

CHEMICALS OF EMERGING CONCERN IN THE GREAT LAKES REGION

Prepared by:

Merih Otker Uslu, Nihar Biswas

Civil and Environmental Engineering, University of Windsor
401 Sunset Ave., Windsor, Ontario N9B 3P4
and

Saad Jasim

Great Lakes Regional Office, International Joint Commission
100 Ouellette Ave., 8th Floor, Windsor, ON N9A 6T3

CHEMICALS OF EMERGING CONCERN IN THE GREAT LAKES REGION

Contents

1. Introduction.....	1
2. Pharmaceutical Substances.....	3
3. Pesticides.....	32
4. Flame Retardants.....	42
5. Perfluorinated Surfactants.....	52
6. Alkyphenolic Substances.....	56
7. Synthetic Musk Fragrances.....	58
8. Plasticizers.....	61
9. Polycyclic Aromatic Hydrocarbons.....	61
10. Conclusions.....	62
11. References.....	64

1. INTRODUCTION

Pharmaceutical compounds, personal care products and endocrine disrupting compounds have been detected in municipal wastewaters, surface and ground waters, drinking waters as well as sediments and aquatic biota all around the world. Pharmaceutically active compounds are subdivided into several groups like anti inflammatories, antibiotics, anti epileptics, beta blockers, etc. A number of chemical substances are included in personal care products such as musk fragrances and cosmetics. A broad range of compounds have been identified as endocrine disruptors, such as hormones, pesticides and alkylphenols. These compounds were lumped into a group under the term “Chemicals of Emerging Concern” and are receiving attention due to their potential adverse effects on animals and humans at low levels of exposure. The toxic effects on

aquatic organisms, alterations on the reproductive system of aquatic organisms and the promotion of the development of resistant bacterial strains representing a health risk to humans, are among the adverse effects of these compounds.

Although chemicals of emerging concern have been detected in different environmental compartments for a long time period, their environmental releases have not been completely regulated by the regulatory communities in the United States and Canada. A comprehensive risk assessment for each chemical of emerging concern should be conducted by scientific and regulatory authorities. For this purpose, environmental analysis and monitoring should be undertaken especially in areas where toxic chemicals are released into the aquatic environment.

Environmental contamination by the chemicals of emerging concern due to the discharges from agricultural, industrial, and municipal activities is also known within the Great Lakes basin and many such locations are listed as Areas of Concern by the International Joint Commission. In the present report, a review of the literature data on the occurrence of chemicals of emerging concern in the Great Lakes Basin between the years of 2007-2011 was performed using Web of Science to compile the peer-reviewed scientific studies and reports. The chemicals identified as emerging chemicals by the International Joint Commission are synthetic musks, fluorinated surfactants, brominated and chlorinated flame retardants, alkylphenol-ethoxylates, short chain chlorinated paraffins, phthalates, pharmaceuticals and personal care products, pesticides and hydroxylated polychlorinated biphenyls (PCBs). Based on the given list and literature data, the emerging chemicals summarized in the current review are classified as pharmaceutical substances, pesticides, flame retardants (brominated and chlorinated flame retardants, chlorinated paraffins), perfluorinated surfactants, alkylphenolic substances, synthetic musk fragrances, plasticizers and polycyclic aromatic hydrocarbons. The literature data on the historical contaminant, polychlorinated biphenyls is excluded in the current report. The occurrence of all these chemicals in wastewater treatment plant influents and effluents, surface and ground waters, drinking water treatment plant influents and effluents, sediments and biota are discussed throughout the report.

2. PHARMACEUTICAL SUBSTANCES

Pharmaceutical substances are extensively used to treat diseases in humans and animals. They are emerging pollutants in water and their presence in the environment is of growing interest worldwide. Due to the continuous load of pharmaceuticals into sewage treatment plants (STPs) through the human excretion, the effluents from hospitals and manufacturing plants, they have been detected in STP influents (Watkinson et al., 2009). Conventional treatment processes in STPs generally failed in the complete removal of pharmaceutically active substances (Carballa et al., 2004), so that they have also been detected in STP effluents. Improper discharge of STP effluents, surface runoff and leaching in agricultural areas and irrigation with treated or untreated wastewater are responsible for the presence of pharmaceutical residues in surface and ground waters that are sources of drinking water supply (Jasim et al., 2006; Benotti et al., 2009). Conventional drinking water treatment processes including coagulation, flocculation, sedimentation, filtration and chlorination have been demonstrated to be ineffective in complete destruction of pharmaceutical compounds (Westerhoff et al., 2005; Jasim et al., 2006).

The main concern regarding the presence of pharmaceutical residues in the aquatic environment has been focused on antibacterials which may promote the development of resistant bacteria strains representing a health risk to humans. A wide range of antibiotic resistance has been detected in natural waters (De Oliveira and Pinhata 2008). Presence of another emerging pollutant, endocrine disrupting chemicals such as hormones, may alter the reproduction of aquatic organisms. Additionally, the toxic effects of several pharmaceutical classes such as, analgesics/anti-inflammatories, antibiotics, antiepileptics and steroid hormones to aquatic organisms have been demonstrated to occur even at low concentrations (Hernando et al., 2006). Existence of these substances in drinking water sources may also pose adverse effects on humans.

A wide variety of prescription and non-prescription drugs have been detected in sewage treatment plants (Table 1a), in natural waters (Table 1b), in drinking water treatment plants (Table 1c) as well as in aquatic biota (Table 1d) in the Great Lakes Basin. These drugs include

anti-inflammatories, lipid regulators, anti-depressants, beta blockers, antibiotics, anti-epileptics, analgesics, antihistamines, antihypertensives, stimulants and hormones.

The incomplete elimination of pharmaceuticals in wastewater treatment plants has been shown by several studies (Table 1a). Scheurer et al. (2010) analyzed the beta blocker compounds, atenolol, sotalol, metoprolol and propranolol in the effluents of WWTPs in Kitchener, Windsor, Elmira and Galt where treatment technologies differed from secondary to tertiary treatment plants. Analyzed beta blockers were found in all effluent samples with atenolol and metoprolol present at the highest concentrations. The modest elimination of beta blockers was attributed to microbial biodegradation rather than sorption as the partition coefficients of the compounds were found to be quite low ($K_d < 500$ l/kg). Of the 12 analyzed beta blockers, Lee et al. (2007) detected propranolol, sotalol, metoprolol, atenolol, acebutolol, labetalol, bisoprolol and nadolol in all primary (sedimentation) and final (activated sludge with or without sand filtration) effluents of WWTPs collected from Brantford, Galt, Guelph and Toronto in May and June 2006. The concentrations of beta blockers detected in all samples ranged from 32 to 1370 ng/l. The authors indicated that the stability of beta blockers in wastewater treatment plants might be a reason for the presence of these compounds in surface water samples.

The same group of authors analyzed lipid regulators atorvastatin (ATO), rosuvastatin (RST) and a metabolite rosuvastatin lactone (RSTL), in the influents and effluents of WWTPs located in Brantford, Burlington, Guelph, Hamilton, Mississauga and Niagara, Pickering, Thunder bay and Toronto (Lee et al., 2009). Both ATO and RST and their metabolites were detected in all influent and effluent samples. The concentrations of ATO and RST in the influents of WWTPs ranged from 72 to 263 ng/l and 134 to 604 ng/l, respectively. The elimination of total RST in WWTPs varied between 4-57 %, whereas that of ATO was ranged from 17% to 91 %. The lower elimination rates of RST compared to ATO was attributed to its lower metabolic rate and greater resistance to sewage treatment processes. The authors also analyzed the surface water samples from Hamilton Harbor that were impacted by the discharge of local STPs and detected ATO, RST and RSTL up to 59.1 ng/l, 74.9 ng/l and 66.2 ng/l, respectively. The presence of other lipid regulating drugs, gemfibrozil, bezafibrate and clofibrac acid, anti inflammatory drugs, several antibiotics and carbamazepine both in influents and effluents from Windsor and Western Ohio treatment plants is also an indicator for incomplete elimination of these substances during treatment processes in WWTPs (Spongberg and Witter,

2008; Tabe et al., 2009). On the other hand, although the concentrations of stimulants caffeine and cotinine in WWTP influents were relatively higher compared to other pharmaceuticals (up to 4865 and 1581 ng/l, respectively), they were not resistant to sewage treatment processes as their effluents concentrations were very low (Spongberg and Witter, 2008; Tabe et al., 2009).

The influence of WWTP discharges on the contamination of surface waters was evaluated in a recent study (Metcalf et al., 2010) in which several anti depressants were detected in WWTP influents, effluents and surface water of the Grand River up to 100 m downstream of the WWTP discharge. The mean concentrations of venlafaxine, fluoxetine, sertraline, citalopram and their metabolites, bupropion and paroxetine in WWTP influents and effluents ranged from 0.011 to 2.6 µg/l and from < Limit of Quantification (LOQ) to 1.637µg/l, respectively. There was a modest removal of the compounds in WWTPs where tertiary aerobic treatment technologies were used. This led to contamination of river water at the point of wastewater discharge, with surface water chemical concentrations similar to those observed in the effluents. The concentrations of the antidepressants and metabolites declined with distance downstream and ranged from not determined (ND) to 0.274 µg/l at a point 100 m downstream of the WWTP discharge. The authors also claimed that the analyzed compounds have the potential for modest bioaccumulation (bioconcentration factors < 100) in fish that inhabit impacted rivers.

In addition to effluent discharges, sludge from WWTPs is also an important source of aquatic pharmaceutical contamination through the land application of contaminated sludge with a subsequent runoff into surface water. Some pharmaceuticals are able to adsorb on sludge particles and have been detected in biosolids from WWTPs at higher concentrations compared to effluents. Ding et al. (2011) collected the treated sewage sludge samples in 2009 from WWTPs in six cities of Michigan. The samples were analyzed for pharmaceuticals and 4 sulfonamide group antibiotics, 5 tetracycline group antibiotics, 3 macrolide group antibiotics, acetaminophen, caffeine, and carbamazepine were detected. Tetracycline and sulfonamide antibiotics were frequently detected with the concentrations ranging from 36.6 to 743.6 ng/g and from 4.8 to 668.9 ng/g, respectively.

Table 1a. The occurrence of pharmaceuticals in sewage treatment plants in the Great Lakes Basin

Compound	Matrix	Location	Concentration	Frequency	Reference
<i>Anti inflammatory</i>					
Diclofenac	WWTP influents	Northwestern Ohio	ND-13.9 ng/l	2/3	Spongberg and Witter, 2008
Diclofenac	WWTP effluents	Northwestern Ohio	8.3-177.1 ng/l	3/3	Spongberg and Witter, 2008
Diclofenac	Biosolid samples	Northwestern Ohio	ND-23.09 ng/g	2/3	Spongberg and Witter, 2008
Ibuprofen	WWTP effluents	Windsor	157-203 ng/l	3/8	Tabe et al. (2009)
Indomethacin	WWTP effluents	Windsor	19-46 ng/l	8/8	Tabe et al. (2009)
Ketoprofen	WWTP effluents	Windsor	11-16 ng/l	4/8	Tabe et al. (2009)
Naproxen	WWTP effluents	Windsor	126-555 ng/l	8/8	Tabe et al. (2009)
Salicylic acid	WWTP influents	Northwestern Ohio	433.9-8036.1 ng/l	3/3	Spongberg and Witter, 2008
Salicylic acid	WWTP effluents	Northwestern Ohio	ND-47.2 ng/l	2/3	Spongberg and Witter, 2008
Salicylic acid	Biosolid samples	Northwestern Ohio	ND-252.86 ng/g	2/3	Spongberg and Witter, 2008
<i>Lipid regulating</i>					
Bezafibrate	WWTP effluents	Windsor	145-315 ng/l	8/8	Tabe et al. (2009)
Clofibric acid	Biosolid samples	Northwestern Ohio	ND-8.05 ng/g	1/3	Spongberg and Witter, 2008
Clofibric acid	WWTP effluents	Windsor	10-43 ng/l	8/8	Tabe et al. (2009)
Gemfibrozil	WWTP influents	Northwestern Ohio	181.8-451.3 ng/l	3/3	Spongberg and Witter, 2008
Gemfibrozil	WWTP effluents	Northwestern Ohio	ND-83.5 ng/l	2/3	Spongberg and Witter, 2008
Gemfibrozil	WWTP effluents	Windsor	19-206 ng/l	8/8	Tabe et al. (2009)
Gemfibrozil	Biosolid samples	Northwestern Ohio	ND-3.4 ng/g	2/3	Spongberg and Witter, 2008

Table 1a continued

Atorvastatin	STP influents	Ontario	72-263 ng/l	11/11	Lee et al. (2009)
Atorvastatin	STP effluents	Ontario	10-122 ng/l	11/11	Lee et al. (2009)
Rosuvastatin	STP influents	Ontario	134-604 ng/l	11/11	Lee et al. (2009)
Rosuvastatin	STP effluents	Ontario	190-552 ng/l	11/11	Lee et al. (2009)
Rosuvastatin lactone	STP influents	Ontario	35-315 ng/l	11/11	Lee et al. (2009)
Rosuvastatin lactone	STP effluents	Ontario	8-86 ng/l	11/11	Lee et al. (2009)
<i>Anti-depressants</i>					
Fluoxetine	WWTP influent-effluent	Grand River	0.191-0.122 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Norfluoxetine	WWTP influent-effluent	Grand River	0.011-0.005 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Citalopram	WWTP influent-effluent	Grand River	0.223-0.203 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Desmethyl citalopram	WWTP influent-effluent	Grand River	0.133-0.111 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Venlafaxine	WWTP influent-effluent	Grand River	1.155-0.808 µg/l	1/1 – 1/1	Metcalf et al. (2010)
N-desmethyl venlafaxine	WWTP influent-effluent	Grand River	0.259-0.217 µg/l	1/1 – 1/1	Metcalf et al. (2010)
O- desmethyl venlafaxine	WWTP influent-effluent	Grand River	2.6-1.637 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Bupropion	WWTP influent-effluent	Grand River	0.191-0.104 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Sertraline	WWTP influent-effluent	Grand River	0.034-0.016 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Desmethyl sertraline	WWTP influent-effluent	Grand River	0.021-<LOQ µg/l	1/1 – 1/1	Metcalf et al. (2010)

Table 1a continued

Paroxetine	WWTP influent-effluent	Grand River	0.016-<LOQ µg/l	1/1 – 1/1	Metcalf et al. (2010)
<i>Beta blockers</i>					
Acebutolol	STP primary effluent	Southern Ontario	221-1090 ng/l	7/7	Lee et al. (2007)
Acebutolol	STP final effluent	Southern Ontario	184-662 ng/l	7/7	Lee et al. (2007)
Atenolol	WWTP effluents	Kitchener, Windsor, Elmira, Galt	Up to ~ 1100 ng/l	-	Scheurer et al. (2010)
Atenolol	STP primary effluent	Southern Ontario	1180-2210 ng/l	7/7	Lee et al. (2007)
Atenolol	STP final effluent	Southern Ontario	642-1680 ng/l	7/7	Lee et al. (2007)
Metoprolol	WWTP effluents	Kitchener, Windsor, Elmira, Galt	Up to ~ 700 ng/l	-	Scheurer et al. (2010)
Metoprolol	STP primary effluent	Southern Ontario	214-664 ng/l	7/7	Lee et al. (2007)
Metoprolol	STP final effluent	Southern Ontario	177-402 ng/l	7/7	Lee et al. (2007)
Sotalol	WWTP effluents	Kitchener, Windsor, Elmira, Galt	Up to ~ 150 ng/l	-	Scheurer et al. (2010)
Sotalol	STP primary effluent	Southern Ontario	180-567 ng/l	7/7	Lee et al. (2007)
Sotalol	STP final effluent	Southern Ontario	162-429 ng/l	7/7	Lee et al. (2007)
Propranolol	WWTP effluents	Kitchener, Windsor, Elmira, Galt	Up to ~ 80 ng/l	-	Scheurer et al. (2010)
Propranolol	STP primary effluent	Southern Ontario	15-79 ng/l	7/7	Lee et al. (2007)
Propranolol	STP final effluent	Southern Ontario	22-50 ng/l	7/7	Lee et al. (2007)
Labetalol	STP primary effluent	Southern Ontario	70-279 ng/l	7/7	Lee et al. (2007)
Labetalol	STP final effluent	Southern Ontario	64-90 ng/l	7/7	Lee et al. (2007)
Bisoprolol	STP primary effluent	Southern Ontario	25-74 ng/l	7/7	Lee et al. (2007)

Table 1 a continued

Bisoprolol	STP final effluent	Southern Ontario	20-71 ng/l	7/7	Lee et al. (2007)
Timolol	STP primary effluent	Southern Ontario	ND-7 ng/l	2/7	Lee et al. (2007)
Nadolol	STP primary effluent	Southern Ontario	74-146 ng/l	7/7	Lee et al. (2007)
Nadolol	STP final effluent	Southern Ontario	26-76 ng/l	7/7	Lee et al. (2007)
<i>Antibiotics</i>					
Sulfadiazine	Biosolid samples	WWTPs in Michigan	ND-562.2 ng/g	1/6	Ding et al. (2011)
Sulfadimethoxine	WWTP influents	Northwestern Ohio	ND-2.6 ng/l	1/3	Spongberg and Witter, 2008
Sulfadimethoxine	WWTP effluents	Northwestern Ohio	ND-1.9 ng/l	1/3	Spongberg and Witter, 2008
Sulfadimethoxine	Biosolid samples	Northwestern Ohio	ND-8.14 ng/g	2/3	Spongberg and Witter, 2008
Sulfamerazine	Biosolid samples	WWTPs in Michigan	ND-668.9 ng/g	2/6	Ding et al. (2011)
Sulfamethoxazole	Biosolid samples	WWTPs in Michigan	ND-35.9 ng/g	4/6	Ding et al. (2011)
Sulfamethoxazole	WWTP effluents	Windsor	229-516 ng/l	8/8	Tabe et al. (2009)
Sulfamethoxazole	WWTP influents	Northwestern Ohio	13.5-261 ng/l	3/3	Spongberg and Witter, 2008
Sulfamethoxazole	WWTP effluents	Northwestern Ohio	79.4-472.4 ng/l	3/3	Spongberg and Witter, 2008
Sulfamethazine	Biosolid samples	WWTPs in Michigan	ND-131.8 ng/g	3/6	Ding et al. (2011)
Sulfamethazine	Biosolid samples	Northwestern Ohio	ND-26.65 ng/g	2/3	Spongberg and Witter, 2008
Sulfamethazine	WWTP influents	Northwestern Ohio	ND-26.9 ng/l	1/3	Spongberg and Witter, 2008

Table 1 a continued

Chlortetracycline	Biosolid samples	WWTPs in Michigan	ND-346.6 ng/g	3/6	Ding et al. (2011)
Chlortetracycline	Biosolid samples	Northwestern Ohio	ND-14.74 ng/g	2/3	Spongberg and Witter, 2008
Chlortetracycline	WWTP influents	Northwestern Ohio	ND-15.9 ng/l	1/3	Spongberg and Witter, 2008
Demeclocycline	Biosolid samples	WWTPs in Michigan	ND-131.2 ng/g	3/6	Ding et al. (2011)
Doxycycline	Biosolid samples	WWTPs in Michigan	149.6-292.4 ng/g	6/6	Ding et al. (2011)
Oxytetracycline	Biosolid samples	WWTPs in Michigan	ND-743.6 ng/g	4/6	Ding et al. (2011)
Tetracycline	Biosolid samples	WWTPs in Michigan	ND-281.9 ng/g	1/6	Ding et al. (2011)
Tetracycline	Biosolid samples	Northwestern Ohio	ND-15.75 ng/g	2/3	Spongberg and Witter, 2008
Tetracycline	WWTP influents	Northwestern Ohio	ND-38.9 ng/l	2/3	Spongberg and Witter, 2008
Tetracycline	WWTP effluents	Northwestern Ohio	ND-34.4 ng/l	2/3	Spongberg and Witter, 2008
Tetracycline	WWTP effluents	Windsor	48-102 ng/l	8/8	Tabe et al. (2009)
Lincomycin	Biosolid samples	WWTPs in Michigan	ND-8.7 ng/g	4/6	Ding et al. (2011)
Lincomycin	WWTP effluents	Windsor	4.2-20.6 ng/l	8/8	Tabe et al. (2009)
Monensin sodium	WWTP effluents	Windsor	22 ng/l	1/8	Tabe et al. (2009)
Clindamycin	WWTP influents	Northwestern Ohio	6.8-13.3 ng/l	3/3	Spongberg and Witter, 2008
Clindamycin	WWTP effluents	Northwestern Ohio	14.9-32.5 ng/l	3/3	Spongberg and Witter, 2008
Clindamycin	Biosolid samples	Northwestern Ohio	3.7-15.4 ng/g	3/3	Spongberg and Witter, 2008

Table 1a continued

Clarithromycin	WWTP influents	Northwestern Ohio	ND-742.2 ng/l	2/3	Spongberg and Witter, 2008
Clarithromycin	WWTP effluents	Northwestern Ohio	ND-610.6 ng/l	2/3	Spongberg and Witter, 2008
Clarithromycin	Biosolid samples	Northwestern Ohio	ND-30.24 ng/g	2/3	Spongberg and Witter, 2008
Erythromycin	Biosolid samples	WWTPs in Michigan	ND-62.8 ng/g	3/6	Ding et al. (2011)
Erythromycin	WWTP effluents	Windsor	91-281 ng/l	8/8	Tabe et al. (2009)
Tylosin	WWTP effluents	Windsor	22-26 ng/l	2/8	Tabe et al. (2009)
Ciprofloxacin	WWTP effluents	Windsor	132-344 ng/l	8/8	Tabe et al. (2009)
Ciprofloxacin	WWTP influents	Northwestern Ohio	11.4-377.2 ng/l	3/3	Spongberg and Witter, 2008
Ciprofloxacin	WWTP effluents	Northwestern Ohio	8.8-67.4 ng/l	3/3	Spongberg and Witter, 2008
Ciprofloxacin	Biosolid samples	Northwestern Ohio	ND-46.3 ng/g	2/3	Spongberg and Witter, 2008
Trimethoprim	WWTP effluents	Windsor	164-486 ng/l	8/8	Tabe et al. (2009)
<i>Anti epileptic</i>					
Carbamazepine	Biosolid samples	WWTPs in Michigan	ND-22.3 ng/g	5/6	Ding et al. (2011)
Carbamazepine	Biosolid samples	Northwestern Ohio	4.75-12.85 ng/g	3/3	Spongberg and Witter, 2008
Carbamazepine	WWTP effluents	Windsor	361-735 ng/l	8/8	Tabe et al. (2009)
Carbamazepine	WWTP influents	Northwestern Ohio	24.8-50.9 ng/l	3/3	Spongberg and Witter, 2008
Carbamazepine	WWTP effluents	Northwestern Ohio	33.7-111.2 ng/l	3/3	Spongberg and Witter, 2008

Table 1 a continued

<i>Antihypertension</i>					
Diltiazem	WWTP influents	Northwestern Ohio	ND-69.1 ng/l	2/3	Spongberg and Witter, 2008
Diltiazem	WWTP effluents	Northwestern Ohio	ND-107.3 ng/l	2/3	Spongberg and Witter, 2008
Diltiazem	Biosolid samples	Northwestern Ohio	ND-12.8 ng/g	2/3	Spongberg and Witter, 2008
<i>Anelgesic &Antipyretic</i>					
Acetaminophen	Biosolid samples	WWTPs in Michigan	ND-370.4 ng/g	3/6	Ding et al. (2011)
<i>Stimulants</i>					
Caffeine	Biosolid samples	WWTPs in Michigan	ND-75.5 ng/g	5/6	Ding et al. (2011)
Caffeine	Biosolid samples	Northwestern Ohio	ND-5.20 ng/g	2/3	Spongberg and Witter, 2008
Caffeine	WWTP influents	Northwestern Ohio	2448-4865 ng/l	3/3	Spongberg and Witter, 2008
Caffeine	WWTP effluents	Northwestern Ohio	3.9-23.1 ng/l	3/3	Spongberg and Witter, 2008
Cotinine	WWTP influents	Northwestern Ohio	41.2-1581.1 ng/l	3/3	Spongberg and Witter, 2008
<i>Hormones</i>					
Esterone	WWTP effluents	Windsor	0.4-12 ng/l	7/8	Tabe et al. (2009)

The presence of a vast number of pharmaceuticals in natural waters of the Great Lakes at trace levels is in agreement with the ineffective elimination of these compounds in wastewater treatment plants (Table 1b). Rahman et al. (2010) collected the surface water samples from a drinking water treatment plant intake on Lake Huron. Carbamazepine, fluoxetine, ibuprofen and atorvastatin were detected in at least one of five samples at average concentrations of 29, 20, 17.2 and 1.1 ng/l, respectively. Li et al. (2010) estimated the water concentrations of different groups of pharmaceuticals in Lake Ontario, based on the accumulated amounts on a passive polar organic chemical integrative (POCIS) sampler and the sampling rates. For this purpose, they deployed the POCIS samplers at selected near shore stations in Lake Ontario (Hamilton Harbor, Humber Bay, Toronto Harbor, Trenton, Niagara River and an open water site) in 2006. Estimated concentrations of pharmaceuticals belonging to the groups of antibiotics, anti-depressants, anti-inflammatories, beta blockers, lipid regulators, antipyretic, anti epileptics and stimulants ranged from ND to 34.6 ng/l. Caffeine, carbamazepine, citalopram, venlafaxine and its metabolites were found in all samples from different parts of Lake Ontario. The degree of pharmaceutical contamination at the near shore sites decreased in the order of Hamilton Harbor > Toronto Harbor > Humber Bay > Newcastle, Bay of Quinte and Niagara River. The estimated water concentrations for the pharmaceuticals were in agreement with the measured concentrations of grab samples except for beta blockers and caffeine which the measured concentrations were higher than the estimated data.

Several classes of pharmaceuticals were also analyzed in surface water samples collected after a rainfall event in December 2007 from the Maumee Bay Lake Erie coastal area of Oregon, OH (Wu et al., 2008). The water samples from a stream that drains agricultural lands amended with treated sludge and lake water from the shore were found to be contaminated with pharmaceuticals including, cotinine, trimethoprim, sulfamethoxazole, sulfamethazine, paraxanthine, caffeine, carbamazepine, clindamycin, diltiazem, erythromycin, clarithromycin, ofloxacin, gemfibrozil, diclofenac, indomethacin and salicylic acid. Compared to other pharmaceuticals, the concentrations of sulfamethoxazole (35-211 ng/l), caffeine (60-144 ng/l), salicylic acid (70-121) and trimethoprim (21- 212 ng/l) were higher and detected in all water samples. Another sampling campaign was implemented in 2008 in the same area, which is characterized by a mix of urban, suburban and agricultural landscapes and water samples were (n = 161) analyzed for the same pharmaceutical compounds (Wu et al., 2009). Caffeine (88%) and

its metabolite paraxanthine (56%) were detected in more than half of the samples at maximum concentrations of 4275 ng/l and 1822 ng/l, respectively. The authors suggested the use of caffeine as an anthropogenic marker for wastewater associated contaminants due to its existence in many beverage and food products as well as its therapeutic use. The detection frequency of carbamazepine, an anti epileptic, was also high (57%) suggesting its high persistence in the environment. The occurrence of pharmaceuticals in surface waters was related to the use of septic systems.

Milwaukee Water Works Water Quality section analyzed the Lake Michigan surface water (source of Milwaukee drinking water) for the presence of a vast number of pharmaceuticals as well as conventional water quality parameters (Milwaukee, 2008). In their annual water quality report for 2008, almost all compounds in surface water were below the detection limit except gemfibrozil (0.8 ng/l) and nicotine (5 ng/l).

Carrara et al. (2008) collected water samples from groundwater plumes at varying depths and different geochemical zones located at Point Pelee national Park near Leamington and Long Point Provincial Park, on the north shore of Lake Erie. Only salicylic acid and diclofenac was detected at the edge of the tile bed in Point Pelee groundwater with concentrations of approximately 30 ng/l. Low concentrations of these pharmaceuticals were attributed to hydrogeochemical and microbiological processes at this site. On the other hand, in addition to salicylic acid and diclofenac; ketoprofen, gemfibrozil, indomethacin, ibuprofen and naproxen were also found in groundwater samples at Long Point. Ibuprofen concentrations were the highest in the thousands of ng/l followed by naproxen and gemfibrozil in the hundreds and thousands of ng/l. The elevated concentrations of some pharmaceuticals far from the tile bed were explained by groundwater transport. Authors correlated the extents of groundwater transport of pharmaceuticals with the oxidation-reduction conditions in the wastewater plumes. At Long Point elevated concentrations of all pharmaceuticals were detected in NO_3^- , Mn (IV) and Fe (III) reducing zones but not in aerobic zones due to the preferential removal of organic compounds in oxic zones of a plume relative to anoxic zones. Buszka et al. (2009) analyzed the ground water samples affected by the landfill leachate near Elkhart, Indiana. They collected water samples from different depths of wells. Acetaminophen, cotinine, caffeine and ibuprofen were detected in well samples.

Table 1b. The occurrence of pharmaceuticals in natural waters in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
<i>Anti-inflammatory</i>					
Diclofenac	Groundwater	Point Pelee	ND-31.7 ng/l	1/9	Carrara et al. (2008)
Diclofenac	Groundwater	Long Point	ND-20 ng/l	7/15	Carrara et al. (2008)
Diclofenac	Surface water	Lake Erie / Maumee Bay	11-82 ng/l	4/4	Wu et al. (2008)
Diclofenac	Surface water	Lake Erie / Maumee Bay	Up to 42 ng/l	15 %	Wu et al. (2009)
Salicylic acid	Groundwater	Point Pelee	ND-29 ng/l	1/9	Carrara et al. (2008)
Salicylic acid	Groundwater	Long Point	ND-480 ng/l	4/15	Carrara et al. (2008)
Salicylic acid	Surface water	Lake Erie / Maumee Bay	70-121 ng/l	4/4	Wu et al. (2008)
Ibuprofen	Groundwater	Long Point	ND-12200 ng/l	11/15	Carrara et al. (2008)
Ibuprofen	Ground water	Elkhart, Indiana	ND-3100 ng/l	1/5	Buszka et al. (2009)
Ibuprofen	Surface water	Lake Ontario	ND-34.6 ng/l	6/7 sites	Li et al. (2010)
Ibuprofen	Surface water	Lake Erie / Maumee Bay	Up to 2796 ng/l	9 %	Wu et al. (2009)
Naproxen	Groundwater	Long Point	ND-5580 ng/l	9/15	Carrara et al. (2008)
Naproxen	Surface water	Lake Ontario	ND-6.64 ng/l	4/7sites	Li et al. (2010)
Ketoprofen	Groundwater	Long Point	ND-30 ng/l	4/15	Carrara et al. (2008)
Indomethacin	Groundwater	Long Point	ND-20 ng/l	6/15	Carrara et al. (2008)
Indomethacin	Surface water	Lake Erie / Maumee Bay	Up to 26 ng/l	2 %	Wu et al. (2009)
<i>Lipid regulating</i>					
Gemfibrozil	Groundwater	Long Point	ND-1950 ng/l	10/15	Carrara et al. (2008)
Gemfibrozil	Surface water	Lake Michigan	0.8 ng/l	-	Milwaukee Water (2009)
Gemfibrozil	Surface water	Lake Ontario	ND-14.1 ng/l	3/7 sites	Li et al. (2010)
Gemfibrozil	Surface water	Lake Erie / Maumee Bay	ND-16 ng/l	2/4	Wu et al. (2008)
Gemfibrozil	Surface water	Lake Erie / Maumee Bay	Up to 16 ng/l	4 %	Wu et al. (2009)

Table 1b continued

Bezafibrate	Groundwater	Long Point	ND-350 ng/l	4/15	Carrara et al. (2008)
Atorvastatin	Surface water	Hamilton Harbor	8.7-59.1 ng/l ng/l	5/16	Lee et al. (2009)
Rosuvastatin	Surface water	Hamilton Harbor	16.9-74.9 ng/l	7/14	Lee et al. (2009)
Rosuvastatin lactone	Surface water	Hamilton Harbor	10.2-66.2 ng/l	6/16	Lee et al. (2009)
<i>Anti-depressants</i>					
Fluoxetine	Surface water (0-100 m below WWTP)	Grand River	0.141-ND µg/l	1/1 – 0/1	Metcalf et al. (2010)
Norfluoxetine	Surface water (0-100 m below WWTP)	Grand River	0.004-ND µg/l	1/1 – 0/1	Metcalf et al. (2010)
Citalopram	Surface water	Lake Ontario	0.01-1.39 ng/l	7/7 sites	Li et al. (2010)
Citalopram	Surface water (0-100 m below WWTP)	Grand River	0.206-0.029 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Desmethyl citalopram	Surface water	Lake Ontario	ND-0.64 ng/l	5/7 sites	Li et al. (2010)
Desmethyl citalopram	Surface water (0-100 m below WWTP)	Grand River	0.11-0.017 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Venlafaxine	Surface water	Lake Ontario	0.14-15.8 ng/l	7/7 sites	Li et al. (2010)
Venlafaxine	Surface water (0-100 m below WWTP)	Grand River	0.901-0.138 µg/l	1/1 – 1/1	Metcalf et al. (2010)
N-desmethyl venlafaxine	Surface water	Lake Ontario	0.03-2.01 ng/l	7/7 sites	Li et al. (2010)
O- desmethyl venlafaxine	Surface water	Lake Ontario	0.1-3.62 ng/l	7/7 sites	Li et al. (2010)
N-desmethyl venlafaxine	Surface water (0-100 m below WWTP)	Grand River	0.206-0.044 µg/l	1/1 – 1/1	Metcalf et al. (2010)

Table 1b continued

O- desmethyl venlafaxine	Surface water (0-100 m below WWTP)	Grand River	1.472 -0.274 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Bupropion	Surface water (0-100 m below WWTP)	Grand River	0.12-0.019 µg/l	1/1 – 1/1	Metcalf et al. (2010)
Sertraline	Surface water (0-100 m below WWTP)	Grand River	0.017-ND µg/l	1/1 – 0/1	Metcalf et al. (2010)
Desmethyl sertraline	Surface water (0-100 m below WWTP)	Grand River	0.005-ND µg/l	1/1 – 0/1	Metcalf et al. (2010)
Paroxetine	Surface water (0-100 m below WWTP)	Grand River	0.007-ND µg/l	1/1 – 0/1	Metcalf et al. (2010)
Paroxetine	Surface water	Lake Erie / Maumee Bay	Up to 90 ng/l	4 %	Wu et al. (2009)
<i>Beta blockers</i>					
Atenolol	Surface water	Lake Ontario	ND-28.2 ng/l	3/7 sites	Li et al. (2010)
Metoprolol	Surface water	Lake Ontario	ND-4.67 ng/l	2/7 sites	Li et al. (2010)
Nadolol	Surface water	Lake Ontario	ND-2.17 ng/l	5/7 sites	Li et al. (2010)
<i>Antibiotics</i>					
Triclosan	Surface water	Hamilton Harbor	~ 20 ng/l	-	Andresen et al. (2007)
Triclosan	Surface water	Lake Ontario (open)	~ 1 ng/l	-	Andresen et al. (2007)
Sulfamethoxazole	Surface water	Lake Ontario	ND-1.4 ng/l	6/7 sites	Li et al. (2010)
Sulfamethoxazole	Groundwater wells	Southern Ontario	ND-13 ng/l	4/8	Kormos (2007)
Sulfamethoxazole	Surface water	Lake Erie / Maumee Bay	35-211 ng/l	4/4	Wu et al. (2008)

Table 1b continued

Sulfamethoxazole	Surface water	Lake Erie / Maumee Bay	Up to 112 ng/l	24 %	Wu et al. (2009)
Sulfamethazine	Surface water	Lake Erie / Maumee Bay	8.5-38 ng/l	4/4	Wu et al. (2008)
Sulfamethazine	Surface water	Lake Erie / Maumee Bay	Up to 10 ng/l	7 %	Wu et al. (2009)
Sulfapyridine	Surface water	Lake Ontario	ND-0.58 ng/l	6/7 sites	Li et al. (2010)
Erythromycin	Surface water	Lake Erie / Maumee Bay	Up to 438 ng/l	6 %	Wu et al. (2009)
Erythromycin-H ₂ O	Surface water	Lake Erie / Maumee Bay	ND-12 ng/l	1/4	Wu et al. (2008)
Lincomycin	Groundwater wells	Southern Ontario	1.5-4.8 ng/l	8/8	Kormos (2007)
Clindamycin	Surface water	Lake Erie / Maumee Bay	0.5-1.7 ng/l	4/4	Wu et al. (2008)
Clindamycin	Surface water	Lake Erie / Maumee Bay	Up to 11 ng/l	32 %	Wu et al. (2009)
Clarithromycin	Surface water	Lake Erie / Maumee Bay	ND-9.6ng/l	2/4	Wu et al. (2008)
Clarithromycin	Surface water	Lake Erie / Maumee Bay	Up to 72 ng/l	6 %	Wu et al. (2009)
Trimethoprim	Surface water	Lake Ontario	ND-5.51ng/l	6/7 sites	Li et al. (2010)
Trimethoprim	Surface water	Lake Erie / Maumee Bay	21-212 ng/l	4/4	Wu et al. (2008)
Trimethoprim	Surface water	Lake Erie / Maumee Bay	Up to 252 ng/l	5 %	Wu et al. (2009)
<i>Anti epileptic</i>					
Carbamazepine	Surface water	Lake Ontario	0.84-16.3 ng/l	7/7 sites	Li et al. (2010)
Carbamazepine	Groundwater wells	Southern Ontario	3.2-12 ng/l	8/8	Kormos (2007)
Carbamazepine	Surface water	Lake Erie / Maumee Bay	2.7-20 ng/l	4/4	Wu et al. (2008)

Table 1b continued

Carbamazepine	Surface water	Lake Erie / Maumee Bay	Up to 1238 ng/l	57 %	Wu et al. (2009)
<i>Anelgesic &Antipyretic</i>					
Acetaminophen	Surface water	Lake Ontario	ND-17.1 ng/l	3/7 sites	Li et al. (2010)
<i>Antihypertension</i>					
Diltiazem	Surface water	Lake Erie / Maumee Bay	ND-3.7 ng/l	1/4	Wu et al. (2008)
Diltiazem	Surface water	Lake Erie / Maumee Bay	Up to 130 ng/l	19 %	Wu et al. (2009)
<i>Anelgesic &Antipyretic</i>					
Acetaminophen	Ground water	Elkhart, Indiana	ND-380 ng/l	2/5	Buszka et al. (2009)
<i>Stimulants</i>					
Caffeine	Surface water	Lake Ontario	2.15-32.7 ng/l	7/7 sites	Li et al. (2010)
Caffeine	Surface water	Lake Erie / Maumee Bay	60-144 ng/l	4/4	Wu et al. (2008)
Caffeine	Surface water	Lake Erie / Maumee Bay	Up to 4275 ng/l	88 %	Wu et al. (2009)
Caffeine	Ground water	Elkhart, Indiana	ND-130 ng/l	1/5	Buszka et al. (2009)
Nicotine	Surface water	Lake Michigan	5 ng/l	-	Milwaukee Water Works (2009)
Cotinine	Surface water	Lake Erie / Maumee Bay	ND-55 ng/l	2/4	Wu et al. (2008)
Cotinine	Ground water	Elkhart, Indiana	ND-100 ng/l	1/5	Buszka et al. (2009)
Paraxanthine	Surface water	Lake Erie / Maumee Bay	5.7-31 ng/l	4/4	Wu et al. (2008)
Paraxanthine	Surface water	Lake Erie / Maumee Bay	Up to 1822 ng/l	56 %	Wu et al. (2009)

The existence of pharmaceutical compounds in drinking water sources led to extensive research on the effectiveness of drinking water treatment plants on the removal of these compounds. For this purpose, many researchers analyzed the influents and effluents of different water treatment plants along the Great Lakes basin (Table 1c). Tabe et al. (2009) collected raw (n=22) and treated water (n=32) samples from the A.H. Weeks WTP in Windsor and the Detroit Water Works Park WTPs in 2005-2006. In addition to conventional treatment technologies, both drinking water treatment plants contain ozonation units for disinfection purposes. Ozone was used at 1-3 mg/l and 0.6-1.5 mg/l doses for Windsor and Detroit water treatment plants, respectively. The detection frequencies of carbamazepine, gemfibrozil and ibuprofen in 22 raw water samples were more than 50 % and ranged from 0.1 to 2 ng/l, from 0.2 to 4 ng/l and from 2 to 42 ng/l, respectively. In order to evaluate the removal extents of pharmaceuticals precisely, the authors analyzed the pharmaceuticals in 22 paired raw and treated water samples. The water treatment plants in Detroit and Windsor generally failed in the complete removal of pharmaceutical substances ibuprofen, gemfibrozil, ketoprofen, naproxen, lasaloid, erythromycin, tylosin and ciprofloxacin. The concentrations of macrolide antibiotics, erythromycin and tylosin in treated water were substantially higher compared to raw water.

In a survey conducted by the Ontario Ministry of the Environment in 2006, a total of 258 samples were collected from selected source waters and drinking water treatment systems and analyzed for pharmaceuticals and endocrine disruptors (Kleywegt et al., 2011). Drinking water systems that participated in the drinking water surveillance program had different types of filtration and disinfection units. Among 48 compounds, 27 were detected in source waters and finished drinking waters. In accordance with the study of Tabe et al. (2009), the most frequently detected compounds were carbamazepine, gemfibrozil and ibuprofen. In contrast, however, carbamazepine was also detected in 25 % of the treated samples from eight different sites at a maximum value of 601 ng/l. The range of removal efficiency of carbamazepine was between 71-93% in drinking water systems including granulated activated carbon and ultraviolet radiation. The modest removal (44-55%) of gemfibrozil in treatment plants using granulated activated carbon was increased to 82 % when granulated activated carbon was followed by ultraviolet radiation. The removal of ibuprofen was substantially low and ranged between 15-21%. Other pharmaceuticals that were frequently detected (>10%) in source water were naproxen, lincomycin, sulfamethoxazole, acetaminophen, bezafibrate and trimethoprim. However, their

detection frequencies in treated water were less than 2%. Higher concentrations of the antibiotics erythromycin, roxithromycin, tylosin, tetracycline, enrofloxacin and norfloxacin were reported in finished water compared to source water. This observation was mainly attributed to discounting the hydraulic retention times at treatment plants throughout the sampling.

The occurrence and the removal of pharmaceuticals at two municipal drinking treatment facilities (Facility A and B) were compared by analyzing the influent and effluent water samples collected in 2005-2006 (Komos 2007). Both of the facilities use river water as their raw water source and are located within the same watershed in Southern Ontario. Facility A consisted of coagulation, flocculation, sedimentation, filtration, chlorination and chloramination processes, ozonation, GAC filters and ultra-violet (UV) irradiation. Facility B includes screening, coagulation, flocculation (sand ballasted flocculation), sedimentation, chlorination, filtration, chloramination and fluoridation. The most frequently detected compounds in raw samples were carbamazepine, gemfibrozil, ibuprofen, bezafibrate, naproxen, sulfamethoxazole, trimethoprim and lincomycin HCl. The antibiotics, lincomycin HCl, sulfamethoxazole and trimethoprim and an anti-inflammatory naproxen could not be detected at any of the treated samples explaining their potential to react with both chlorine and ozone. Bezafibrate was only detected in the effluents of Facility B suggesting the high efficiency of GAC filters and ozone in the removal of this compound. The concentrations of gemfibrozil in water samples treated at Facility A were below the detection limit, while the maximum concentration in the samples treated at facility B was 3 ng/l. The detection frequencies of ibuprofen in raw and treated water samples were 67% and 50%, respectively with maximum concentrations of 54 and 44 ng/l. The concentrations of ibuprofen in treated waters at Facility A was lower than that of at Facility B. Carbamazepine was found in all raw water samples from Facility A and B and ranged from 2.7 to 1015 ng/l. Carbamazepine was completely eliminated at Facility A, while it was frequently detected in all treated samples from Facility B. Based on the results of the study, the author concluded that the application of conventional treatment technologies were not very efficient in reducing some compounds, whereas ozonation and GAC filters were able to reduce the concentrations of these contaminants. Sulfamethoxazole was detected in an urban located well and was explained by higher loads of the human antibiotic being discharged into surface waters in areas with greater population. On the other hand, lincomycin HCl was found at a rural located well and was

attributed to the application of livestock manure to agricultural fields with a subsequent runoff into the surface waters that infiltrated groundwater supplies.

Raw and finished drinking water samples were collected from Chicago, Elgin, Aurora, Rock Island and East St. Louis in 2008 by the Bureau of Water, Illinois EPA. Several pharmaceuticals including cotinine, monensin, nicotine, gemfibrozil, carbamazepine, paraxanthine, sulfadimethoxine, naproxen and fluoxetine were detected in both raw and finished drinking water samples. The agency calculated the hazard index (HI) of these compounds, which is the ratio of the actual exposure to the acceptable exposure. The HI for each pharmaceutical was lower than the critical value of 1, indicating that the concentrations of the compounds in the influent and effluent samples do not pose a public hazard.

Table1c. The occurrence of pharmaceuticals in drinking water treatment facilities (DWTF) in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
<i>Anti-inflammatory</i>					
Ibuprofen	DWTF influent	Lake Huron	ND-17.2 ng/l	1/5	Rahman et al. (2010)
Ibuprofen	DWTF influent	Southern Ontario	ND-54 ng/l	16/24	Kormos (2007)
Ibuprofen	DWTF effluent	Southern Ontario	ND-44 ng/l	14/24	Kormos (2007)
Ibuprofen	DWTF influent	Ontario	Up to 79 ng/l	21 %	Kleywegt et al. (2011)
Ibuprofen	DWTF effluent	Ontario	Up to 25 ng/l	15 %	Kleywegt et al. (2011)
Ibuprofen	DWTF influent	Detroit-Windsor	2-42 ng/l	11/22	Tabe et al. (2009)
Ibuprofen	DWTF effluent	Detroit-Windsor	2-39 ng/l	13/32	Tabe et al. (2009)
Naproxen	DWTF influent	Southern Ontario	4.8-64 ng/l	24/24	Kormos (2007)
Naproxen	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-4 ng/l	2/5	EPA (2008)
Naproxen	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-3 ng/l	1/5	EPA (2008)
Naproxen	DWTF influent	Ontario	Up to 199 ng/l	21 %	Kleywegt et al. (2011)
Naproxen	DWTF influent	Detroit-Windsor	1-14 ng/l	4/22	Tabe et al. (2009)
Naproxen	DWTF effluent	Detroit-Windsor	ND-2.9 ng/l	1/32	Tabe et al. (2009)
Ketopofen	DWTF influent	Detroit-Windsor	0.4-0.8 ng/l	2/22	Tabe et al. (2009)
Ketoprofen	DWTF effluent	Detroit-Windsor	0.6-1 ng/l	2/32	Tabe et al. (2009)
<i>Lipid regulating</i>					
Gemfibrozil	DWTF influent	Southern Ontario	0.7-6 ng/l	24/24	Kormos (2007)
Gemfibrozil	DWTF effluent	Southern Ontario	ND-3 ng/l	15/24	Kormos (2007)

Table 1c continued

Gemfibrozil	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	0.9-17.4 ng/l	5/5	EPA (2008)
Gemfibrozil	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	0.6-10.6 ng/l	5/5	EPA (2008)
Gemfibrozil	DWTF influent	Ontario	Up to 9 ng/l	33 %	Kleywegt et al. (2011)
Gemfibrozil	DWTF effluent	Ontario	Up to 4 ng/l	15 %	Kleywegt et al. (2011)
Gemfibrozil	DWTF influent	Detroit-Windsor	0.2-4 ng/l	14/22	Tabe et al. (2009)
Gemfibrozil	DWTF effluent	Detroit-Windsor	0.1-2 ng/l	8/32	Tabe et al. (2009)
Bezafibrate	DWTF influent	Southern Ontario	1.1-11.6 ng/l	24/24	Kormos (2007)
Bezafibrate	DWTF effluent	Southern Ontario	ND-14.3 ng/l	17/24	Kormos (2007)
Bezafibrate	DWTF influent	Ontario	Up to 3.6 ng/l	10 %	Kleywegt et al. (2011)
Bezafibrate	DWTF effluent	Ontario	Up to 1 ng/l	2 %	Kleywegt et al. (2011)
Bezafibrate	DWTF influent	Detroit-Windsor	0.5-4 ng/l	7/22	Tabe et al. (2009)
Clofibric acid	DWTF influent	Detroit-Windsor	2-12 ng/l	3/22	Tabe et al. (2009)
Atorvastatin	DWTF influent	Lake Huron	ND-17.7 ng/l	1/5	Rahman et al. (2010)
<i>Anti-depressants</i>					
Fluoxetine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-2 ng/l	1/5	EPA (2008)
Fluoxetine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-1 ng/l	1/5	EPA (2008)
Fluoxetine	DWTF influent	Lake Huron	ND-47.5 ng/l	4/5	Rahman et al. (2010)

Table 1c continued

<i>Antibiotics</i>					
Sulfamethoxazole	DWTF influent	Southern Ontario	2.6-35 ng/l	24/24	Kormos (2007)
Sulfamethoxazole	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-12 ng/l	4/5	EPA (2008)
Sulfamethoxazole	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-5 ng/l	1/5	EPA (2008)
Sulfamethoxazole	DWTF influent	Ontario	Up to 284 ng/l	18 %	Kleywegt et al. (2011)
Sulfamethoxazole	DWTF effluent	Ontario	Up to 2 ng/l	1 %	Kleywegt et al. (2011)
Sulfamethoxazole	DWTF influent	Detroit-Windsor	0.2-2 ng/l	9/22	Tabe et al. (2009)
Sulfamethazine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-1 ng/l	1/5	EPA (2008)
Sulfamethazine	DWTF influent	Ontario	Up to 34 ng/l	10 %	Kleywegt et al. (2011)
Sulfamethazine	DWTF influent	Detroit-Windsor	0.1-1.1 ng/l	5/22	Tabe et al. (2009)
Sulfamethazine	DWTF effluent	Detroit-Windsor	ND-0.1 ng/l	1/32	Tabe et al. (2009)
Sulfadimethoxine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-11 ng/l	4/5	EPA (2008)
Sulfadimethoxine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-7 ng/l	1/5	EPA (2008)
Tetracycline	DWTF influent	Ontario	Up to 35 ng/l	2 %	Kleywegt et al. (2011)

Table 1c continued

Tetracycline	DWTF effluent	Ontario	Up to 15 ng/l	4 %	Kleywegt et al. (2011)
Erythromycin	DWTF influent	Ontario	Up to 145 ng/l	10 %	Kleywegt et al. (2011)
Erythromycin	DWTF effluent	Ontario	Up to 155 ng/l	3 %	Kleywegt et al. (2011)
Erythromycin	DWTF influent	Detroit-Windsor	3-34 ng/l	4/22	Tabe et al. (2009)
Erythromycin	DWTF effluent	Detroit-Windsor	3-136 ng/l	9/32	Tabe et al. (2009)
Tylosin	DWTF influent	Ontario	Up to 39 ng/l	4 %	Kleywegt et al. (2011)
Tylosin	DWTF effluent	Ontario	Up to 31 ng/l	6 %	Kleywegt et al. (2011)
Tylosin	DWTF influent	Detroit-Windsor	2-40 ng/l	5/22	Tabe et al. (2009)
Tylosin	DWTF effluent	Detroit-Windsor	0.3-29 ng/l	6/32	Tabe et al. (2009)
Roxithromycin	DWTF influent	Ontario	Up to 66 ng/l	2 %	Kleywegt et al. (2011)
Roxithromycin	DWTF effluent	Ontario	Up to 41 ng/l	2 %	Kleywegt et al. (2011)
Roxithromycin	DWTF influent	Detroit-Windsor	0.3-1.7 ng/l	2/22	Tabe et al. (2009)
Roxithromycin	DWTF effluent	Detroit-Windsor	0.2-9 ng/l	7/32	Tabe et al. (2009)
Lincomycin	DWTF influent	Southern Ontario	1.1-40 ng/l	24/24	Kormos (2007)
Lincomycin	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-8.5 ng/l	4/5	EPA (2008)
Lincomycin	DWTF influent	Detroit-Windsor	0.1-1.8 ng/l	8/22	Tabe et al. (2009)
Lincomycin	DWTF effluent	Detroit-Windsor	0.1-0.2 ng/l	2/32	Tabe et al. (2009)
Monensin	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-1.4 ng/l	4/5	EPA (2008)

Table 1c continued

Monensin	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-2.8 ng/l	3/5	EPA (2008)
Monensin Na	DWTF influent	Ontario	Up to 810 ng/l	11 %	Kleywegt et al. (2011)
Monensin Na	DWTF effluent	Ontario	Up to 76 ng/l	7 %	Kleywegt et al. (2011)
Monensin Na	DWTF influent	Detroit-Windsor	ND-2.4 ng/l	1/22	Tabe et al. (2009)
Monensin Na	DWTF effluent	Detroit-Windsor	7-10 ng/l	2/32	Tabe et al. (2009)
Trimethoprim	DWTF influent	Southern Ontario	0.4-14 ng/l	24/24	Kormos (2007)
Trimethoprim	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-4 ng/l	3/5	EPA (2008)
Trimethoprim	DWTF influent	Ontario	Up to 25 ng/l	10 %	Kleywegt et al. (2011)
Trimethoprim	DWTF effluent	Ontario	Up to 15 ng/l	1 %	Kleywegt et al. (2011)
Trimethoprim	DWTF influent	Detroit-Windsor	0.3-1 ng/l	2/22	Tabe et al. (2009)
Enrofloxacin	DWTF influent	Ontario	Up to 13 ng/l	2 %	Kleywegt et al. (2011)
Enrofloxacin	DWTF effluent	Ontario	Up to 13 ng/l	3 %	Kleywegt et al. (2011)
Ciprofloxacin	DWTF influent	Detroit-Windsor	ND-8 ng/l	1/22	Tabe et al. (2009)
Ciprofloxacin	DWTF effluent	Detroit-Windsor	ND-7 ng/l	1/32	Tabe et al. (2009)
<i>Anti epileptic</i>					
Carbamazepine	DWTF influent	Southern Ontario	2.7-1015 ng/l	24/24	Kormos (2007)
Carbamazepine	DWTF effluent	Southern Ontario	ND-721 ng/l	12/24	Kormos (2007)
Carbamazepine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-9 ng/l	4/5	EPA (2008)

Table 1c continued

Carbamazepine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-7 ng/l	3/5	EPA (2008)
Carbamazepine	DWTF influent	Lake Huron	2.6-77.9 ng/l	5/5	Rahman et al. (2010)
Carbamazepine	DWTF influent	Ontario	Up to 749 ng/l	50 %	Kleywegt et al. (2011)
Carbamazepine	DWTF effluent	Ontario	Up to 601 ng/l	25 %	Kleywegt et al. (2011)
Carbamazepine	DWTF influent	Detroit-Windsor	0.1-2 ng/l	19/22	Tabe et al. (2009)
Carbamazepine	DWTF effluent	Detroit-Windsor	0.1-0.4 ng/l	8/32	Tabe et al. (2009)
<i>Anelgesic &Antipyretic</i>					
Acetaminophen	DWTF influent	Ontario	Up to 298 ng/l	11 %	Kleywegt et al. (2011)
Acetaminophen	DWTF effluent	Ontario	Up to 17 ng/l	1 %	Kleywegt et al. (2011)
<i>Antihypertension</i>					
Diltiazem	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-3 ng/l	2/5	EPA (2008)
<i>Stimulants</i>					
Nicotine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	6-59 ng/l	5/5	EPA (2008)
Nicotine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-11 ng/l	3/5	EPA (2008)
Cotinine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	1-12ng/l	5/5	EPA (2008)

Table 1c continued

Cotinine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-6 ng/l	4/5	EPA (2008)
Paraxanthine	DWTF influent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-10 ng/l	3/5	EPA (2008)
Paraxanthine	DWTF effluent	Chicago, Rock Island, Elgin, Aurora, St Louis	ND-14 ng/l	1/5	EPA (2008)
<i>Hormones</i>					
Estrone	DWTF influent	Detroit-Windsor	ND-1 ng/l	2/22	Tabe et al. (2009)
Estrone	DWTF effluent	Detroit-Windsor	ND-1 ng/l	1/32	Tabe et al. (2009)

Pharmaceutical compounds have also been analyzed in aquatic biota in order to evaluate the extent of bioaccumulation potential of these substances (Table 1d). Chu and Metcalfe (2007) detected the antidepressants paroxetine, fluoxetine and norfluoxetine in different fish species (n=7) collected in 2002 from Hamilton Harbor in Lake Ontario. The most frequently detected pharmaceutical was fluoxetine with a maximum concentration of 1.02 ng/g ww. Relatively higher concentrations of fluoxetine (up to 23 ng/g) and norfluoxetine (up to 130 ng/g) were reported in a fish liver obtained from North Shore Channel receiving discharge from WWTP in Chicago (Ramirez et al., 2009). In addition, another antidepressant sertraline, antihistamine diphenhydramine, antihypertension diltiazem, and anti epileptic carbamazepine were detected in all fish samples. The authors also analyzed the fish samples from other parts of the U.S and concluded that the exposure and thereby tissue accumulation in organisms in water resources receiving discharges from WWTPs with advanced technology is lower compared to other WWTPs using conventional treatment systems. In a more recent study, Al Ansari et al. (2010) collected redhorse sucker fish samples downstream of a municipal effluent in the St. Clair River. They detected 17 α -ethinylestradiol, the synthetic hormone and the active ingredient of oral contraceptives, in 50 % of the male fish samples at up to 1.6 ng/g concentration.

Table 1d. The occurrence of pharmaceuticals in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
<i>Anti-depressants</i>					
Fluoxetine	Fish species	Hamilton Harbor	ND-1.02 ng/g	6/7	Chu and Metcalfe (2007)
Fluoxetine	Fish tissues	North Shore Channel	Up to 23 ng/g	3/6	Ramirez et al. (2009)
Norfluoxetine	Fish species	Hamilton Harbor	ND-1.08 ng/g	4/7	Chu and Metcalfe (2007)
Norfluoxetine	Fish tissues	North Shore Channel	Up to 130 ng/g	6/6	Ramirez et al. (2009)
Sertraline	Fish tissues	North Shore Channel	Up to 149 ng/g	6/6	Ramirez et al. (2009)
Paroxetine	Fish species	Hamilton Harbor	ND-0.58 ng/g	3/7	Chu and Metcalfe (2007)
<i>Anti epileptic</i>					
Carbamazepine	Fish tissues	North Shore Channel	Up to 8 ng/g	6/6	Ramirez et al. (2009)
<i>Antihistamine</i>					
Diphenhydramine	Fish tissues	North Shore Channel	Up to 10 ng/g	6/6	Ramirez et al. (2009)
<i>Antihypertension</i>					
Diltiazem	Fish tissues	North Shore Channel	Up to 0.9 ng/g	6/6	Ramirez et al. (2009)
<i>Hormones</i>					
17 α -ethinylestradiol	Redhorse suckers	Stag island- St Clair River	0.48-2.3 ng/g	10/20	Al-Ansari et al. (2010)

3. PESTICIDES

Pesticides, including herbicides, insecticides and fungicides, have commonly been used in agriculture and lawn care activities in order to prevent, destroy or mitigate any pest. However, they are considered as priority pollutants due to their adverse effects on the aquatic/ terrestrial organisms and human health. Many pesticides are suspected of being endocrine disruptors which can cause sexual abnormalities and reproductive failure. In Canada, the governments have responsibility for pesticide regulation to protect public health and environment through a number of acts, regulations, guidelines and bylaws. Pest Management Regulatory Agency (PMRA) registers all manufactured or imported pesticides in Canada. The use, sale and disposal of pesticide products are governed by the provincial acts and regulations. Additionally, local governments may restrict the use of pesticides for the purpose of maintaining outdoor trees, shrubs, flowers, other ornamental plants and turf on residential or municipal land to protect human health and environment. In a similar way, in USA under Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) which requires the registration by the US EPA to sell, distribute or use a pesticide. Registration also includes approval by the EPA of the pesticide's label with detailed information for its safe use. The pesticides are classified as general use and/or restricted use (<http://www.epa.gov/compliance/civil/fifra/>). Despite their ban or restricted use, pesticides are still present in different environmental compartments.

A number of studies have been published regarding the occurrence of pesticides in natural waters of the Great Lakes Basin (Table 2a). The regional and seasonal variations of atrazine and metolachlor, common agricultural herbicides, in Great Lakes/St Lawrence watersheds have been investigated by Byer et al (2011). Water samples (n=739) were collected monthly from April to October of 2007. The maximum detected concentration of atrazine was 3.91 µg/l which exceeded Canadian Water Quality Guidelines for the protection of aquatic life (1.8 µg/l) while that of metolachlor was 1.83 µg/l. Detection frequencies of atrazine and metolachlor were higher in agricultural areas (54 % and 37% for atrazine and metolachlor, respectively) compared with urban streams (36% and 32% for atrazine and metolachlor, respectively). Similar concentrations of neutral atrazine (3.13 µg/l) and metolachlor (2.4µg/l) herbicides in surface waters at agricultural sites in the Chatham and London, (ON) area were

reported by McDaniel et al. (2008). The moderate concentrations of acid herbicides, clopyralid, dicamba, MCPA, 2-4 D and mecoprop were also detected in many of the samples periodically collected from August 2003 to July 2005. However, none of them exceeded Canadian Water Quality Guidelines for the protection of aquatic life (Mc Daniel et al., 2008). An increasing trend in the pesticide concentrations was demonstrated during the late spring/early summer period when agricultural activities and precipitation is elevated (McDaniel et al., 2008; Byer et al., 2011).

An increasing trend of pesticide concentrations and water quality parameters was shown with increasing agricultural activity. In a similar way, Kurt-Karakus et al. (2010b) analyzed a total of 203 surface water samples from Ontario streams for the presence of mecoprop, dichlorprop and metolachlor between 2006 April and 2007 December. Metolachlor was detected more frequently in agricultural areas with the highest concentration of 5.16 µg/l compared to urban areas while mecoprop, a common lawn care herbicide, was higher in streams draining urban watersheds. Struger and Fletcher (2007) analyzed a total of 262 surface water samples from the Don and Humber rivers for 152 pesticides and 8 metabolites between the years of 1998-2002. Approximately 75 % of all samples contained at least one of 11 pesticides and one metabolite. The detection frequency and concentrations of atrazine were found to be significantly higher in the Humber River watershed which has more agricultural area compared to the Don River watershed. On the contrary, the higher concentration of mecoprop was detected in the more urbanized Don River watershed. The concentrations of atrazine, carbofuran and chlorpyrifos, were beyond the federal or provincial water quality standards in 1% of the samples, while diazinon exceeded these values in 28 % of the samples. The authors demonstrated the potential risk for the contamination of Lake Ontario with agricultural and urban pesticides through the Don and Humber River watersheds.

Another commonly used herbicide, glyphosate, was also detected in surface waters (rivers, small streams, low-flow wetlands and urban creeks) of southern Ontario up to 40.8 µg/l (Byer et al., 2008; Struger et al., 2008). None of the reported concentrations of glyphosate in southern Ontario streams exceeded the Canadian Council of Ministers of the Environment guideline for the protection of aquatic life (65µg/l). In 2004 and 2005 glyphosate was found in 17 of 502 surface water samples in the concentration range of 1.17-40.8 µg/l (Struger et al., 2008). In addition to its agricultural use, glyphosate is also used for residential and recreational

purposes. Byer et al. (2008) detected higher glyphosate concentrations in urban areas (12 µg/l) than in rural areas (5.38µg/l) within the Great Lakes basin, although both samples had similar detection frequencies (33 and 32 %, respectively).

Table 2a. The occurrence of pesticides in natural waters in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
2,4 D	Surface water	Chatham, London	Up to 1010 ng/l	14/16	McDaniel et al. (2008)
2,4 D	Surface water	Don and Humber rivers	Up to 3.2 µg/l	12%	Struger& Fletcher (2007)
Atrazine	Surface water	Lake Huron	30.1-110.2 ng/l	6/6	Rahman et al. (2010)
Atrazine	Surface water	Great Lakes/St.Lawrence	ND-3.91 µg/l	359/739	Byer et al. (2011)
Atrazine	Surface water	Laurentian Great Lakes	4.7-151 ng/l	100%	Kurt-Karakus et al. (2010)
Atrazine	Surface water	Chatham, London	Up to 3130 ng/l	41/44	McDaniel et al. (2008)
Atrazine	Surface water	Don and Humber rivers	Up to 3.6 µg/l	11.10%	Struger& Fletcher (2007)
Bromacil	Surface water	Don and Humber rivers	Up to 1.7 µg/l	4.20%	Struger& Fletcher (2007)
Carbamates Organophosphates	Surface and drinking water	Ontario DWTPs	at sub µg/l	0.02 % in drinking 0.5 % in surface	Hao et al. (2010)
Carbofuran	Surface water	Don and Humber rivers	Up to 3 µg/l	0.80%	Struger& Fletcher (2007)
Chlorpyrifos	Surface water	Don and Humber rivers	Up to 0.52 µg/l	0.40%	Struger& Fletcher (2007)
cis-chlordane	Surface water	Great Lakes	ND-11 pg/l	100%	Jantunen et al. (2008)
Clopyralid	Surface water	Chatham, London	Up to 4.4 ng/l	9/16	McDaniel et al. (2008)
Cypermethrin	Surface water	Don and Humber rivers	Up to 0.38 µg/l	0.40%	Struger& Fletcher (2007)
D-atrazine	Surface water	Chatham, London	Up to 113 ng/l	9/16	McDaniel et al. (2008)

Table 2a continued

Desethyl atrazine	Surface water	Don and Humber rivers	Up to 1.7 µg/l	0.80%	Struger& Fletcher (2007)
Diazinon	Surface water	Don and Humber rivers	Up to 1 µg/l	36.30%	Struger& Fletcher (2007)
Dicamba	Surface water	Chatham, London	Up to 252 ng/l	15/16	McDaniel et al. (2008)
Dicamba	Surface water	Don and Humber rivers	Up to 2.2 µg/l	2.70%	Struger& Fletcher (2007)
Dichlorprop	Surface water	Ontario streams	ND-31 ng/l	21%	Kurt-Karakus et al. (2010)b
Dichlorprop	Surface water	Lake Ontario	0.26-1.07 ng/l	5/5	Kurt-Karakus et al. (2010)b
Dieldrin	Surface water	Great Lakes	ND-220 pg/l	100%	Jantunen et al. (2008)
Glyphosate	Surface water	Great Lakes basin	ND-12 µg/l	240/739	Byer et al. (2008)
Glyphosate	Surface water	Southern Ontario	1.17-40.8 µg/l	5%	Struger et al. (2008)
Heptachlor exo epoxide	Surface water	Great Lakes	ND-70 pg/l	100%	Jantunen et al. (2008)
Hexachlorobenzene	Water	Golf course watersheds in Muskoka Region	ND-51 ng/SPMD ^a	9/10	Metcalf et al. (2008)
MCPA	Surface water	Chatham, London	Up to 81 ng/l	11/16	McDaniel et al. (2008)
Mecoprop	Surface water	Ontario streams	ND-829 ng/l	53%	Kurt-Karakus et al. (2010)b
Mecoprop	Surface water	Lake Ontario	1.7-53 ng/l	5/5	Kurt-Karakus et al. (2010)b
Mecoprop	Surface water	Chatham, London	Up to 475 ng/l	11/16	McDaniel et al. (2008)

Table 2a continued

Mecoprop	Surface water	Don and Humber rivers	Up to 2.4 µg/l	39.70%	Struger& Fletcher (2007)
Metolachlor	Surface water	Great Lakes/St.Lawrence	ND-1.83 µg/l	266/739	Byer et al. (2011)
Metolachlor	Surface water	Laurentian Great Lakes	0.2-23 ng/l	100%	Kurt-Karakus et al. (2010)
Metolachlor	Surface water	Ontario streams	ND-5160 ng/l	88%	Kurt-Karakus et al. (2010) ^b
Metolachlor	Surface water	Chatham, London	Up to 2400 ng/l	28/44	McDaniel et al. (2008)
Metolachlor	Surface water	Sub-watersheds in Yamaska drainage	ND-0.70 µg/l	>15 %	Spear et al. (2009)
Metolachlor	Surface water	Don and Humber rivers	Up to 1.6 µg/l	5%	Struger& Fletcher (2007)
Metribuzin	Surface water	Don and Humber rivers	Up to 0.12 µg/l	0.40%	Struger& Fletcher (2007)
Pentachloroaniline	Water	Golf course watersheds in Muskoka Region	ND-28.7 ng/SPMD ^a	5/10	Metcalf et al. (2008)
Pentachloronitro benzene	Water	Golf course watersheds in Muskoka Region	ND-334 ng/SPMD ^a	8/10	Metcalf et al. (2008)
<i>trans</i> -chlordane	Surface water	Great Lakes	ND-7.9 pg/l	100%	Jantunen et al. (2008)
<i>trans</i> -nonachlor	Surface water	Great Lakes	ND-8.4 pg/l	100%	Jantunen et al. (2008)
α-hexachlorocyclohexone	Surface water	Great Lakes	190-3600 pg/l	100%	Jantunen et al. (2008)
β-hexachlorocyclohexone	Surface water	Great Lakes	ND-93 pg/l	100%	Jantunen et al. (2008)

^a semipermeable membrane devices

Surface runoff, especially from agricultural areas has been shown as a major source pathway to pesticide contamination of waters. Prince Edward Island initiated buffer legislation to minimize the contamination of receiving waters by runoff from row crops. For moderate and steep sloped agricultural fields that border streams, the legislation mandates 10 m and 20 m buffers, respectively. Dunn et al. (2011) sampled runoff waters at the edge of the field (0 m) and 10-30 m down slope in the buffer from 2001 through to 2006 (Table 2b). They detected 9 pesticides, α -endosulfan, β -endosulfan, chlorothalonil, carbofuran, metribuzin, linuron, metalaxyl, mancozeb and ethylene thiourea, at the edge of the field and 10 m down slope buffer with the concentration range of 2.94-296.5 $\mu\text{g/l}$ and 0.19-140.99 $\mu\text{g/l}$, respectively. Based on the *Daphnia Magna* toxicity results at 10 m and beyond, authors concluded that Prince Edward Island's mandated 10 m buffer is not sufficient to protect aquatic life for shallow sloped fields.

Table 2b. Occurrence of pesticides in agricultural runoff from Prince Edward Island and effect of buffer legislation (10 m buffer).

Compound	Mean Concentration (0-10 m) ($\mu\text{g/l}$)
Carbofuran	7.96-2.09
Chlorothalonil	57.3-0.67
Ethylene thiourea	184.5-58.75
Linuron	7.08-2.43
Mancozeb	296.5-140.99
Metalaxyl	3.46-2.27
Metribuzin	2.94-0.98
α -endosulfan	7.45-0.19
β -endosulfan	11.97-0.31

The toxicity of pesticides to aquatic organisms in agricultural and urban areas has been verified by other studies. For example, Metcalfe et al. (2008) deployed semipermeable membrane devices (SPMDs) into streams that drain the golf courses in the Muskoka Region, Ontario. Fungicide related compounds, pentachloronitrobenzene, hexachlorobenzene and pentachloroaniline, were detected in the extracts from the SPMDs. The toxicity in the extracts was determined using bioassays with early life stages of an aquarium fish. Toxicity to fish was found to be highest in the SPDM extracts of pentachloronitrobenzene at concentrations up to 334 ng/SPMD.

Potential endocrine disruption was evaluated in northern leopard frogs and green frogs from the agricultural water bodies that are contaminated with pesticides (mainly atrazine and metolachlor) and nutrients (McDaniel et al., 2008). Significantly higher occurrence of the testicular ovarian follicles male northern leopard frog (42%) was reported compared to male frogs from reference sites (7%). A correlation between the proportion of testicular oocytes and pesticide nutrient mixture was demonstrated in waters from agricultural sites.

Recent studies have shown that even open lake waters and drinking waters are also contaminated with pesticide residuals at ng/l concentration ranges. For example, in a study performed by Kurt-Karakus et al. (2010), Great Lakes surface samples (n=101) were collected as a part of Environment Canada's Great Lakes Surveillance Program in 2005-2007 and analyzed for metolachlor and atrazine. Their concentrations were significantly higher in lakes Ontario, Erie and Michigan than in lakes Superior and Huron. Authors attributed this result to higher number of watersheds that border agricultural land in the area of lakes Ontario, Erie and Michigan. A number of organochlorine pesticides (hexachlorocyclohexanes, chlordanes, dieldrin and a metabolite heptachlor exo-epoxide, trans-nonachlor) were also detected in open Great Lakes water samples up to low ng/l concentrations (Jantunen et al., 2008). Between 2006-2008, sub µg/l concentrations of carbamate (carbaryl) and organophosphate pesticides (azinphos-methyl, ethion, malathion, parathion, temephos, terbufos and diazinon) were detected in 0.02 % of drinking water samples collected under the Drinking Water Surveillance Program of Ontario Ministry of Environment (Hao et al., 2010). In another study, Rahman et al. (2010) analyzed the water samples (n = 5) collected from a drinking water treatment plant intake on Lake Huron between April – October 2008. They detected atrazine in all samples at an average concentration of 57 ng / l that was considerably lower than Ontario and USEPA drinking water quality standards (5 and 3 µg/l, respectively).

The occurrence of pesticides is not only restricted by surface waters. Sediments could be considered as an important reservoir for pesticide compounds due to their adsorption capabilities. Accordingly sediments are also used as an indicator for pesticide contamination (Table 2c). In the study of Wong et al.(2009), lake sediment samples were collected from two urban, four suburban and one rural site of Toronto. Samples were analyzed for several organochlorine pesticides. The concentrations of total DDTs, chlordanes and hexachlorocyclohexanes were significantly higher in the urban site (High Park) compared to the rural site (Borden). This

observation was attributed to heavy usage of organochlorine pesticides in High Park for recreational purposes or runoff from storm water.

Table 2c. Occurrence of pesticides in sediments in the Great Lake Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Chlordanes	Sediments	Toronto	0.051-6.5 ng/g	7/7	Wong et al. (2009)
Dieldrin	Sediments	Toronto	<0.05-0.67 ng/g	1/7	Wong et al. (2009)
DDTs	Sediments	Toronto	0.2-472 ng/g	7/7	Wong et al. (2009)
Endosulfans	Sediments	Toronto	<0.01-0.61 ng/g	5/7	Wong et al. (2009)
Hexachlorocyclohexanes	Sediments	Toronto	0.0075-0.035 ng/g	7/7	Wong et al. (2009)
Mirex	Sediments	Laurentian Great Lakes	ND-10000 pg/g	23/24	Shen et al. (2010)

Aside from surface waters and sediments, many fish or wildlife species have been used as a bioindicator and analyzed for organic contaminants for monitoring purposes (Table 2d). Champoux et al.(2010) used great blue heron to evaluate the extent of pesticide contamination in St Lawrence River. Seven great blue heron colonies were sampled from freshwater and estuarine part of the river in 2001 and 2002. Samples were analyzed for 21 pesticides and more than half was detected in about 50% of the samples. Toxaphene congeners (octachlorobornanes B8-2229 (P44), B8-810, and B8-1471, and the nonachlorobornane B9-1679 (P50)), *p,p'*-DDE, *trans*-nonachlor, oxychlordane and dieldrin were detected in all samples. Higher concentrations of pesticides were reported in freshwater portion of the river compared to estuarine part. Eggs of six seabird species that were sampled from the St Lawrence River in 2006 and 2007 were also analyzed for chlorinated pesticides (Lavoie et al., 2010). Of the 5 chlorinated pesticides, concentration of DDE was the highest for all seabird eggs and ranged between 229-5438 ng/g. Increasing trends were observed in the concentrations of pesticides with the increasing trophic level of seabirds. Another species, red-breasted merganser was used as a bioindicator of the state of the Lake Michigan (Heinz and Stromborg, 2009). Eggs of red-breasted merganser were sampled from Pilot and Hog Islands in Lake Michigan in 1977-78, 1990 and 2002 (n = 36) and analyzed for dieldrin, heptachlorepoxide, toxaphene, HCB, mirex, endrin, oxychlordane, cis-

nonachlor, trans-nonachlor, cis-chlordane and DDTs. Results of the long term monitoring study showed an encouraging decline in organochlorine pesticides over 24 years.

Table 2d. Occurrence of pesticides in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
cis-chlordane	Breasted mergansers egg	Lake Michigan	ND-0.14 µg/g	13<n<35/36	Heinz&Stromborg (2009)
cis-nonachlor	Breasted mergansers egg	Lake Michigan	0.02-0.3 µg/g	36/36	Heinz&Stromborg (2009)
DDE	Seabirds eggs	St Lawrence	229-5438 ng/g	116/116	Lavoie et al. (2010)
Dieldrin	Great blue huron egg	St Lawrence River	<0.1-208 ng/g	100%	Champoux et al. (2010)
Dieldrin	Bald eagle plasma	Great Lakes	ND-7.27 ng/g	7/15	Venier et al. (2010)
Dieldrin	Seabirds eggs	St Lawrence	ND-346 ng/g	98/116	Lavoie et al. (2010)
Dieldrin	Breasted mergansers egg	Lake Michigan	ND-1.4 µg/g	25<n<35/36	Heinz&Stromborg (2009)
Endrin	Breasted mergansers egg	Lake Michigan	ND-0.05 µg/g	24/36	Heinz&Stromborg (2009)
HCB	Breasted mergansers egg	Lake Michigan	ND-0.18 µg/g	25<n<35/36	Heinz&Stromborg (2009)
Heptachlor epoxide	Breasted mergansers egg	Lake Michigan	0.02-0.41 µg/g	36/36	Heinz&Stromborg (2009)
Hexachloro benzenes	Seabirds eggs	St Lawrence	18.8-267 ng/g	116/116	Lavoie et al. (2010)
Mirex	Breasted mergansers egg	Lake Michigan	ND-0.3 µg/g	25<n<35/36	Heinz&Stromborg (2009)
Mirex	White fish&Lake trout	Laurentian Great Lakes	480-540000 pg/g	23/23	Shen et al. (2010)
Oxychlordan	Great blue huron egg	St Lawrence River	4-124 ng/g	100%	Champoux et al. (2010)

Table 2d continued

Oxychlordan	Breasted mergansers egg	Lake Michigan	ND-0.52 µg/g	25<n<35/36	Heinz&Stromborg (2009)
Oxychlordan	Seabirds eggs	St Lawrence	ND-336 ng/g	76/116	Lavoie et al. (2010)
<i>p-p'</i> DDD	Breasted mergansers egg	Lake Michigan	ND-0.43 µg/g	25<n<35/36	Heinz&Stromborg (2009)
<i>p-p'</i> DDE	Great blue huron egg	St Lawrence River	174-3469 ng/g	100%	Champoux et al. (2010)
<i>p-p'</i> DDE	Breasted mergansers egg	Lake Michigan	0.66-11 µg/g	36/36	Heinz&Stromborg (2009)
<i>p-p'</i> DDE	Bald eagle plasma	Great Lakes	ND-62.6 ng/g	12/15	Venier et al. (2010)
<i>p-p'</i> DDT	Breasted mergansers egg	Lake Michigan	0.02-0.45 µg/g	36/36	Heinz&Stromborg (2009)
Toxaphene	Great blue huron egg	St Lawrence River	4.2-433.3 ng/g	100%	Champoux et al. (2010)
Toxaphene	Breasted mergansers egg	Lake Michigan	ND-3.6 µg/g	24/36	Heinz&Stromborg (2009)
<i>trans</i> -nonachlor	Breasted mergansers egg	Lake Michigan	0.02-0.45 µg/g	36/36	Heinz&Stromborg (2009)
<i>trans</i> -nonachlor	Great blue huron egg	St Lawrence River	7-612 ng/g	100%	Champoux et al. (2010)
<i>trans</i> -nonachlor	Seabirds eggs	St Lawrence	11-603 ng/g	116/116	Lavoie et al. (2010)

4. FLAME RETARDANTS

Flame retardants are used in different materials (e.g. plastics, textiles, foams, electronics) that inhibit or resist the spread of fire. Flame retardants, especially brominated flame retardants (BFRs) have become widespread environmental pollutants as they have been detected in various environmental compartments and wildlife. These substances are highly toxic and persistent in the environment. Due to high lipophilicity and stability, they have the potential for accumulation in sediments and bioaccumulation in wildlife. As some commonly used BFRs have chemical

structures similar to well known endocrine disruptors like polychlorinated biphenyls (PCB), they are also considered potential endocrine disruptors. Several types of polybrominated diphenyl ethers (PBDEs) have been banned by the European Union in 2008. United States Environmental Protection Agency (US EPA) regulated the manufacture, use and import of pentaBDE and octaBDE under the Significant New Use Rule (SNUR). Accordingly, the only US manufacturer of pentaBDE and octaBDE ceased the production of these chemicals voluntarily. In addition, based on the negotiations between EPA and the U.S. producers, production, importation and sales of deca BDE will be phased out for most uses in the U.S. The use of pentaBDE and octaBDE were voluntarily phased out in Canada in 2006. Based on the regulation under the Canadian Environmental Protection Act, the manufacture of all PBDEs and the import and use of tetra to hexaBDEs has been banned in 2008.

A number of studies have been performed in the Great Lakes region to screen for the occurrence of flame retardants in sediments (Table 3a) and aquatic biota (Table 3b) and to determine the biota-sediment accumulation factors of these flame retardants.

Table 3a. The occurrence of flame retardants in sediments in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
CP ^a	Sediments	Laurentian Great Lakes	ND-270 pg/g dw	80/84	Shen et al. (2011)
Dechlorane 602	Sediments	Laurentian Great Lakes	ND-13 ng/g dw	82/84	Shen et al. (2011)
Dechlorane 603	Sediments	Laurentian Great Lakes	0.61-600 pg/g dw	24/24	Shen et al. (2010)
Dechlorane 602	Sediment	Laurentian Great Lakes	0.97-11000 pg/g dw	24/24	Shen et al. (2010)
Dechlorane 603	Sediments	Laurentian Great Lakes	ND-1.1 ng/g dw	81/84	Shen et al. (2011)
Dechlorane 604	Sediments	Laurentian Great Lakes	ND-4.8 ng/g dw	45/84	Shen et al. (2011)
Dechlorane 604	Sediments	Laurentian Great Lakes	ND-8 ng/g dw	12/24	Shen et al. (2010)
DP ^a	Sediments	Laurentian Great Lakes	ND-310 ng/g dw	84/84	Shen et al. (2011)
DP	Sediments	Lower Great Lakes	0.061-586 ng/g dw	100 %	Sverko et al. (2008)
DP (syn+anti)	Sediments	Laurentian Great Lakes	13.8-90000 pg/g dw	24/24	Shen et al. (2010)
ΣPBDE ^a	Sediments	Rochester Harbor	100 pg/g dw	-	Lotufo&Pickard (2010)
ΣPBDE	Sediments	(open)Lake Ontario	48 pg/g dw	-	Lotufo&Pickard (2010)

^a PBDE = polybrominated diphenylether, DP = Dechlorane Plus, CP = Chlordane Plus

Table3b. The occurrence of flame retardants in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Brominated Flame Retardants	Seabird eggs	St Lawrence River	160-4181 ng/g lw	-	Lavoie et al. (2010)
BTBPE ^a	Lake trout	Lake Ontario	0.62-2.6 ng/g lw	100 %	Ismail et al. (2009)
Dechlorane 602	White fish&Lake trout	Laurentian Great Lakes	470-34000 pg/g dw	23/23	Shen et al. (2010)
Dechlorane 603	White fish&Lake trout	Laurentian Great Lakes	14-550 pg/g dw	23/23	Shen et al. (2010)
Dechlorane 604	White fish&Lake trout	Laurentian Great Lakes	ND-1300 pg/g dw	10/23	Shen et al. (2010)
DP ^a	Bald eagle plasma	Laurentian Great Lakes	ND-0.68 ng/g ww	6/15	Venier et al. (2010)
DP (syn +anti)	Herring Gulls egg	Laurentian Great Lakes	ND - 18 ng/g ww	101/101	Gauthier&Letcher 2009
DP	Lake trout	Lake Ontario	2.3-7.2 ng/g lw	100 %	Ismail et al. (2009)
DP (syn+anti)	White fish&Lake trout	Laurentian Great Lakes	61-2600 pg/g dw	23/23	Shen et al. (2010)
ΣHBCD ^a	Lake trout	Lake Ontario	16-33 ng/g lw	100 %	Ismail et al. (2009)
ΣHBCD	Bald eagle plasma	Laurentian Great Lakes	ND-0.56 ng/g ww	7/15	Venier et al. (2010)
MCCP ^a	Food web	Lake Ontario & Lake Michigan	ND-109 ng/g ww	57%	Houde et al. (2008)
MCCP	Lake trout	Lake Ontario	50-187 ng/g lw	100 %	Ismail et al. (2009)
ΣOH-PBDE ^a	Plasma of peregrine nestlings	Great Lakes Basin	0.01-12.06 ng/g ww	34/34	Fernie&Letcher (2010)
Σ PBDE ^a	Great blue heron eggs	St Lawrence River	70-1377 ng/g ww	100 %	Champoux et al. (2010)
ΣPBDE	Plasma of peregrine nestlings	Great Lakes Basin	0.87-195.79 ng/g ww	34/34	Fernie&Letcher (2010)

Table 3b continued

ΣPBDE	Forage fish	Lake Michigan	149-1094 ng/g lw	88/88	Hahm et al. (2008)
ΣPBDE	Lake trout	Lake Ontario	269-3339 ng/g lw	100 %	Ismail et al. (2009)
ΣPBDE	L.variegatus tissue	Rochester Harbor	Up to 460 pg/g dw	-	Lotufo&Pickard (2010)
ΣPBDE	L.variegatus tissue	(open)Lake Ontario	Up to 13.3 ng/g dw	-	Lotufo&Pickard (2010)
ΣPBDE	Common carp muscle	Lake Erie	1.5-100 ng/g lw	BDE47-100 :18/18 BDE 154 : 14/18 BDE99-153: 1/18	Perez et al. (2010)
ΣPBDE	Bald eagle plasma	Laurentian Great Lakes	0.35-29.3 ng/g ww	15/15	Venier et al. (2010)
ΣPBDE	Stranded belugas liver (male-female)	St Lawrence River	404-489 ng/g lw	-	Raach et al. (2011)
PEB ^a	Lake trout	Lake Ontario	17-320 ng/g lw	100 %	Ismail et al. (2009)
SCCP ^a	Food web	Lake Ontario & Lake Michigan	1.02—123 ng/g ww	100 %	Houde et al. (2008)
SCCP ^a	Lake trout	Lake Ontario	107-748 ng/g lw	100 %	Ismail et al. (2009)
TBBP-A-ae ^a	Herring gull eggs	St Lawrence River and Great Lakes Basin	ND-0.56 ng/g ww	8/11	Letcher and Chu (2010)
TBBP-A-dbpe ^a	Herring gull eggs	St Lawrence River and Great Lakes Basin	ND-0.36 ng/g ww	3/11	Letcher and Chu (2010)

^a BDE = brominated diphenylether, PBDE = polybrominated diphenylether, HBCD = hexabromocyclododecane, BTBPE = 1,2-bis(2,4,6 tribromophenoxy)ethane, PEB = pentabromoethylbenzene, DP = Dechlorane Plus, SCCP = short-chain chlorinated paraffins, MCCP = medium-chain chlorinated paraffins, TBBP-A-ae = tetrabromobisphenol-A-bis(allyl ether), TBBP-A-dbpe = Tetrabromobisphenol-A-bis(2,3-dibromopylether)

Lotufo and Pickard (2010) evaluated the bioavailability of PBDEs in surface sediments that were collected from Lake Ontario and Rochester Harbor reach of the lower Genesee River. Among the analyzed PBDE congeners, only BDE 153 (26 pg/g) and BDE 154 (22 pg/g) were found in open lake sediments. The concentrations of these congeners were higher in Rochester Harbor sediment samples (BDE153 = 45 pg/g; BDE 154 = 37 pg/g) where an additional PBDE congener, BDE 28, was also detected at a concentration of 18 pg/g. The bioavailability of PBDE congeners was determined by estimating the biota-sediment accumulation factors using a freshwater bioaccumulation test with the aquatic oligochaete worm. The biota-sediment accumulation factors were higher for the open lake sediments than for the Rochester Harbor sediments. This observation was explained by the possibility of higher fraction of black carbon in Rochester Harbor sediment which have high sorption strength for planar hydrophobic organic carbons. However, the authors could not establish any relationship between PBDE biota-sediment bioaccumulation factors and log K_{ow} values.

Due to their high bioaccumulation tendency, screening studies for brominated flame retardants have generally been performed in aquatic biota (Table 3b). Wild common carp samples from eastern Lake Erie were analyzed for PBDEs (Perez et al., 2010). The detection frequencies of BDE 47, BDE 28 and BDE 100 in fish muscle were 100% and the total PBDE concentration ranged from 1.5 to 100 ng/g. The highest concentration was detected for BDE 47 which is known to be predominant congener that bioaccumulates in fish. In line with this result, BDE 47 was found to be most abundant congener in forage fish samples collected from Lake Michigan in 1995 and 2002/2003. The lipid normalized total PBDE concentrations in fish ranged from 149 to 1094 ng/g. Similar concentrations of PBDEs were observed in liver of stranded belugas collected from St. Lawrence Estuary shores between 1993 and 2007. The mean lipid normalized PBDE concentrations were 404 ng/g and 489 ng/g for male and female stranded belugas, respectively (Raach et al., 2011). The authors could not observe any temporal change of PBDEs between 1993 and 2007. On the other hand, Ismail et al., (2009) reported a significant temporal change in the concentrations of PBDEs in lake trout samples from Lake Ontario from 1979 to 2004. They observed a significant increase in PBDE congeners from 1979 until mid-1990s. Subsequent decrease or stability in concentrations of these congeners was detected between 1998 and 2004 except for BDE 209 which increased substantially during this period.

Several bird species which are found near large bodies of open water have also been used as an indicator of PBDE contamination of the environment (Table 3b). Fernie and Letcher (2010) collected peregrine falcon samples from the urban region in southern Ontario, the small industry city of Thunder Bay region and the North Shore region of Lake Superior in 2004 and 2005. The plasmas of nestling peregrine samples were analyzed for 14 congeners of PBDEs and the arithmetic mean concentration of total PBDEs was reported as 37.62 ng/g ww. BDE 99, 153, 47, 100 and 183 congeners of 14 measured accounted for 92.7 % of total PBDEs. The concentration of BDE 47 congener, which generally predominates in birds with an aquatic sourced diet, was higher in the North Shore area compared to Thunder Bay and urban regions. This spatial difference was explained by the dietary habit of the birds, because the aquatic based prey was reported only for North Shore nests. In 2005, a total of 15 bald eagle samples were collected from the southern shore of Lake Superior, the Lake Michigan watershed and the Michigan side of Lake Huron from May to June of 2005 (Venier et al., 2010). PBDEs were detected in the plasma of all samples with an average of 5.7 ng/g ww. Since the bald eagles also have aquatic based diet, the most abundant congener detected in plasma samples was BDE-47. The higher PBDE level (430 ng/g ww) was reported in great blue heron eggs from the St. Lawrence River (2001-2002) (Champoux et al., 2010). Among the seven congeners detected, BDE 47, 99 and 100 were the most abundant congeners confirming the previous studies. In 2006 and 2007, eggs of different bird species were sampled from the Gulf of St Lawrence River and analyzed for several PBDE congeners (Lavoie et al., 2010). The total lipid normalized concentrations of 5 PBDE congeners (BDE-47, 99, 100, 153, 154) in seabird species ranged from 134-1721 ng/g. Total PBDE concentration tended to increase with tropic levels of seabirds and higher connectivity with the benthos. The authors also showed that the resident species in St Lawrence ecosystem has higher PBDE concentrations than migratory species.

Due to the banning of the penta and octa BDE congeners by the European Union and several states of the United States and voluntary phase out in the U.S and Canada in 2006, they are being replaced with other brominated flame retardants (Ismail et al., 2009). Temporal changes of brominated flame retardants, Hexabromocyclododecane (HBCD), 1,2-bis[2,4,6-tribromophenoxy]ethane (BTBPE) and pentabromoethylbenzene (PEB) was assessed by Ismail et al. (2009) in lake trout samples collected from Lake Ontario between 1979 and 2004 (Table 3b). Total concentrations of lipid normalized HBCD isomers ranged from 16 to 33 ng/g with a

significant decline during the sampling period. On the other hand, BTBPE concentrations increased from 0.6 ng/g to 2.6 ng/g between the years of 1979 and 1993 and then decreased to about 1.6 ng/g at 2004. No temporal change was observed by the authors for PEN concentration which ranged from 17 to 320 ng/g.

Letcher and Chu (2010) collected the herring gull egg samples during 2008-2009 from the St Lawrence River and Lake Ontario, Lake Huron and Lake Erie. The samples were analyzed for tetrabromobisphenol-A (TBBP-A) derivative, which is one of the most extensively used brominated flame retardants (Table 3b). The maximum detected concentrations of TBBP-A-bis(allyl ether) and TBBP-A-bis(2,3-dibromopropyl ether) were 0.56 and 0.36 ng/g ww, respectively. The authors concluded that TBBP-A-ae and TBBP-A-dbpe are bioaccumulated in the food web of herring gulls from across the Great Lakes-St. Lawrence basin, and transferred to their eggs. Up to 116 ng/g lipid normalized concentration of HBCD was detected in the eggs of different seabird species from the Gulf of St. Lawrence River (Lavoie et al., 2010).

Aside from brominated flame retardants, chlorinated flame retardants, especially dechloranes, have also been widely detected in various sediment and biota samples in the Great Lakes region (Table 3a and 3b). The contamination of Great Lakes with these substances was mainly attributed to the manufacturing facilities along the Niagara River.

Sverko et al. (2008) analyzed the archived sediment samples collected from the Niagara River, during the period from 1980 to 2002 and found a decreasing trend in DP concentration from 89 to 7 ng/g suggesting a possible decrease in production or the reduction of DP released to the environment from the manufacturing plant. Similar trend in the temporal distribution of Dechlorane plus in lake trout samples from Lake Ontario was evaluated by Ismail et al. (2009) between 1979-2004. Lipid normalized DP concentrations ranged between 2.3-7.2 ng/g with a significant decrease during the sampling periods. Dechloranes 602, 603, 604, Dechlorane Plus and Chlordane Plus was found in surficial sediment samples collected from Canadian tributaries to the Laurentian Great Lakes in 2002-2006 (Shen et al., 2011). The more developed and industrialized areas were the most contaminated ones as the elevated concentrations of dechloranes were detected in sediment samples from these areas. The highest concentrations of Dechlorane 602, 604 and Dechlorane Plus were observed in Niagara River tributaries associated with the manufacturing plants along the river. In a previous study of the same authors (Shen et al., 2010) sediment, lake trout and white fish samples were collected from Great Lakes in 1998-

2002. Based on the spatial trends in sediments and fish samples, authors concluded that the major source of Dechlorane 602, 604 and Dechlorane Plus is manufacturing plants along the Niagara River, whereas the source of Dechlorane 603 is more likely atmospheric deposition. The highest concentrations of Dechlorane 602, 604 and Plus in sediments were, 11 ng/g, 8 ng/g and 90 ng/g, respectively. A significant relationship between the Dechlorane Plus concentration in herring gull eggs and distance from the DP production facility in North America at Niagara Falls was specified by Gauthier and Letcher (2009). Based on their biomonitoring results during 1982-2006, the authors stated that DP isomers have accumulated in the food web of female herring gulls with subsequent transfer during ovogenesis. DP was also monitored in Great Lakes region using the bald eagles plasma samples collected in 2005 (Venier et al., 2010). It was detected in 6 of 15 samples at an average concentration of 0.19 ng/g.

Chlorinated paraffins (CP) are divided into groups according to their carbon chain length, namely short chain (SCCP), medium chain (MCCP) and long chain (LCCP) chlorinated paraffins. They have been used as flame retardants and plasticizers and as additives in metal working fluids, in sealants, paints and coatings. In a final follow-up assessment report published in 2008, Environment Canada and Health Canada concluded that all CPs are “toxic” as they constitute or may constitute a danger in Canada to human life or health under the paragraph 64(c) of Canadian Environmental Protection Act (CEPA), 1999. It was also concluded that SCCPs meet the criteria under paragraph of 64(a) of CEPA in which a substance is defined as “toxic” as they have or may have an immediate or long-term harmful effect on the environment or its biological diversity. In USA, EPA is initiating action under the Toxic Substances Control Act (TSCA) to regulate the manufacture, import, export, processing, distribution and use of SCCPs due to their persistence, bioaccumulation potential and toxicity to aquatic organisms. Likewise PBDEs and DPs, Ismail et al. (2009) detected high concentrations of chlorinated paraffins in Lake Trout samples from Lake Ontario (Table 3b). For SCCPs and MCCPs, concentrations ranged from 107 to 748 ng/g lipid (17 to 91 ng/g ww) and from 50 to 187 ng/g lipid (7.9 to 34 ng/g wet wt), respectively. Similar concentrations of CPs in lake trout samples from Lake Ontario (SCCP = 34 ng/g ww; MCCP = 24 ng/g ww) and Lake Michigan (SCCP = 123 ng/g ww; MCCP = 5.6 ng/g ww) were also reported by Houde et al. (2008).

Fewer data has been published for the contamination of surface waters with flame retardants compared to sediments and biota (Table 3c). Ueno et al. (2008) detected PBDEs and

their metabolites OH-PBDEs in surface water samples collected in 2002-2004 from Great Lakes region in Ontario. Hydroxylated PBDE concentrations were higher within 0.5–2 km from two major STP outfalls in Hamilton Harbour and near a large STP in eastern Toronto. The microbial oxidation of PBDEs in municipal wastewater or their reaction with OH radicals during disinfection with ozone was suggested as formation pathways of OH-PBDEs. Lake Ontario surface water samples were also analyzed for chlorinated paraffins (Houde et al., 2008). Over the three sampling periods from 2000 to 2004, concentrations of SCCPs ranged from 1039 to 1935 pg/l at the West Lake Ontario sites and from 606 to 1488 pg/l in the central basin site.

Table 3c. Occurrence of flame retardants in natural waters in the Great Lakes Basin

Compound	Matrix	Location	Concentration	Frequency	Reference
MCCP	Surface water	Lake Ontario	ND-47 pg/l	67 %	Houde et al. (2008)
ΣOH-PBDE	Surface water	Lake Ontario	2.2-70 pg/l	13/13	Ueno et al. (2008)
ΣPBDE	Surface water	Lake Ontario	17-250 pg/l	13/13	Ueno et al. (2008)
SCCP	Surface water	Lake Ontario	606-1935 pg/l	100 %	Houde et al. (2008)

5. PERFLUORINATED SURFACTANTS

Perfluorinated surfactants, perfluorinated carboxylates and perfluorinated sulfonates are used for industrial and commercial purposes such as in lubricants, paints, polishes, food packaging, and fire-fighting foams. Perfluoroalkanesulfonate salts and perfluorocarboxylates are present in fire-fighting foam formulations, including aqueous film forming foams which are proprietary mixtures used to extinguish hydrocarbon fuel fires and are often found where there are large volumes of flammable liquids and the potential for a fire exists (Moody et al., 2002).

Many studies have been reported about the presence of perfluorinated chemicals (PFC), especially perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in the environment, particularly in wildlife animal and human samples (Houde et al., 2006). Perfluorinated surfactants have shown different potentials for reproductive interference and carcinogenicity in animal experiments as well as partly long half-lives in humans. They are extremely recalcitrant compounds against microbiological and chemical degradation and they have the bioaccumulation potential in animals and humans (Houde et al., 2006). Considering these facts, in January 2006, the US EPA invited perfluorinated compound manufacturers to participate in a global stewardship program on PFOA, PFOA precursors, and related chemicals, asking them to commit towards eliminating these chemicals from emissions and products by 2015 (US EPA, 2006 - <http://www.epa.gov/oppt/pfoa/>). In Canada, most uses of PFOS and its salts has been prohibited with exemptions of specific uses and published in 2008 (<http://www.ec.gc.ca/toxiques-toxics/Default.asp?lang=En&n=98E80CC6-1&xml=ECD5A576-CEE5-49C7-B26A-88007131860D>).

The studies with perfluorinated surfactants in Great Lakes region have mainly focused on the contamination of surface waters and biota. As shown at Table 4a, among all detected perfluorinated surfactants, the levels of PFOA and PFOS were substantially high at STP effluents (up to 54.7 and 208.5 ng/l) in southern Ontario (Furdui et al., 2008). PFOA and PFOS were also determined frequently in the effluents of Little River STP in Windsor at maximum concentrations of 141 ng/l and 82 ng/l, respectively (Tabe et al., 2009). Furdui et al. (2008) analyzed the surface water samples from Lakes Ontario, Huron, Erie, Michigan and Superior (2002-2005) in order to evaluate the spatial distribution of perfluorinated compounds (Table 4b). PFOA and PFOS were detected in all samples at a maximum concentration of 6.7 and 37.6 ng/l,

respectively, in Hamilton Harbor samples. In addition, Tabe et al. (2009) determined these substances in the influents and effluents of drinking water treatment facilities in Detroit and Windsor frequently (Table 4c).

Table4a. The occurrence of perfluorinated surfactants in STP effluents in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Heptadecafluorooctane sulfonamide	STP effluents	Southern Ontario	ND-3.8 ng/l	5/7	Furdui et al. (2008)
Perfluorodecanoic acid	STP effluents	Southern Ontario	0.8-4.9 ng/l	7/7	Furdui et al. (2008)
Perfluorododecanoic acid	STP effluents	Southern Ontario	ND-8.1 ng/l	5/7	Furdui et al. (2008)
Perfluoroheptanoic acid	STP effluents	Southern Ontario	1.9-6.5 ng/l	7/7	Furdui et al. (2008)
Perfluorononanoic acid	STP effluents	Southern Ontario	1.6-5.4 ng/l	7/7	Furdui et al. (2008)
Perfluorooctanoic acid	STP effluents	Southern Ontario	0.1-54.7 ng/l	7/7	Furdui et al. (2008)
Perfluorooctanoic acid	STP effluents	Windsor	27-141 ng/l	8/8	Tabe et al. (2009)
Perfluorooctanoic sulfonate	STP effluents	Southern Ontario	8.6-208.5 ng/l	7/7	Furdui et al. (2008)
Perfluorooctanoic sulfonate	STP effluents	Windsor	9-82 ng/l	8/8	Tabe et al. (2009)
Perfluoroundecanoic acid	STP effluents	Southern Ontario	ND-5.7 ng/l	5/7	Furdui et al. (2008)
Potassium perfluorohexane sulfonate	STP effluents	Southern Ontario	3-10.7 ng/l	7/7	Furdui et al. (2008)

Table4b. The occurrence of perfluorinated surfactants in natural waters in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Heptadecafluorooctane sulfonamide	Surface water	Laurentian Great Lakes	ND-0.6 ng/l	17/23	Furdui et al. (2008)
Perfluorodecanoic acid	Surface water	Laurentian Great Lakes	ND-2.4 ng/l	9/23	Furdui et al. (2008)
Perfluorododecanoic acid	Surface water	Laurentian Great Lakes	ND-2.6 ng/l	12/23	Furdui et al. (2008)
Perfluoroheptanoic acid	Surface water	Laurentian Great Lakes	ND-2.1 ng/l	5/23	Furdui et al. (2008)
Perfluorononanoic acid	Surface water	Laurentian Great Lakes	ND-2 ng/l	18/23	Furdui et al. (2008)
Perfluorooctanoic acid	Surface water	Laurentian Great Lakes	0.1-6.7 ng/l	23/23	Furdui et al. (2008)
Perfluorooctanoic sulfonate	Surface water	Laurentian Great Lakes	0.1-37.6 ng/l	23/23	Furdui et al. (2008)
Perfluoroundecanoic acid	Surface water	Laurentian Great Lakes	ND-1.4 ng/l	10/23	Furdui et al. (2008)
Potassium perfluorohexane sulfonate	Surface water	Laurentian Great Lakes	ND-1.8 ng/l	11/23	Furdui et al. (2008)

Table 4c. The occurrence of perfluorinated surfactants in DWTFs in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Perfluorooctanoic acid	DWTF influent	Windsor-Detroit	2-22 ng/l	20/22	Tabe et al. (2009)
Perfluorooctanoic sulfonate	DWTF influent	Windsor-Detroit	2-16 ng/l	18/22	Tabe et al. (2009)
Perfluorooctanoic acid	DWTF effluent	Windsor-Detroit	2-32 ng/l	30/32	Tabe et al. (2009)
Perfluorooctanoic sulfonate	DWTF effluent	Windsor-Detroit	2-12 ng/l	31/32	Tabe et al. (2009)

The spatial distribution of perfluorinated carboxylates and perfluorinated sulfonates in Laurentian Great Lakes was also studied by Furdui et al. (2007) using lake trout samples (Table 4d). A total of 46 lake trout samples were collected in 2001 from Lake Superior, Lake Michigan, Lake Huron, Lake Erie and Lake Ontario. The order of decreasing PFC concentrations was Lake Erie (152 ng/g) > Lake Ontario (60 ng/g) > Lake Huron (58 ng/g) > Lake Michigan (27 ng/g) > Lake Superior (13.1 ng/g). Among 13 PFCs, PFOS was the most frequently detected compound with the highest concentration of 121 ng/g in Lake Erie samples. In another study, perfluorinated carboxylates and perfluorinated sulfonates were analyzed in herring gull eggs collected from Laurentian Great lakes in 2007. In confirmation with the study of Furdui et al. (2007) the highest total PFC concentration (601 ng/g) was reported in Lake Erie samples (Gebbink et al., 2009). More than 90 % of total perfluorinated sulfonates were comprised of PFOS. The authors emphasized the significance of herring gull diet as a major factor regulating the exposure of PFCs. They also suggested that aquatic prey may be the main source of PFCs accumulation to herring gulls.

Table 4d. The occurrence of perfluorinated surfactants in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Perfluorinated Carboxylates	Herring gull eggs	Laurentian Great Lakes	32-113 ng/g	> 60%	Gebbink et al. (2009)
Perfluorinated Carboxylates	Lake trout	Laurentian Great Lakes	6.9-19 ng/g	Generally > 60%	Furdui et al. (2007)
Perfluorinated Sulfonates	Herring gull eggs	Laurentian Great Lakes	91-507 ng/g	Generally > 60%	Gebbink et al. (2009)
Perfluorinated Sulfonates	Lake trout	Laurentian Great Lakes	5.8-130 ng/g	Generally > 60%	Furdui et al. (2007)

6. ALKYLPHENOLIC SUBSTANCES

Alkylphenols are formed by the alkylation of phenols and mostly used as precursors to detergents, as additives for fuels and lubricants and as antioxidants in plastics and rubber products. Alkylphenol ethoxylates are made from alkylphenols and used as synthetic surfactants in detergents and cleaning products. Alkylphenol ethoxylates could not be degraded effectively in sewage treatment plants; however the ethoxylate groups could easily break down releasing alkylphenols and alkylphenoxy carboxylic acids into the environment. Nonylphenol and octylphenol are the most common alkylphenols and have hormone disrupting effects as they have been found to alter reproduction, to feminize and to lower the survival rates of fish in contaminated water.

Regulatory criteria or guidelines have been developed in both the United States and Canada. In the United States, the acute Ambient Water Quality Criterion (WQC) for nonylphenol in fresh water is 28 µg/l while a chronic freshwater criterion is 6.6 µg/l (US EPA 2005). In Canada, an Environmental Quality Guideline for nonylphenol in freshwater is 1 µg/L and determined by using the lowest observable effect concentration for the most sensitive organism (Canadian Council of Ministers of the Environment (CCME) 2001).

Mayer et al. (2007) investigated the occurrence of alkylphenolic compounds in water, sediment and invertebrates in a Great Lakes coastal marsh, Cootes Paradise and evaluated their bioaccumulation potential (Table 5a-c). Seven water samples and 21 sediment samples were collected from both shoreline sites and open water between the years 2001-2002. The total concentrations of alkylphenolic compounds in water samples ranged from 1.05 to 96.9 µg/l (Table 5a). The highest concentration of alkylphenolic substances was found in the West Pond sediments, which are at the site nearest to the Dundas WTP effluent pipe (Table 5b). The hydrophobic 4-nonyl phenol comprised 52 % of total alkylphenolic compounds, whereas polar carboxylic acids could not be detected in surficial sediments. Accordingly, the major component in sediment dwelling invertebrates was also 4-nonylphenol (Table 5c). Sediment ingestion was proposed as a major pathway for the contamination of invertebrates with hydrophobic 4-nonylphenol, while the direct uptake from the external environment was shown to be main route of exposure for dissolved compounds.

Table5a. The occurrences of alkylphenolic substances in natural water in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Nonylphenol	Water	Muskoka Region	ND-19.83 µg/SPMD	7/10	Metcalfe et al. (2008)
4-nonylphenol	Water column	Cootes Paradise	ND-0.286 µg/l	4/7	Mayer et al. (2007)
Nonylphenoxyacetic acid	Water column	Cootes Paradise	0.025-2.49 µg/l	7/7	Mayer et al. (2007)
Nonylphenoxyethoxy acetic acid	Water column	Cootes Paradise	0.025-9.67 µg/l	7/7	Mayer et al. (2007)
Nonylphenol ethoxylates (n=1-17)	Water column	Cootes Paradise	0.076-95.87 µg/l	7/7 NPE1 4/7 NPE2 7/7 NPE3-17	Mayer et al. (2007)
4-tert-octylphenol	Water column	Cootes Paradise	ND-0.012 µg/l	2/7	Mayer et al. (2007)
Octylphenoxyacetic acid	Water column	Cootes Paradise	ND-0.083 µg/l	6/7	Mayer et al. (2007)

Table5b. The occurrences of alkylphenolic substances in sediments in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
4-nonylphenol	Sediment	Cootes Paradise	ND-1.75 µg/g	52 % of total alkyl phenolics	Mayer et al. (2007)
Nonylphenoxyacetic acid	Sediment	Cootes Paradise	ND-0.03 µg/g	-	Mayer et al. (2007)
Nonylphenol ethoxylates (n=1-17)	Sediment	Cootes Paradise	ND-3.26 µg/g	-	Mayer et al. (2007)
4-tert-octylphenol	Sediment	Cootes Paradise	ND-0.052 µg/g		Mayer et al. (2007)

Table5c. The occurrences of alkylphenolic substances in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
4-nonylphenol	Invertebrates	Cootes Paradise	1.85-6.33 µg/g	37.5 % of total alkyl phenolics	Mayer et al. (2007)
Nonylphenoxyacetic acid	Invertebrates	Cootes Paradise	0.31 µg/g	-	Mayer et al. (2007)
Nonylphenoxyethoxy acetic acid	Invertebrates	Cootes Paradise	2.1-5 µg/g	-	Mayer et al. (2007)

7. SYNTHETIC MUSK FRAGRANCES

Synthetic musks are widely used in a vast majority of personal care products such as, perfumes, cosmetics, detergents and cleaning products. They are generally divided into two classes, aromatic nitro musks and polycyclic musks. The nitro musks include musk ketone (1-[4-(1,1-dimethyl-ethyl)-2,6-dimethyl-3,5-dinitrophenyl]-ethanone) and musk xylene (1-(1,1-dimethylethyl)-3,5-dimethyl-2,4,6-trinitrobenzene). The most common polycyclic musks include 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta(*g*)-2-benzopyran (HHCB), 6-acetyl-1,1,2,4,4,7-hexamethyltetralin (AHTN), 5-acetyl-3-isopropyl-1,1,2,6-tetramethylindane (ATII), 6-acetyl-1,1,2,3,3,5-hexamethylindane (AHMI), 4-acetyl-6-*tert*-butyl-1,1-dimethylindane (ADBI), and 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5*H*)-indanone (DPMI). Due to their lipophilic nature, synthetic musks could not be effectively removed in sewage treatment facilities and are retained in sewage sludges. Therefore, nitro and polycyclic nitro musks have been detected in different environmental samples and have potential to bioaccumulate in aquatic organisms.

The effectiveness of six different wastewater treatment plants on the removal of synthetic musks was evaluated in the study of Smyth et al. (2008) in which influent and effluents samples from WWTPs along the Grand River were collected from November 2003 to July 2004 (Table 6a). The treatment types represented by the six plants included; facultative lagoon, oxidation ditch with tertiary sand filtration, extended aeration activated sludge plant and three conventional activated sludge plant. The polycyclic musks, HHCB (Galaxolide) and AHTN (Tonalide) were detected in all influents samples up to 40 and 14 µg/l, respectively and consisted of more than 90 % of the total influent musk concentration. The polycyclic musks ATII (Traseolide), AHDI (Phantolide), ADBI (Celestolide) and nitro musks Musk Xylene and Musk ketone were also detected in all influent samples. The removal of polycyclic and nitro musks in wastewater treatment systems ranged from 50% to 97%. However, based on the correlation between removal rates of synthetic musks and their concentrations in raw sludge, the authors concluded that the reduction of musks in effluent samples mainly occurred due to their partitioning to sewage sludge.

Table 6a. The occurrence of musk fragrances in WWTPs in the Great Lakes Basin.

Total Polycyclic (Cashmeran, celestolide, crysolide, phantolide, traseolide, galaxolide, abbalide, pearlide, tonalide, fixolide, astralide) and Nitro (musk ambrette, musk xylene, musk moskene, musk tibetene, musk ketone) musks	Facultative Lagoon Influent	Grand River	9.7-20.9 µg/l	100 % Galaxolide	Smyth et al. (2008)
	Oxidation Ditch Influent	Grand River	2.4-9.7µg/l	Tonalide	Smyth et al. (2008)
	Extended Aeration Influent	Grand River	10.9-17.4 µg/l	Traseolide	Smyth et al. (2008)
	Activated Sludge 1 Influent	Grand River	6.7-56.6 µg/l	Celestolide	Smyth et al. (2008)
	Activated Sludge 2 Influent	Grand River	8.94-14.7 µg/l	Phantolide	Smyth et al. (2008)
	Activated Sludge 3 Influent	Grand River	5.2-26.3 µg/l	Musk xylene Musk ketone	Smyth et al. (2008)
				50% Cashmeran	Smyth et al. (2008)
				Musk ambrette Musk oskene	Smyth et al. (2008)
	Facultative Lagoon effluent	Grand River	0.076-0.834 µg/l	100 % Galaxolide	Smyth et al. (2008)
	Oxidation Ditch effluent	Grand River	0.641-1.35 µg/l	Tonalide	Smyth et al. (2008)
	Extended Aeration effluent	Grand River	3.07-4.64 µg/l	Musk xylene Musk ketone	Smyth et al. (2008)
	Activated Sludge 1 effluent	Grand River	3.04-4.04 µg/l		Smyth et al. (2008)
	Activated Sludge 2 effluent	Grand River	2.95-4.17 µg/l		Smyth et al. (2008)
	Activated Sludge 3 effluent	Grand River	1.16-2.2 µg/l		Smyth et al. (2008)

Andresen et al. (2007) determined the AHTN, HHCB, HHCB-lactone, musk xylene and musk ketone in the samples collected from Hamilton Harbor and open Lake Ontario surface waters in 2005 (Table 6b). The musk concentrations near Hamilton Harbor ranged from 0.04 to 7 ng/l and decreased with increasing distance from Hamilton Harbor. Dilution, sorption and remobilization in offshore areas were suggested for the spatial distribution of the compound concentrations in Lake Ontario. In a recent study, Ramirez et al. (2009) collected fish samples during late summer and fall of 2006, from North Shore Channel receiving discharge from WWTP in Chicago. Among the 5 synthetic musks, galaxolide and tonalide were detected in all samples (n=6) up to 1800 and 230 ng/g, respectively (Table 6c).

Table6b. The occurrence of musk fragrances in natural waters in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Musk xylene	Surface water	Hamilton Harbor	0.04 ng/l	-	Andresen et al. (2007)
Musk xylene	Surface water	Lake Ontario (open)	0.04 ng/l	-	Andresen et al. (2007)
Musk ketone	Surface water	Hamilton Harbor	0.04 ng/l	-	Andresen et al. (2007)
Musk ketone	Surface water	Lake Ontario (open)	0.04 ng/l		Andresen et al. (2007)
Galaxolide	Surface water	Hamilton Harbor	7 ng/l	-	Andresen et al. (2007)
Galaxolide	Surface water	Lake Ontario (open)	2 ng/l	-	Andresen et al. (2007)
Galaxolide lactone	Surface water	Hamilton Harbor	4 ng/l	-	Andresen et al. (2007)
Galaxolide lactone	Surface water	Lake Ontario (open)	1 ng/l		Andresen et al. (2007)
Tonalide	Surface water	Hamilton Harbor	0.8 ng/l		Andresen et al. (2007)
Tonalide	Surface water	Lake Ontario (open)	0.2 ng/l	-	Andresen et al. (2007)

Table6c. The occurrence of musk fragrances in biota in the Great Lakes Basin.

Compound	Matrix	Location	Concentration	Frequency	Reference
Galaxolide	Fish tissues	North Shore Channel	Up to 1800 ng/g	6/6	Ramirez et al. (2009)
Tonalide	Fish tissues	North Shore Channel	Up to 230 ng/g	6/6	Ramirez et al. (2009)

8. PLASTICIZERS

Bisphenol A is a well known plasticizer used to make polycarbonate plastics and epoxy resins. It is a highly persistent endocrine disruptor and therefore subjected to risk assessment studies by regulatory authorities around the world. Environment Canada and Health Canada (2008) set the Predicted No Effect Concentration (PNEC) for aquatic organisms in water and sediment as 0.175 µg/l and 0.01 mg/l, respectively. In a study of Tabe et al. (2009), bisphenol A was detected in WWTP effluents, DWTP influents and effluents from Windsor and Detroit at concentration ranges of 7-42 ng/l, 1-1967 ng/l and 0.3-26 ng/l and detection frequencies of 50%, 50%, and 40%, respectively. It was also detected in source water and drinking water from 17 drinking water systems in Ontario at frequencies of 22% and 12 %, respectively. The maximum concentrations of Bisphenol A in source water and drinking water were 87 and 99 ng/l, respectively (Kleywegt et al., 2011). In addition, Bisphenol A was detected in well samples affected by landfill leachate near Elkhart, Indiana up to 1.3 µg/l (Buszka et al., 2009). The authors also determined other commonly used plasticizers, ethanol-2-butoxy phosphate and diethylphthalate in well samples up to 1 and 1.2 µg/l.

9. POLYCYCLIC AROMATIC HYDROCARBONS

Polycyclic aromatic hydrocarbons are among the most widespread organic pollutants with potential endocrine disrupting properties. They are mainly formed by incomplete combustion of carbon containing wood, coal, diesel, fat and tobacco and therefore are mainly potent atmospheric products. However, PAHs have been detected in sediment samples from the Great Lakes basin as well as air samples. Total PAH concentrations in sediment samples from Toronto ranged from 42 ng/g (suburban site) to 3300 ng/g (urban site) and the composition of PAHs was dominated by fluoranthene (6-22%) followed by pyrene (5-20%) and phenanthrene (2-13%) (Wong et al., 2009). Similar concentration range of ΣPAHs (50-7590 ng/g) in sediment samples collected from Saginaw River watershed in 2004 was also observed by Horii et al. (2009). Fourteen of 16 EPA priority PAHs were detected in all sediment samples (n=10) at high concentrations, especially fluoranthene (8.4-1230 ng/g), pyrene (6.5-1100 ng/g) and phenanthrene (3.6-1000 ng/g). Chlorinated PAHs were also detected in Saginaw sediment

samples at a relatively lower concentration range (49-2490 pg/g) (Horii et al., 2009). In a recent study, much higher PAH concentrations were reported in suspended sediments from Detroit River, Lake St. Clair and St. Clair River corridor. Heavy historical industrial activities such as steel manufacturing and chlor-alkali production near the Trenton Channel area of Detroit River and the upper reaches of the St. Clair River resulted in a high sediment contamination with a maximum PAH concentration of 82,000 and 52,000 ng/g in 2000 and 2004, respectively.

10. CONCLUSION

In the current report, the review of the environmental occurrence of several chemicals of emerging concern in the Great Lakes region was conducted. For this purpose about 60 scientific papers published between 2007-2011 were identified that evaluated the presence of a variety of pharmaceutical substances, pesticides, flame retardants, surfactants, alkylphenolic substances, synthetic musk fragrances, and other endocrine disrupting chemicals in aquatic environment, sediments and biota.

Based on the data derived from the literature, the most frequently detected pharmaceutical in drinking water treatment facility influents and effluents was an antiepileptic drug, carbamazepine with the maximum concentrations of 1015 ng/l and 721 ng/l, respectively. Carbamazepine was followed by anti-inflammatory drugs, ibuprofen and naproxen and lipid regulating drugs gemfibrozil and bezafibrate. A widely used sulfonamide group antibiotic, sulfamethoxazole was also detected frequently in drinking water treatment facility influents, but not in effluents. Although their detection frequencies were relatively low, high concentrations of macrolide antibiotics, especially erythromycin was detected in the effluents of drinking water treatment facilities compared to the influents. Several pharmaceuticals were detected at high ng/l levels in natural water samples from the Great Lakes region including, carbamazepine, caffeine, its metabolite paraxanthine, ibuprofen, gemfibrozil and sulfamethoxazole and were the most frequently studied pharmaceuticals, with reported maximum concentrations of 1238 ng/l, 4275 ng/l, 1822 ng/l, 12200 ng/l, 1950 ng/l and 211 ng/l respectively. The occurrence of lipid regulating drugs, antidepressants, beta blockers and antibiotics were mostly reported in sewage treatment plants where their elimination is poor. Although several pharmaceuticals have been

detected in aquatic environment, so far there are no regulatory standards for their occurrence in freshwater or drinking water.

Agricultural activities were mainly responsible for the contamination of surface water and sediments with pesticides as they were frequently detected at locations receiving runoff from rural lands. Atrazine, metolachlor and mecoprop were consistently detected in surface water samples from the Great Lakes region. Only atrazine was found to exceed Canadian Water Quality Guideline levels for the protection of aquatic life in some of the water samples. The occurrence of diazinon in surface waters was limited to only one study in which diazinon exceeded both US and Canadian water quality standards in 28 % of samples. Bioaccumulation potential of a vast number of pesticides was confirmed by several studies through their detection in a variety of seabirds.

Among all chemicals of emerging concern discussed in the current report, brominated and chlorinated flame retardants and alkylphenolic substances had the highest bioaccumulation potential, as their elevated concentrations in aquatic biota had been reported in many articles. Among flame retardants, PBDEs, especially the congeners BDE 47 and BED 100, and Dechloranes were the most frequently detected compounds in aquatic biota and sediments. The detection frequency of nonylphenol was quite high in water, sediment and invertebrates at high concentrations. The maximum concentration of nonylphenol in sediment (1.75 mg/kg) was beyond the Canadian regulatory criteria. Its accumulation in invertebrates was also substantially high and concentrations ranged from 1.9 to 6.3 mg/kg.

Another group of chemicals of emerging concern with high bioaccumulation potential was perfluorinated surfactants. The mostly detected surfactants in biota were perfluorooctanoic sulfonate (PFOS) and perfluorooctanoic acid (PFOA). These substances were also detected in surface water samples at a maximum concentration of 0.038 µg/l which is far below the estimated no effect value (0.491 µg/l) set by Environment Canada.

Of the several polycyclic and nitro musks, galaxolide, tonalide, musk ketone and musk xylene have been found in surface water samples consistently at maximum concentrations of 7 ng/l, 0.8 ng/l, 0.04 ng/l and 0.04 ng/l, respectively. Ineffective elimination of these substances by several treatment facilities in WWTPs was also reported. Galaxolide and tonalide was also detected in fish tissues up to 1.8 mg/kg and 0.23 mg/kg, respectively.

11. REFERENCES

- Al-Ansari A.M., Saleem A., Kimpe L.E., Sherry J.P., McMaster M.E., Trudeau V.L., Blais J.M. 2010. Bioaccumulation of the pharmaceutical 17 α -ethinylestradiol in shorthead redhorse suckers (*Moxostoma macrolepidotum*) from the St. Clair River, Canada. *Environmental Pollution*, 158, 2566-2571.
- Andresen J. A., Muir D., Ueno D., Darling C., Theobald N., Bester K. 2007. Emerging pollutants in the north sea in comparison to Lake Ontario, Canada, data. *Environmental Toxicology and Chemistry* 26, 1081-1089.
- Benotti M. J., Trenholm R. A., Vanderford B. J., Holady J. C., Stanford B. D., Snyder S. A. 2009. Pharmaceuticals and Endocrine Disrupting Compounds in U.S. Drinking Water. *Environmental Science and Technology*, 43, 597–603.
- Buszka, P.M., Yeskis D.J., Kolpin D.W., Furlong E.T., Zaugg S.D., Meyer M.T. 2009. Waste indicator and pharmaceutical compounds in landfill leachate affected ground water near Elkhart, Indiana, 2000-2002. *Bulletin of Environmental Contamination and Toxicology*, 82, 653-659.
- Byer JD, Struger J, Sverko E, Klawunn P, Todd A. 2011. Spatial and seasonal variations in atrazine and metolachlor surface water concentrations in Ontario (Canada) using ELISA. *Chemosphere*, 82, 1155-1160.
- Byer JD, Struger J, Klawunn P, Todd A, Sverko E. 2008. Low cost monitoring of glyphosate in surface waters using the ELISA method: an evaluation. *Environmental Science and Technology*, 42, 6052-6057.
- Carballa M., Omil F., Lema J.M., Llompart M., Garcia-Jares C., Rodriguez I., Gomez M., Ternes T., 2004. Behavior of Pharmaceuticals, Cosmetics, and Hormones in a Sewage Treatment Plant. *Water Research*, 38 (12), 2918–2926.

Carrara C., Ptacek C.J., Robertson W.D., Blowes D.W., Moncur M.C., Sverko E., Backus S. 2008. Fate of Pharmaceutical and Trace Organic Compounds in Three Septic System Plumes, Ontario, Canada. *Environmental Science and Technology*, 42, 2805-2811.

Champoux L., Moisey J., Muir D.C.G. 2010. Polybrominated diphenyl ethers, toxaphenes and other halogenated organic pollutants in Great Blue Heron eggs. *Environmental Toxicology and Chemistry*, 29, 243-249.

Chu S., Metcalfe C.D. 2007. Analysis of paroxetine, fluoxetine and norfluoxetine in fish tissues using pressurized liquid extraction, mixed mode solid phase extraction cleanup and liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A*, 1163, 112-118.

De Oliveira A. J. F., Pinhata J. M. W., 2008. Antimicrobial resistance and species composition of *Enterococcus* spp. isolated from waters and sands of marine recreational beaches in Southeastern Brazil. *Water Research*, 42, 2242-2250.

Ding Y., Zhang W., Gu C., Xagorarakis I., Li H. 2011. Determination of pharmaceuticals in biosolids using accelerated solvent extraction and liquid chromatography/tandem mass spectrometry. *Journal of Chromatography A*, 1218, 10-16.

Dunn A.M., Julien G., Ernst W.R., Cook A., Doe K.G., Jackman P.M. 2011. Evaluation of buffer zone effectiveness in mitigating the risks associated with agricultural runoff in Prince Edward Island. *Science of the Total Environment*, 409, 868-882.

EPA, 2008. Report on Pharmaceuticals and Personal Care Products in Illinois Drinking Water Bureau of Water, Illinois EPA.

Fernie K.J., Letcher R.J. 2010. Historical Contaminants, Flame Retardants, and Halogenated Phenolic Compounds in Peregrine Falcon (*Falco peregrinus*) Nestlings in the Canadian Great Lakes Basin. *Environmental Science and Technology*, 44, 3520-3526.

Furdui V.I., Stock N.L., Ellis D.A., Butt C.M., Whittle D.M., Crozier P.W., Reiner E.J., Muir D.C.G., Mabury S.A. 2007. Spatial Distribution of Perfluoroalkyl Contaminants in Lake Trout from the Great Lakes. *Environmental Science and Technology*, 41, 1554 – 1559.

Furdui V.I., Crozier P.W., Reiner E.J., Mabury S.A. 2008. Trace level determination of perfluorinated compounds in water by direct injection. *Chemosphere*, 73, S24-S30.

Gauthier L.T., Letcher R.J. 2009. Isomers of Dechlorane Plus flame retardant in the eggs of herring gulls (*Larus argentatus*) from the Laurentian Great Lakes of North America: Temporal changes and spatial distribution. *Chemosphere*, 75, 115-120.

Gebbink W.A., Hebert C.E., Letcher R.J. 2009. Perfluorinated Carboxylates and Sulfonates and Precursor Compounds in Herring Gull Eggs from Colonies Spanning the Laurentian Great Lakes of North America. *Environmental Science and Technology*, 43, 7443-7449.

Hahm J., Manchester-Neesvig J.B., DeBord D., Sonzogni W.C. 2009. Polybrominated diphenyl ethers (PBDEs) in Lake Michigan forage fish. *Journal of Great Lakes Research*, 35, 154-158.

Hao C., Nguyen B., Zhao X., Chen E., Yang P. 2010. Determination of Residual Carbamate, Organophosphate, and Phenyl Urea Pesticides in Drinking and Surface Water by High-Performance Liquid Chromatography/Tandem Mass Spectrometry. *Journal of AOAC International*, 93, 400-410.

Heinz G.H., Stromborg K.L. 2009. Further declines in organochlorines in eggs of red-breasted mergansers from Lake Michigan, 1977–1978 versus 1990 versus 2002. *Environmental Monitoring and Assessment*, 159, 163-168.

Hernando M.D., Mezcua M., Fernández-Alba A.R., Barceló D. 2006. Environmental risk assessment of pharmaceutical residues in wastewater effluents, surface waters and sediments. *Talanta*, 69, 334-342.

Horii Y, Ohura T., Yamashita N., Kannan K. 2009. Chlorinated polycyclic aromatic hydrocarbons in sediments from industrial areas in Japan and United States. *Archives of Environmental Contamination and Toxicology*, 57, 651-660.

Houde M., Martin J.W., Letcher R.J., Solomon K.R., Muir D.C.G. 2006. Biological monitoring of polyfluoroalkyl substances: A review. *Environmental Science and Technology*, 40, 3463-3473.

Houde M., Muir D.C.G., Tomy G.T., Whittle D.M., Teixeira C., Moore S. 2008. Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environmental Science and Technology*, 42, 3893–3899.

Ismail N., Gewurtz S.B., Pleskach K., Whittle M., Helm P.A., Marvin C.H., Tomy G.T. 2009. Brominated and chlorinated flame retardants in Lake Ontario, Canada, lake trout (*Salvelinus namaycush*) between 1979 and 2004 and possible influences of food-web changes. *Environmental Toxicology and Chemistry*, 28, 910-920.

Jasim S. Y., Irabelli A., Yang P., Ahmed S., Schweitzer L. 2006. Presence of Pharmaceuticals and Pesticides in Detroit River Water and the Effect of Ozone on Removal. *Ozone Science and Engineering*, 28 (6), 415-423.

Jantunen L.M., Helm P.A., Ridal J.J., Bidleman T.F. 2008. Air–water gas exchange of chiral and achiral organochlorine pesticides in the Great Lakes. *Atmospheric Environment*, 42, 8533-8542.

Kurt-Karakus P.B., Muir D.C., Bidleman T.F., Small J., Backus S., Dove A., 2010. Metolachlor and atrazine in the Great Lakes. *Environmental Science and Technology* 44, 4678–4684.

Kurt-Karakus P.B., Bidleman T.F., Muir D.C., Struger J., Sverko E., Cagampan S.J., Small J.M., Jantunen L.M. 2010. Comparison of concentrations and stereoisomer ratios of mecoprop,

dichlorprop and metolachlor in Ontario streams, 2006-2007 vs. 2003-2004. *Environmental Pollution*, 158, 1842-1849.

Kleywegt S., Pileggi V., Yang P., Hao C., Zhao X., Rocks C., Thach S., Cheung P., Whitehead B. 2011. Pharmaceuticals, hormones and bisphenol A in untreated source and finished drinking water in Ontario, Canada - Occurrence and treatment efficiency. *Science of the Total Environment*, 409, 1481-1488.

Kormos, J.L. 2007. Occurrence and seasonal variability of selected pharmaceuticals in Southern Ontario drinking water supplies. Msc. Thesis, Biology, University of Waterloo.

Lavoie R.A., Champoux L., Rail J.F., Lean D.R.S. 2010. Organochlorines, brominated flame retardants and mercury levels in six seabird species from the Gulf of St. Lawrence (Canada): Relationships with feeding ecology, migration and molt. *Environmental Pollution*, 158, 2189-2199.

Lee H.B., Sarafin K., Peart T.E. 2007. Determination of β -blockers and β 2-agonists in sewage by solid-phase extraction and liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A*, 1148, 158-167.

Lee H.B., Peart T.E., Svoboda M.L., Backus S. 2009. Occurrence and fate of rosuvastatin, rosuvastatin lactone, and atorvastatin in Canadian sewage and surface water samples. *Chemosphere*, 77, 1285-1291.

Letcher R.J., Chu S. 2010. High-Sensitivity Method for Determination of Tetrabromobisphenol-S and Tetrabromobisphenol-A Derivative Flame Retardants in Great Lakes Herring Gull Eggs by Liquid Chromatography-Atmospheric Pressure Photoionization-Tandem Mass Spectrometry. *Environmental Science and Technology*, 44, 8615-8621.

Li H., Helm P.A., Metcalfe C.D. 2010. Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine-disrupting substances using passive polar organic chemical integrative sampler, *Environmental Toxicology and Chemistry*, 29, 751-762.

Lotufo G.R., Pickard S.W. 2010. Benthic Bioaccumulation and Bioavailability of Polybrominated Diphenyl Ethers from Surficial Lake Ontario Sediments Near Rochester, New York, USA. *Bulletin of Environmental Contamination and Toxicology*, 85, 348-351.

Mayer, T., Bennie D., Rosa F., Rekas G., Palabrica V., Schachtschneider J. 2007. Occurrence of alkylphenolic substances in a Great Lakes coastal marsh, Cootes Paradise, ON, Canada. *Environmental Pollution*, 147, 683-690.

McDaniel T.V., Martin P.A., Struger J., Sherry J., Marvin C.H., McMaster M.E., Clarence S., Tetreault G. 2008. Potential endocrine disruption of sexual development in free ranging male northern leopard frogs (*Rana pipiens*) and green frogs (*Rana clamitans*) from areas of intensive row crop agriculture. *Aquatic Toxicology*, 88, 230-42.

Metcalfe T. L., Dillon P. J., Metcalfe C. D. 2008. Detecting the Transport of Toxic Pesticides from Golf Courses into Watersheds in the Precambrian Shield Region of Ontario, Canada. *Environmental Toxicology and Chemistry*, 27, 811-818

Metcalfe, C.D., Chu, S., Judt, C., Li, H., Oakes, K.D., Servos, M.R., Andrews, D.M. 2010. Antidepressants and their metabolites in municipal wastewater, and downstream exposure in an urban watershed. *Environmental Toxicology and Chemistry*, 29, 79-89

Milwaukee Water Works Water Quality section, Tests of Lake Michigan water- source of Milwaukee Drinking Water, 2008 Annual Water Quality report, 2008.

Moody C.A., Martin J.W., Kwan W.C., Muir D.C.G., Mabuty S.A. 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke creek. *Environmental Science and Technology*, 36, 545–551.

Pérez-Fuentetaja A., Lupton S., Clapsadl M., Samara F., Gatto L., Biniakewitz R., Aga D.S. 2010. PCB and PBDE levels in wild common carp (*Cyprinus carpio*) from eastern Lake Erie. *Chemosphere*, 81, 541-7.

Raach M., Lebeuf M., Pelletier E. 2011. PBDEs and PCBs in the liver of the St Lawrence Estuary beluga (*Delphinapterus leucas*): a comparison of levels and temporal trends with the blubber. *Journal of Environmental Monitoring*, 13, 649-656.

Rahman M.F., Yanful E.K., Jasim S.Y., Bragg L.M., Servos M.R., Ndiongue S., Borikar, D. 2010. Advanced oxidation treatment of drinking water: Part 1. Occurrence and removal of pharmaceuticals and endocrine disrupting compounds from Lake Huron water. *Ozone Science and Engineering*, 32,217-229.

Ramirez A. J., Brain R. A., Usenko S., Mottaleb M. A., O'Donnell J. G., Stahl L. L., Wathen J. B., Snyder B. D., Pitt J. L., Perez-Hurtado P., Dobbins L. L., Brooks B. W., Chambliss, C. K. 2009. Occurrence of pharmaceuticals and personal care products in fish: Results of a national pilot study in the United States. *Environmental Toxicology and Chemistry*, 28, 2587–2597.

Scheurer M., Ramil M., Metcalfe C.D., Groh S., Ternes T.A. 2010. The challenge of analyzing beta-blocker drugs in sludge and wastewater. *Analytical and Bioanalytical Chemistry*, 396, 845-856.

Shen L., Reiner E. J., MacPherson K. A., Kolic T. M., Sverko E., Helm P. A., Bhavsar S. P., Brindle I. D., Marvin C. H. 2010. Identification and screening analysis of halogenated norbornene flame retardants in the Laurentian Great Lakes: Dechloranes 602, 603 and 604. *Environmental Science and Technology*, 44, 760–766.

Shen L., Reiner E.J., MacPherson K.A., Kolic T.M., Helm P.A., Richman L.A., Marvin C.H., Burniston D.A., Hill B., Brindle I.D., McCrindle R., Chittim B.G. 2011. Dechloranes 602, 603,

604, Dechlorane Plus, and Chlordene Plus, a newly detected analogue, in tributary sediments of the Laurentian Great Lakes. *Environmental Science and Technology*, 45, 693-699.

Smyth S.A., Lishman L., McBean E.A., Kleywegt S., Yang J.J., Svoboda M.L., Lee H-B., Seto, P. 2008. Seasonal occurrence and removal of polycyclic and nitro musks from wastewater treatment plants in Ontario, Canada. *Journal of Environmental Engineering and Science*, 7, 299-317.

Spear P.A., Boily M., Giroux I. DeBlois C. Leclair M.H., Levasseur M., Leclair R. 2009. Study design, water quality, morphometrics and age of the bullfrog, *Rana catesbeiana*, in sub-watersheds of the Yamaska River drainage basin, Quebec, Canada. *Aquatic Toxicology*, 91, 110-117.

Spongberg A.L., Witter J.D. 2008. Pharmaceutical compounds in the wastewater process stream in Northwest Ontario. *Science of the Total Environment*, 397, 148-157.

Struger J., Fletcher T. 2007. Occurrence of Lawn Care and Agricultural Pesticides in the Don River and Humber River Watersheds (1998–2002). *Journal of Great lakes Research*, 33, 887-905.

Struger J., Thompson D., Staznik B., Martin P., McDaniel T., Marvin C. 2008. Occurrence of Glyphosate in surface waters of southern Ontario. *Bulletin of Environmental Toxicology and Contamination*, 80, 378-384.

Sverko E., Tomy G. T., Marvin C. H., Zaruk D., Reiner E., Helm P. A., Hill B., McCarry B. E. 2008. Dechlorane Plus levels in sediment of the lower Great Lakes. *Environmental Science and Technology*, 42, 361–366.

Tabe S., Jamal T., Seth R., Yue C., Yang P., Zhao X., Schweitzer L. 2009. PPCPs and EDCs- Occurrence in the Detroit River and Their Removal by Ozonation. *Water Research Foundation*, 1-207.

Ueno D., Darling C., Alaee M., Pacepavicius G., Teixeira C., Campbell L., Letcher R.J., Bergman Å., Marsh G., Muir D. 2008. Hydroxylated Polybrominated Diphenyl Ethers (OH-PBDEs) in the Abiotic Environment: Surface Water and Precipitation from Ontario, Canada. *Environmental Science and Technology*, 42, 1657-1664.

Venier M., Wierda M., Bowerman W.W., Hites R.A. 2010. Flame retardants and organochlorine pollutants in bald eagle plasma from the Great Lakes region. *Chemosphere*, 80, 1234-1240.

Watkinson, A. J., Murby, E. J., Kolpin, D. W., Costanzo, S. D., 2009. The occurrence of antibiotics in an urban watershed: From wastewater to drinking water. *Science of the Total Environment*, 407, 2711-2723.

Wong F., Robson M., Diamond M.L., Harrad S., Truong J. 2009. Concentrations and chiral signatures of POPs in soils and sediments: A comparative urban versus rural study in Canada and UK. *Chemosphere*, 74, 404-411.

Wu C., Spongberg A.L., Witter J.D. 2008. Use of solid phase extraction and liquid chromatography–tandem mass spectrometry for simultaneous determination of various pharmaceuticals in surface water. *International Journal of Environmental Analytical Chemistry*, 88, 1033–1048.

Wu C., Witter J.D., Spongberg A.L., Czajkowski K.P. 2009. Occurrence of selected pharmaceuticals in an agricultural landscape, western Lake Erie basin. *Water Research*, 43, 3407-3416.