipal wastewater effluent (MWWE), Minnow Environmental Inc., Mississauga, Ont.

Monteiro, S.C. and Boxall, A.B.A. (2010) Occurrence and Fate of Human Pharmaceuticals in the Environment. *Reviews of Environmental Contamination and Toxicology, Vol 202* **202**, 53-154.

Morris, J.C. (1988) The aqueous solubility of ozone - A review, pp. 14-16.

Morris, J.C. and McKay, G. (1975) *Formation of halogenated organics by chlorination of water supplies : a review*, Office of Research and Development, U.S. Environmental Protection Agency, Washington.

Muñoz, I., Tomàs, N., Mas, J., García-Reyes, J.F., Molina-Díaz, A. and Fernández-Alba, A.R. (2010) Potential chemical and microbiological risks on human health from urban wastewater reuse in agriculture. Case study of wastewater effluents in Spain. *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes* **45**(4), 300-309.

Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N. and Takada, H. (2007) Removal of selected pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs) during sand filtration and ozonation at a municipal sewage treatment plant. *Water Research* **41**(19), 4373-4382.

Nakada, N., Tanishima, T., Shinohara, H., Kiri, K. and Takada, H. (2006) Pharmaceutical chemicals and endocrine disrupters in municipal wastewater in Tokyo and their removal during activated sludge treatment. *Water Research* **40**(17), 3297-3303.

Nakonechny, M., Ikehata, K. and El-Din, M.G. (2008) Kinetics of estrone ozone/hydrogen peroxide advanced oxidation treatment. *Ozone-Science & Engineering* **30**(4), 249-255.

Nanaboina, V. and Korshin, G.V. (2010) Evolution of Absorbance Spectra of Ozonated Wastewater and Its Relationship with the Degradation of Trace-Level Organic Species. *Environmental Science & Technology* **44**(16), 6130-6137.

Nebel, C., Gottschling, R.D., Hutchison, R.L., McBride, T.J., Taylor, D.M., Pavoni, J.L., Tittlebaum, M.E., Spencer, H.E. and Fleischman, M. (1973) Ozone Disinfection of Industrial-Municipal Secondary Effluents. *Journal Water Pollution Control Federation* **45**(12), 2493-2507.

Nöthe, T., Fahlenkamp, H. and von Sonntag, C. (2009) Ozonation of Wastewater: Rate of Ozone Consumption and Hydroxyl Radical Yield. *Environmental Science & Technology* **43**(15), 5990-5995.
Okuda, T., Kobayashi, Y., Nagao, R., Yamashita, N., Tanaka, H., Tanaka, S., Fujii, S., Konishi, C. and Houwa, I. (2008) Removal efficiency of 66 pharmaceuticals during wastewater treatment process in Japan. *Water Science and Technology* **57**(1), 65-71.
Oneby, M.A., Bromley, C.O., Borchardt, J.H. and Harrison, D.S. (2010) Ozone Treatment of Secondary Effluent at U.S. Municipal Wastewater Treatment Plants. *Ozone-Science & Engineering* **32**(1), 43-55.
Ontario MOE (2008) Design guidelines for sewage works, Ontario Ministry of the Environment.
Ontario MOE (2001) Procedure F-5-4 Effluent Disinfection Requirements for Sewage Works Discharging to Surface Waters. Environment, O.M.o.t. (ed), Ontario Ministry of the Environment.
Oppenheimer, J., Eaton, A., Badruzzaman, M., Haghani, A.W. and Jacangelo, J.G. (2011) Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. *Water Research* **45**(13), 4019-4027.
Pagliaro, L.A. and Benet, L.Z. (1975) Critical Compilation of Terminal Half-Lives, Percent Excreted Unchanged, and Changes of Half-Life in Renal and Hepatic Dysfunction for Studies in Humans with References. *Journal of Pharmacokinetics and Biopharmaceutics* **3**(5), 338-383.
Paraskeva, P. and Graham, N.J.D. (2005) Treatment of a secondary municipal effluent by ozone, UV and microfiltration: microbial reduction and effect on effluent quality. *Desalination* **186**(1-3), 47-56.
Paraskeva, P., Lambert, S.D. and Graham, N.J.D. (1998) Influence of ozonation conditions on the treatability of secondary effluents *Ozone-Science & Engineering* **20**(2), 133-150.
Paraskeva, P., Lambert, S.D. and Graham, N.J.D. (1999) Ozone treatment of sewage works' final effluent. *Journal of the Chartered Institution of Water and Environmental Management* **13**(6), 430-435.
Pedrouzo, M., Borrull, F., Pocurull, E. and Marcé, R.M. (2011) Presence of Pharmaceuticals and Hormones in Waters from Sewage Treatment Plants. *Water Air and Soil Pollution* **217**(1-4), 267-281.
Petala, M., Tsiridis, V., Samaras, P., Zouboulis, A. and Sakellaropoulos, G.P. (2006) Wastewater reclamation by advanced treatment of secondary effluents. *Desalination* **195**(1-3), 109-118.
Petrović, M., Gonzalez, S. and Barceló, D. (2003) Analysis and removal of emerging contaminants in wastewater and drinking water. *Trac-Trends in Analytical Chemistry* **22**(10), 685-696.
Phelps, E.B. (1912) The Chemical Disinfection of Sewage. *American Journal of Public Health* **2**(2), 72-76.
Plósz, B.G., Leknes, H., Liltved, H. and Thomas, K.V. (2010) Diurnal variations in the occurrence and the fate of hormones and antibiotics in activated sludge

wastewater treatment in Oslo, Norway. *Science of the Total Environment* **408**(8), 1915-1924.
Puri, S.K. and Lassman, H.B. (1987) Roxithromycin: a Pharmacokinetic Review of a Macrolide. *Journal of Antimicrobial Chemotherapy* **20**, 89-100.
Race, J. (1918) *Chlorination of water*, J. Wiley and sons, New York.
Radjenovic, J., Petrovic, M. and Barceló, D. (2007) Analysis of pharmaceuticals in wastewater and removal using a membrane bioreactor. *Analytical and Bioanalytical Chemistry* **387**(4), 1365-1377.
Radjenovic, J., Petrovic, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. *Water Research* **43**(3), 831-841.
Rakness, K.L., Najm, I., Elovitz, M., Rexing, D. and Via, S. (2005) Cryptosporidium log-inactivation with ozone using effluent CT_{10}, geometric mean CT_{10}, extended integrated CT_{10} and extended CSTR calculations. *Ozone-Science & Engineering* **27**(5), 335-350.
Rakness, K.L., Stover, E.L. and Krenek, D.L. (1984) Design, Start-up, and Operation of an Ozone Disinfection Unit. *Journal Water Pollution Control Federation* **56**(11), 1152-1159.
Rao, S.S. and Lifshitz, R. (1995) The Muta-Chromoplate Method for Measuring Mutagenicity of Environmental-Samples and Pure-Chemicals. *Environmental Toxicology and Water Quality* **10**(4), 307-313.
Razavi, B., Song, W.H., Cooper, W.J., Greaves, J. and Jeong, J. (2009) Free-Radical-Induced Oxidative and Reductive Degradation of Fibrate Pharmaceuticals: Kinetic Studies and Degradation Mechanisms. *Journal of Physical Chemistry A* **113**(7), 1287-1294.
Real, F.J., Benitez, F.J., Acero, J.L., Sagasti, J.J.P. and Casas, F. (2009) Kinetics of the Chemical Oxidation of the Pharmaceuticals Primidone, Ketoprofen, and Diatrizoate in Ultrapure and Natural Waters. *Industrial & Engineering Chemistry Research* **48**(7), 3380-3388.
Reisz, E., Schmidt, W., Schuchmann, H.P. and von Sonntag, C. (2003) Photolysis of ozone in aqueous solutions in the presence of tertiary butanol. *Environmental Science & Technology* **37**(9), 1941-1948.
Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W. and Keller, J. (2012) Ozonation and biological activated carbon filtration of wastewater treatment plant effluents. *Water Research* **46**(3), 863-872.
Reungoat, J., Escher, B.I., Macova, M. and Keller, J. (2011) Biofiltration of wastewater treatment plant effluent: Effective removal of pharmaceuticals and personal care products and reduction of toxicity. *Water Research* **45**(9), 2751-2762.
Reungoat, J., Macova, M., Escher, B.I., Carswell, S., Mueller, J.F. and Keller, J. (2010) Removal of micropollutants and reduction of biological activity in a full scale reclamation plant using ozonation and activated carbon filtration. *Water Research* **44**(2), 625-637.
Rice, E.W., Allen, M.J. and Edberg, S.C. (1990) Efficacy of β-Glucuronidase Assay for Identification of *Escherichia coli* by the Defined-Substrate Technology. *Applied and Environmental Microbiology* **56**(5), 1203-1205.

Rice, R.G. (1999) Ozone in the United States of America - State-of-the-art. *Ozone-Science & Engineering* **21**(2), 99-118.
Rice, R.G., Evison, L.M. and Robson, C.M. (1981) Ozone Disinfection of Municipal Wastewater - Current State-of-the-Art. *Ozone-Science & Engineering* **3**(4), 239-272.
Ried, A., Mielcke, J. and Wieland, A. (2009) The Potential Use of Ozone in Municipal Wastewater. *Ozone-Science & Engineering* **31**(6), 415-421.
Rivas, F.J., Sagasti, J., Encinas, A. and Gimeno, O. (2011) Contaminants abatement by ozone in secondary effluents. Evaluation of second-order rate constants. *Journal of Chemical Technology and Biotechnology* **86**(8), 1058-1066.
Rivas, J., Gimeno, O., Borralho, T. and Carbajo, M. (2010) UV-C photolysis of endocrine disruptors. The influence of inorganic peroxides. *Journal of Hazardous Materials* **174**(1-3), 393-397.
Rosal, R., Rodríguez, A., Perdigón-Melón, J.A., Petre, A., García-Calvo, E., Gómez, M.J., Agüera, A. and Fernández-Alba, A.R. (2010) Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. *Water Research* **44**(2), 578-588.
Rosario-Ortiz, F.L., Mezyk, S.P., Doud, D.F.R. and Snyder, S.A. (2008) Quantitative correlation of absolute hydroxyl radical rate constants with mon-isolated effluent organic matter bulk properties in water. *Environmental Science & Technology* **42**(16), 5924-5930.
Rosenfeldt, E.J. and Linden, K.G. (2004) Degradation of endocrine disrupting chemicals bisphenol A, ethinyl estradiol, and estradiol during UV photolysis and advanced oxidation processes. *Environmental Science & Technology* **38**(20), 5476-5483.
Ruel, S.M., Choubert, J.M., Esperanza, M., Miège, C., Madrigal, P.N., Budzinski, H., Le Ménach, K., Lazarova, V. and Coquery, M. (2011) On-site evaluation of the removal of 100 micro-pollutants through advanced wastewater treatment processes for reuse applications. *Water Science and Technology* **63**(11), 2486-2497.
Runnalls, T.J., Hala, D.N. and Sumpter, J.P. (2007) Preliminary studies into the effects of the human pharmaceutical Clofibric acid on sperm parameters in adult Fathead minnow. *Aquatic Toxicology* **84**(1), 111-118.
Ryu, J., Yoon, Y. and Oh, J. (2011) Occurrence of endocrine disrupting compounds and pharmaceuticals in 11 WWTPs in Seoul, Korea. *Ksce Journal of Civil Engineering* **15**(1), 57-64.
Sadezky, A., Löffler, D. and Ternes, T. (2008) Proposal of an environmental indicator and classification system of pharmaceutical product residues for environmental management, Federal Insitute of Hydrology BfG, Germany.
Sarmah, A.K., Meyer, M.T. and Boxall, A.B.A. (2006) A global perspective on the use, sales, exposure pathways, occurrence, fate and effects of veterinary antibiotics (VAs) in the environment. *Chemosphere* **65**(5), 725-759.
Sawyer, C.M. (1976) *Wastewater disinfection : a state-of-the-art summary*, Virginia Water Resources Research Center, Virginia Polytechnic Institute and State University, Blacksburg.

Schaar, H., Clara, M., Gans, O. and Kreuzinger, N. (2010) Micropollutant removal during biological wastewater treatment and a subsequent ozonation step. *Environmental Pollution* **158**(5), 1399-1404.

Sedlak, D.L. and Pinkston, K.E. (2001) Factors affecting the concentrations of pharmaceuticals released to the aquatic environment. *Water Resources Update* **120**(September), 56-64.

Shon, H.K., Vigneswaran, S. and Snyder, S.A. (2006) Effluent organic matter (EfOM) in wastewater: Constituents, effects, and treatment. *Critical Reviews in Environmental Science and Technology* **36**(4), 327-374.

Snyder, S.A., Keith, T.L., Verbrugge, D.A., Snyder, E.M., Gross, T.S., Kannan, K. and Giesy, J.P. (1999) Analytical methods for detection of selected estrogenic compounds in aqueous mixtures. *Environmental Science & Technology* **33**(16), 2814-2820.

Snyder, S.A., Wert, E.C., Rexing, D.J., Zegers, R.E. and Drury, D.D. (2006) Ozone oxidation of endocrine disruptors and pharmaceuticals in surface water and wastewater. *Ozone-Science & Engineering* **28**(6), 445-460.

Snyder, S.A., Westerhoff, P., Yoon, Y. and Sedlak, D.L. (2003) Pharmaceuticals, personal care products, and endocrine disruptors in water: Implications for the water industry. *Environmental Engineering Science* **20**(5), 449-469.

Sosiak, A.J., Hebben, T. and Alberta. Alberta, E. (2005) *A preliminary survey of pharmaceuticals and endocrine disrupting compounds in treated municipal wastewaters and receiving rivers of Alberta*, Alberta Environment, Environmental Monitoring and Evaluation Branch, Edmonton.

Sotelo, J.L., Beltrán, F.J., Benitez, F.J. and Beltrán-Heredia, J. (1989) Henry's Law Constant for the Ozone Water-System. *Water Research* **23**(10), 1239-1246.

Sowers, A.D., Mills, M.A. and Klaine, S.J. (2009) The developmental effects of a municipal wastewater effluent on the northern leopard frog, Rana pipiens. *Aquatic Toxicology* **94**(2), 145-152.

Stover, E.L. and Jarnis, R.W. (1981) Obtaining High-Level Wastewater Disinfection with Ozone. *Journal Water Pollution Control Federation* **53**(11), 1637-1647.

Stumpf, M., Ternes, T.A., Wilken, R.D., Rodrigues, S.V. and Baumann, W. (1999) Polar drug residues in sewage and natural waters in the state of Rio de Janeiro, Brazil. *Science of the Total Environment* **225**(1-2), 135-141.

Sui, Q., Huang, J., Deng, S.B., Yu, G. and Fan, Q. (2010) Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. *Water Research* **44**(2), 417-426.

Summerfelt, S.T. (2003) Ozonation and UV irradiation - an introduction and examples of current applications. *Aquacultural Engineering* **28**(1-2), 21-36.

Swan, G., Naidoo, V., Cuthbert, R., Green, R.E., Pain, D.J., Swarup, D., Prakash, V., Taggart, M., Bekker, L., Das, D., Diekmann, J., Diekmann, M., Killian, E., Meharg, A., Patra, R.C., Saini, M. and Wolter, K. (2006) Removing the threat of diclofenac to critically endangered Asian vultures. *Plos Biology* **4**(3), 395-402.

Sweetman, S.C. (2009) *Martindale: The Complete Drug Reference*, Pharmaceutical Press, London; Chicago.

Tabe, S., Jamal, T., Seth, R., Yue, C., Yang, P., Zhao, X. and Schweitzer, L. (2009) PPCPs and EDCs—Occurrence in the Detroit River and Their Removal by Ozonation, p. 236, Denver, Colorado, U.S.A.

Takahara, H., Nakayama, S. and Tsuno, H. (2006) Application of Ozone to Municipal Sewage Treatment, pp. 3-8, Berlin.

Tauxe-Wuersch, A., De Alencastro, L.F., Grandjean, D. and Tarradellas, J. (2005) Occurrence of several acidic drugs in sewage treatment plants in Switzerland and risk assessment. *Water Research* **39**(9), 1761-1772.

Ternes, T.A. (1998) Occurrence of drugs in German sewage treatment plants and rivers. *Water Research* **32**(11), 3245-3260.

Ternes, T.A., Joss, A. and Siegrist, H. (2004) Scrutinizing pharmaceuticals and personal care products in wastewater treatment. *Environmental Science & Technology* **38**(20), 392a-399a.

Ternes, T.A., Kreckel, P. and Mueller, J. (1999a) Behaviour and occurrence of estrogens in municipal sewage treatment plants - II. Aerobic batch experiments with activated sludge. *Science of the Total Environment* **225**(1-2), 91-99.

Ternes, T.A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.J., Haist-Gulde, B., Preuss, G., Wilme, U. and Zulei-Seibert, N. (2002) Removal of pharmaceuticals during drinking water treatment. *Environmental Science & Technology* **36**(17), 3855-3863.

Ternes, T.A., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M. and Teiser, B. (2003) Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? *Water Research* **37**(8), 1976-1982.

Ternes, T.A., Stumpf, M., Mueller, J., Haberer, K., Wilken, R.D. and Servos, M. (1999b) Behavior and occurrence of estrogens in municipal sewage treatment plants - I. Investigations in Germany, Canada and Brazil. *Science of the Total Environment* **225**(1-2), 81-90.

Tomiyasu, H., Fukutomi, H. and Gordon, G. (1985) Kinetics and Mechanism of Ozone Decomposition in Basic Aqueous Solution. *Inorganic Chemistry* **24**(19), 2962-2966.

Tripathi, S., Pathak, V., Tripathi, D.M. and Tripathi, B.D. (2011) Application of ozone based treatments of secondary effluents. *Bioresource Technology* **102**(3), 2481-2486.

Tyrrell, S.A., Rippey, S.R. and Watkins, W.D. (1995) Inactivation of Bacterial and Viral Indicators in Secondary Sewage Effluents, Using Chlorine and Ozone. *Water Research* **29**(11), 2483-2490.

USEPA (1986a) *Ambient water quality criteria for bacteria - 1986*, United States Environmental Protection Agency, Office of Water Regulations and Standards, Washington, DC.

USEPA (1986b) *Design manual : municipal wastewater disinfection*, U.S. Environmental Protection Agency, Office of Research and Development, Water Engineering Research Laboratory, Center for Environmental Research Information, Cincinnati, OH.

USEPA (1999) Disinfection profiling and benchmarking guidance manual, United States Environmental Protection Agency, Office of Water, Washington, D.C.

USEPA (2009) *Method 415.3 Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water*, U.S. Environmental Protection Agency, Ohio.

van Leeuwen, J. and Prinsloo, J. (1980) Ozonation at the Stander water reclamation plant. *Water S.A* **6**(2), 96-102.

van Leeuwen, J.H., Pipe-Martin, C. and Lehmann, R.M. (2003) Water reclamation at South Caboolture, Queensland, Australia. *Ozone-Science & Engineering* **25**(2), 107-120.

Venosa, A.D. and Meckes, M.C. (1983) Control of Ozone Disinfection by Exhaust Gas Monitoring. *Journal Water Pollution Control Federation* **55**(9), 1163-1167.

Vieno, N. (2007) *Occurrence of pharmaceuticals in Finnish sewage treatment plants, surface waters and their elimination in drinking water treatment processes*, Tampere University of Technology, Tampere.

Viglino, L., Aboulfadl, K., Prévost, M. and Sauvé, S. (2008) Analysis of natural and synthetic estrogenic endocrine disruptors in environmental waters using online preconcentration coupled with LC-APPI-MS/MS. *Talanta* **76**(5), 1088-1096.

von Gunten, U. (2003a) Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research* **37**(7), 1443-1467.

von Gunten, U. (2003b) Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water Research* **37**(7), 1469-1487.

von Gunten, U. and Hoigné, J. (1994) Bromate Formation during Ozonation of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions. *Environmental Science & Technology* **28**(7), 1234-1242.

von Gunten, U. and Ramseier, M. (2010) Critical review of literature for rate constants for reaction of chemical oxidants with inorganic and organic pollutants, Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland.

Ward, R.W. and DeGraeve, G.M. (1978) Acute Residual Toxicity of Several Wastewater Disinfectants to Aquatic Life. *Water Resources Bulletin* **14**(3), 696-709.

Wert, E., Gonzales, S., Dong, M.M. and Rosario-Ortiz, F. (2011) Evaluation of Enhanced Coagulation Pretreatment to Improve Ozone Oxidation Efficiency in Wastewater, International Water Association, Costa Mesa, California.

Wert, E.C., Rosario-Ortiz, F.L., Drury, D.D. and Snyder, S.A. (2007) Formation of oxidation byproducts from ozonation of wastewater. *Water Research* **41**(7), 1481-1490.

Wert, E.C., Rosario-Ortiz, F.L. and Snyder, S.A. (2009a) Effect of ozone exposure on the oxidation of trace organic contaminants in wastewater. *Water Research* **43**(4), 1005-1014.

Wert, E.C., Rosario-Ortiz, F.L. and Snyder, S.A. (2009b) Using Ultraviolet Absorbance and Color To Assess Pharmaceutical Oxidation during Ozonation of Wastewater. *Environmental Science & Technology* **43**(13), 4858-4863.

Westerhoff, P., Aiken, G., Amy, G. and Debroux, J. (1999) Relationships between the structure of natural organic matter and its reactivity towards molecular ozone and hydroxyl radicals. *Water Research* **33**(10), 2265-2276.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environmental Science & Technology* **39**(17), 6649-6663.

Whitby, G.E. and Scheible, O.K. (2004) The history of UV and wastewater. *IUVA News* **6**(3), 15-26.

Williams, R.T. (1971) The metabolism of certain drugs and food chemicals in man. *Annals of the New York Academy of Sciences* **179**, 141-154.

Williams, R.T. and Parke, D.V. (1964) The Metabolic Fate of Drugs. *Annu. Rev. Pharmacol. Annual Review of Pharmacology* **4**(1), 85-114.

Winkler, M., Lawrence, J.R. and Neu, T.R. (2001) Selective degradation of ibuprofen and clofibric acid in two model river biofilm systems. *Water Research* **35**(13), 3197-3205.

Wolfe, R.L., Stewart, M.H., Liang, S. and Mcguire, M.J. (1989) Disinfection of Model Indicator Organisms in a Drinking-Water Pilot-Plant by Using PEROXONE. *Applied and Environmental Microbiology* **55**(9), 2230-2241.

Xu, P., Janex, M.L., Savoye, P., Cockx, A. and Lazarova, V. (2002) Wastewater disinfection by ozone: main parameters for process design. *Water Research* **36**(4), 1043-1055.

Xu, W.H., Zhang, G., Li, X.D., Zou, S.C., Li, P., Hu, Z.H. and Li, J. (2007) Occurrence and elimination of antibiotics at four sewage treatment plants in the Pearl River Delta (PRD), South China. *Water Research* **41**(19), 4526-4534.

Yang, L.M., Yu, L.E. and Ray, M.B. (2009) Photocatalytic Oxidation of Paracetamol: Dominant Reactants, Intermediates, and Reaction Mechanisms. *Environmental Science & Technology* **43**(2), 460-465.

Yang, X., Flowers, R.C., Weinberg, H.S. and Singer, P.C. (2011) Occurrence and removal of pharmaceuticals and personal care products (PPCPs) in an advanced wastewater reclamation plant. *Water Research* **45**(16), 5218-5228.

Yoon, Y., Westerhoff, P., Snyder, S.A., Wert, E.C. and Yoon, J. (2007) Removal of endocrine disrupting compounds and pharmaceuticals by nanofiltration and ultrafiltration membranes. *Desalination* **202**(1-3), 16-23.

Zhang, T. and Li, B. (2011) Occurrence, Transformation, and Fate of Antibiotics in Municipal Wastewater Treatment Plants. *Critical Reviews in Environmental Science and Technology* **41**(11), 951-998.

Zhang, Y.J., Geissen, S.U. and Gal, C. (2008) Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies. *Chemosphere* **73**(8), 1151-1161.

Zhou, H.D., Huang, X., Wang, X.L., Zhi, X.H., Yang, C.D., Wen, X.H., Wang, Q.H., Tsuno, H. and Tanaka, H. (2010) Behaviour of selected endocrine-disrupting chemicals in three sewage treatment plants of Beijing, China. *Environmental Monitoring and Assessment* **161**(1-4), 107-121.

Zimmermann, S.G., Wittenwiler, M., Hollender, J., Krauss, M., Ort, C., Siegrist, H. and von Gunten, U. (2011) Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection. *Water Research* **45**(2), 605-617.

Zita, A. and Hermansson, M. (1997) Effects of bacterial cell surface structures and hydrophobicity on attachment to activated sludge flocs. *Applied and Environmental Microbiology* **63**(3), 1168-1170.

Zorita, S., Mårtensson, L. and Mathiasson, L. (2009) Occurrence and removal of pharmaceuticals in a municipal sewage treatment system in the south of Sweden. *Science of the Total Environment* **407**(8), 2760-2770.

Zuccato, E., Calamari, D., Natangelo, M. and Fanelli, R. (2000) Presence of therapeutic drugs in the environment. *Lancet* **355**(9217), 1789-1790.

Zwiener, C. and Frimmel, F.H. (2003) Short-term tests with a pilot sewage plant and biofilm reactors for the biological degradation of the pharmaceutical compounds clofibric acid, ibuprofen, and diclofenac. *Science of the Total Environment* **309**(1-3), 201-211.

VITA AUCTORIS

Name:	Saileshkumar Singh	
Place of birth:	Mumbai, India	
Year of birth:	1973	
Education:	Institution of Mechanical Engineers (India)	
	1993 – 1998	Bachelor of Engineering (Mechanical)
	University of Windsor, Canada	
	2008 – 2010	Master of Engineering (Environmental)
	2010 – 2012	Master of Applied Science (Environmental)