Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Occurrence, removal, and environmental impacts of emerging contaminants detected in water and wastewater in Southern Ontario—Part I: occurrence and removal

Shahram Tabe[a,b,*], Vince Pileggi[a], Monica Nowierski[a], Sonya Kleywegt[a] and Paul Yang[a]

[a] Ministry of the Environment and Climate Change, 40 St. Clair Ave. West, Toronto, Ontario, Canada M4 V 1M2

[b] Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario, Canada N9B 3A8

* Corresponding author. E-mail: shahram.tabe@ontario.ca

Abstract

A comprehensive study was conducted at two wastewater treatment plants (WWTPs) and one water treatment plant (WTP) in Windsor, Ontario, Canada. The occurrence of 220 emerging and legacy compounds, their removal efficiencies by the existing treatment processes, and their potential environmental impacts were studied. The results are reported in a two part paper. In this part (I), the occurrence and removal efficiencies are presented. Three of the 47 target pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) contributed 89–96% of the total concentration of PhACs/EDCs in the WWTP influents. They were acetaminophen, ibuprofen, and naproxen. The existing treatment processes successfully removed between 95 and 98% of 'all' PhACs/EDCs, primarily due to the high removal rates of these three analgesics. Concentrations of PhACs/EDCs detected at the WTP intake were two to three orders of magnitude lower than those in the effluent of the upstream WWTP. These concentrations remained relatively unchanged in the finished drinking water, indicating the WTP's low removal efficiency for trace amounts of them. Polybrominated diphenyl ethers (PBDEs) were detected at concentrations as high as 150 ng/L (for PBDE-209) in the WWTPs' influent, and removed at 86–96% efficiency. PDBE effluent concentrations were mostly below 1 ng/L at both WWTPs, with a maximum of 9 ng/L for PBDE-209. Octylphenol, nonylphenol, and nonylphenol ethoxylates concentrations were monitored in one WWTP's effluent, and ranged between undetectable and 286 ng/L (LoDs varied between 1.3 and 15.2 ng/L).

Key words: emerging contaminants, endocrine disrupting compounds (EDCs), pharmaceutically active compounds (PhACs), water treatment, wastewater treatment

INTRODUCTION

A study on the Detroit River watershed (shared between Ontario, Canada and Michigan, USA) indicated the presence of several pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in the effluents from wastewater treatment plants (WWTPs) discharging to the river (Tabe *et al.* 2009). This encouraged the Ontario Ministry of the Environment and Climate Change (MOECC) to design a comprehensive project to improve understanding of the occurrence, removal, and potential environmental impacts of 220 emerging and legacy contaminants. The study was developed in three stages—Baseline, Phase One, and Phase Two. The Baseline study (5 months) concerned the prevalence of the target substances, the removal efficiency of existing treatment processes, and the toxicity of the WWTP effluents to aquatic organisms. Its outcome helped focus Phase One (13 months) on seasonal

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

variations in occurrence, existing process removal efficiencies, and target substance impacts on aquatic organisms. Phase Two was dedicated to evaluating pilot-scale ozonation in removing or transforming the target substances, and understanding the mechanisms and kinetics of formation of oxidation by-products when selected substances were exposed to ozonation. The results from Phase Two have already been published (Singh *et al.* 2015; Uslu *et al.* 2015).

This paper is the first of a pair reporting the Baseline results. It relates to 47 PhACs/EDCs, 17 polybrominated diphenyl ethers (PBDEs), and four alkylphenols and alkylphenol ethoxilates. In this paper (Part I), findings related to the occurrence of these substances at two WWTPs and one water treatment plant (WTP) in Windsor, Ontario, Canada are presented, and the removal efficiencies of the WTP and WWTP processes are discussed. The environmental impacts are presented in Part II.

The presence of trace organic contaminants (TrOCs) in water sources, and their potential negative impacts on the environment and biota, have been the subject of numerous scientific, social, and political debates (Ternes 1998; Heberer 2002; Heberer *et al.* 2002; Kolpin *et al.* 2002; Metcalfe *et al.* 2003; Sedlak *et al.* 2005; Snyder *et al.* 2007; Tabe *et al.* 2009). The development of novel analytical methods and equipment has enabled detection of extremely low TrOC concentrations—e.g., PhACs and EDCs (Yang *et al.* 2008; Vanderford *et al.* 2012). WWTP effluents have been recognized as a major point discharge source into surface waters. Their negative impacts on the environment and aquatic life have been reported widely (Jobling *et al.* 1998; Westergaard *et al.* 2001; Young *et al.* 2002; Andreozzi *et al.* 2003; Richardson 2003; Laville *et al.* 2004; Sanderson *et al.* 2004; Jobling *et al.* 2009; Tetreault *et al.* 2011; Galus *et al.* 2013). Some investigations suggest a link between increased loads of these contaminants and various environmental and public health risks.

PhACs are used to prevent or treat disease symptoms, in both livestock and humans. This study focuses on PhACs administered to humans. EDCs are thought to interfere with endocrine system functioning. This involves various mechanisms such as mimicking natural hormones, blocking hormone receiving receptors, and disrupting natural hormone synthesis, metabolism, and excretion (Weyer & Riley 2001). Three major EDC categories comprise estrogenic (which mimic natural estrogen), androgenic (mimicking or blocking testosterone), and thyroidal (affecting thyroid glands directly or indirectly) substances (Snyder *et al.* 2002). EDCs can be natural or synthetic—e.g., oral contraceptives (Weyer & Riley 2001).

The concentrations of PhACs and EDCs in water sources are much lower than their therapeutic dosages. However, neither their potential short- and long- term impacts, nor their combined (mixture) effects on the environment and public health are well understood (Boxall *et al.* 2003; Jones *et al.* 2004; Stackelberg *et al.* 2004).

Although WTPs and WWTPs are not designed to remove TrOCs, existing processes remove substantial portions, along with other contaminants. However, limited data are available to determine the removal efficiencies of these plants, which jeopardizes optimization efforts.

PBDEs are flame retardants used to reduce fire hazard in plastics, furniture, and electronic items. In the vapor phase, PBDEs delay combustion and inhibit the spread of fire. Depending on the number and location of bromine atoms in their structure, there are 209 possible PBDE compounds. They are of environmental concern due to their health effects including negative impacts on human fertility (Harley *et al.* 2010).

Several PBDEs have been designated toxic, in Canada, and their manufacture, import, and use were/are being prohibited. (CEPA 2013).

Long-chain alkylphenols and alkylphenol ethoxylates are potential endocrine disruptors and xenoestrogens (Kochukov *et al.* 2009). Of specific concern are octylphenol (OP), nonylphenol (NP), and nonylphenol ethoxylates (NPEs), which are produced in large volumes. Although their use in detergents is banned they still have applications that lead to widespread release into aquatic environment.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

According to the US Environmental Protection Agency (USEPA), NP and NPE show low toxicity to humans, but are highly toxic to fish, and aquatic invertebrates and plants (USEPA 2010).

METHODOLOGY

The target substances' occurrence was studied by monthly 24-hour composite sampling from eight locations in the two WWTPs (WWTP-1 and WWTP-2 hereafter) and one WTP, all in Windsor, Ontario, Canada. Because the WTP is downstream of the discharge from WWTP-1, the sampling locations and times were selected to represent a complete travel path for the target substances from WWTP-1's influent to the finished drinking water leaving the WTP.

Plants and sampling points

WWTP-1 mainly receives residential wastewaters. Its treatment processes consist of primary treatment followed by nitrifying conventional activated sludge (CAS-N) and ultraviolet (UV) irradiation. The UV system operates seasonally and was off during the Baseline Study. WWTP-2 receives both residential (~80%) and industrial (~20%) wastewaters. Its treatment train includes primary treatment followed by a biological aerated filter and UV irradiation. As at WWTP-1, the UV system operates seasonally and was off during the Baseline Study. The processes at the WTP include ozonation, flocculation, sedimentation, and sand filtration. Schematics of the three plants, showing the eight sampling locations, are presented in Figure 1. The sampling points were:

- S1-0: WWTP-1 influent
- S1-1: WWTP-1 primary effluent
- S1-2: WWTP-1 CAS-N treated effluent
- W-0: WTP raw water intake
- W-1: WTP transient water after ozone treatment
- W-2: WTP treated drinking water
- S2-0: WWTP-2 influent
- S2-1: WWTP-2 effluent

Sampling protocol

The samples for PhACs/EDCs were collected monthly for 4 months from all sampling locations except S1-2, where it was collected weekly for 23 weeks to support the toxicity and biological studies. The PBDE samples were collected monthly for 3 months from all three WWTP-1 locations. The alkylphenol and alkylphenol ethoxylate samples were collected S1-2 monthly for 4 months.

The residence time in each process was taken into account so that the same batch of water was sampled along the sampling path. Samples were poured into pre-cleaned, 1L sampling bottles and shipped immediately to the laboratories in ice-packed coolers. The laboratory of MOECC (LaSB) was responsible for all chemical analyses apart from OP, NP and NPEs, which were analyzed at AXYS Laboratories, Surrey, BC.

Target substances

Table 1 is a list of the target substances with their limits of detection (LoDs). Several isotope-labelled substances were used as internal standards, and are italicized and marked with an asterisk (*).

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

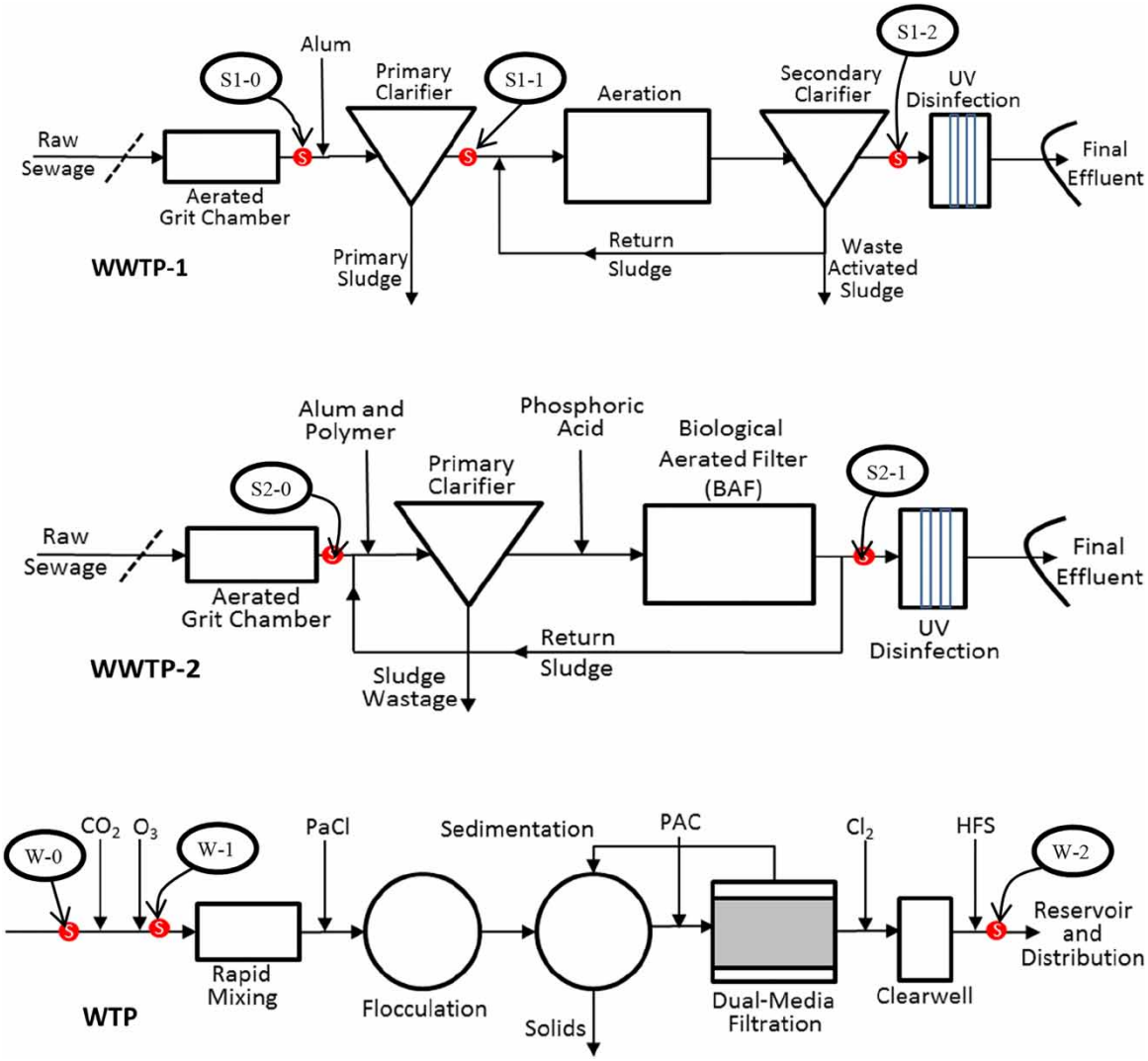

Figure 1 | Schematics of WWTP-1 and WWTP-2, and the WTP, showing the sampling points.

The criteria for choosing the target PhACs/EDCs were their abundance in Detroit River water, as obtained through MOECC monitoring projects and reports in the literature (Metcalfe *et al.* 2003; Hua *et al.* 2006; Lishman *et al.* 2006; Tabe *et al.* 2009; Tabe *et al.* 2010; Kleywegt *et al.* 2011), as well as the availability of analytical methods for their detection at ng/L (PPT) levels.

Chemical analysis and treatment of analytical data

PhACs and EDCs were analyzed using state-of-the art liquid chromatography-tandem mass spectrometry as described in Hao *et al.* (2008). The maximum acceptable range of recovery was set at 100 ± 20%. All compounds were analyzed using two kinds of standards: standard chemical solutions (of known chemical composition) and isotope labelled standards (readily distinguished by mass spectrometry) to verify specific compound concentrations.

All standard solutions and heptafluorobutyric acid (99%) were obtained from Sigma Aldrich (Oakville, Ontario, Canada). Deuterium-labelled surrogates came from CDN-Isotope (Pointe-Claire, Quebec, Canada), except sulfamethazine (phenyl-^{13}C6, 98%) from Cambridge Isotope Laboratories (Andover, MA). Methanol, acetonitrile and sulfuric acid were supplied by Caledon Inc. (Georgetown, Ontario, Canada), ammonium acetate (>99%) by Fluka (Mississauga, Ontario,

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Table 1 | List of targeted substances and associated LoDs

Alkylphenols (APs) and alkylphenol ethoxylates (APEs) and associated LoDs (ng/L)

		LoD			LoD
1	4-Nonylphenol diethoxylates	169	3	4-Nonylphenols	
2	4-Nonylphenol monoethoxylates	61	4	OP	5.6

PBDEs and associated LoDs (ng/L)

1	PBDE-100	0.5	10	PBDE-28	0.09
2	PBDE-119	0.02	11	PBDE-47	3
3	PBDE-126	0.02	12	PBDE-49	0.07
4	PBDE-138	0.07	13	PBDE-66	0.08
5	PBDE-153	0.06	14	PBDE-71	0.07
6	PBDE-154	0.08	15	PBDE-77	0.02
7	PBDE-17	0.03	16	PBDE-85	0.07
8	PBDE-183	0.05	17	PBDE-99	2
9	PBDE-209	4			

PhACs & EDCs and associated LoDs (ng/L)

Analgesic & Painkillers			27	Sulfathiazole	2
1	*Acetaminophen**	2	28	Tetracycline	10
2	*Ibuprofen**	0.5	29	Trimethoprim	1
3	*Indomethacin**	5	**Hormones, ovulation inhibitors, estrogen replacements**		
4	Ketoprofen	2			
5	*Naproxen**	2	30	17-α-Estradiol	5
Antibiotics			31	17-α-Ethynyl Estradiol	5
6	Carbadox	10	32	17-β-Estradiol	2
7	Chloramphenicol	2	33	19-Norethisterone	5
8	Chlorotetracycline	10	34	Diethylstilbestrol	10
9	*Ciprofloxacin**	0.5	35	*Equilin**	2
10	*Diclofenac**	1	36	Estriol	5
11	Doxycycline	5	37	*Estrone**	2
12	Enrofloxacin	5	38	*Progesterone**	20
13	Erythromycin	10	**Lipid regulators, anti-coagulants**		
14	Lasalocid A	10	39	Bezafibrate	1
15	Lincomycin	0.5	40	*Clofibric acid**	0.5
16	Meclocycline	10	41	*Gemfibrozil**	1
17	Norfloxacin	10	42	Warfarin	5
18	Oxytetracycline	5	**Perfluoro surfactants**		
19	Roxithromycin	2	43	PFOA	1
20	Sulfachloropyridazine	5	44	PFOS	0.5
21	Sulfadiazine	5	**EDC**		
22	Sulfadimethoxine	1	45	*Bisphenol A**	2
23	Sulfamerazine	1	**Others (antiepileptic, ionophore)**		
24	*Sulfamethazine**	1	46	*Carbamazepine**	1
25	Sulfamethizole	2	47	Monensin sodium	10
26	*Sulfamethoxazole**	2			

*Indicates use of isotope-labelled substance as internal standard.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Table 2 | Summary of analytical results for occurrence and removal of PhACs in two WWTPs and one WTP in Windsor

Location	Total Analyses	No. of detects	Median Monthly Conc, ng/L	Mean monthly Conc ± SE, ng/L	Mean Removal ± SE
WWTP-1					
S1-0	188	133	212,049	183,000 ± 46,000	
S1-1	188	135	182,951	173,000 ± 38,000	
S1-2	1,081	701	3,638	3,600 ± 100	98% ± 1%
WTP					
W-0	188	85	546	730 ± 290	
W-1	141	58	615	640 ± 100	
W-2	188	72	622	650 ± 170	−8% ± 24%
WWTP-2					
S2-0	188	132	206,876	197,000 ± 14,000	
S2-1	188	121	10,312	10,000 ± 1,000	95.0% ± 0.5%

Canada) and ethylene diamine acetic acid (disodium salt, ACS reagent grade) by BioRad (Mississauga, Ontario, Canada).

Removal efficiencies were determined using Equation (1):

$$R = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

where, R is removal efficiency (%);

C_{in} is the target pollutant concentration entering the process/plant, (ng/L, μg/L, or mg/L); and,

C_{out} is the target pollutant concentration in the process/plant effluent, (ng/L, μg/L, or mg/L).

For compounds with undetectable concentrations, a statistical approach using censored data analysis was used, as recommended by Helsel (2012).

RESULTS AND DISCUSSION

PhACs and EDCs

A summary of results is shown in Table 2. The 188 analytical results shown for S1-0 and S1-1 refer to the 47 substances sampled monthly for 4 months. The 1,081 results shown for S1-2 relate to the 23 weekly sets of samples taken for toxicology tests and also used for chemical analysis. Removal efficiencies were only calculated for paired samples (those relating to the same batch of water). One set of analytical results, including samples taken from W-1 was lost, leaving just 141 analyses for that location. The median and mean overall concentrations shown in Table 2 refer to the total concentrations of all 47 PhACs and EDCs over the sampling period.

Approximately 70% of the analytes in the WWTP influents were detected at least once over the 4-month sampling period. Some substances detected in the influents were removed by treatment to below their LoDs and were thus reported as undetected in the effluents.

After discharge to the surface water, further reductions in target substance concentrations were noted, arising through natural processes like dilution, biodegradation, photo-degradation, adsorption and sedimentation. As a result, fewer substances were detected at the WTP intake than in WWTP-1's effluent discharge a few kilometers downstream. The detection frequency of substances at the WTP intake was also lower than in WWTP-1's effluent and, for the concentrations of those detected were up three orders of magnitude lower. Consequently, target substance concentrations at W-1

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

and W-2 were very low and, in many cases, close to their LoDs. This caused inaccuracies in calculating the WTP's removal efficiency, as reported in Table 2.

The median and mean monthly concentrations of the target PhACs/EDCs at both S1-0 and S2-0 were around 200,000 ng/L (0.2 mg/L). The secondary treatments of both WWTPs successfully removed between 95 and 98% of the total concentrations.

Table 3 categorizes the target PPCPs/EDCs by removal efficiency in the WWTPs and WTP. The categories include:

1. Undetected: substances were not detected in any sample.
2. Negative or Zero: substances whose concentrations were higher or similar in the effluent than in the influent.
3. Low: removal efficiencies between 0 and 50%.
4. Moderate: removal efficiencies between 50 and 75%.
5. High: removal efficiencies between 75 and 95%.
6. Excellent: removal efficiencies exceeding 95%.
7. Inconclusive: removal efficiencies with standard errors spread over three or more categories.

Accordingly, the treatment efficiency of WWTP-1 is higher than that of WWTP-2, as the former removed more substances at moderate to excellent efficiency. The two plants, however, performed similarly towards certain substances. For example, both removed acetaminophen, ibuprofen, estriol, and bisphenol A at high/excellent efficiency, clofibric acid, gemfibrozil, and lasalocid A at low efficiency, and had no impact on carbamazepine or diclofenac. The WTP was only efficient in removing ibuprofen and carbamazepine, and to some extent acetaminophen.

The occurrence and removal information of the ten commonest PhACs/EDCs at different sampling locations is shown in Table 4. The highest concentrations in the raw sewage belonged to the three analgesics; acetaminophen, ibuprofen, and naproxen. These, together, formed 96% and 89% of the total concentration of PhACs/EDCs in the influents of WWTP-1 and WWTP-2, respectively. Acetaminophen alone contributed 87% and 72% of the total concentration of PhACs/EDCs in the WWTP-1 and WWTP-2 influents, respectively. Bisphenol A (BPA) was also a major substance in the influent of WWTP-2, contributing 9% to the PhACs/EDCs concentrations. This may demonstrate the impact of the industrial wastewater load entering WWTP-2.

The high general efficiencies of the WWTPs arose from the $99+\%$ removal of acetaminophen. WWTP-1 also removed $99+\%$ of ibuprofen and naproxen. The removal efficiencies of the latter two substances at WWTP-2 were 88% and 58%, respectively. This could be due to the difference in the treatment trains of the two plants. The removal efficiencies of the WWTPs for substances other than the three analgesics and BPA were low at $42 \pm 7\%$ and $15 \pm 7\%$, respectively. Table 4 also shows the frequency and concentrations of the target substances in transit through the WTP. Only 17-α-estradiol was detected in all 4 sampling events at the WTP intake.

Figure 2 illustrates the concentration variations of the ten commonest substances from the influent of WWTP-1 to the WTP's finished water. The high removal efficiencies for the three analgesics are clear, with 2–3 orders of magnitude reduction in concentration from the influent to the effluent of WWTP-1.

Figure 3 shows the concentration history of the ten commonest substances in the finished drinking water, traced back through the sampling locations in the WWTP and WTP. Nine substances persisted through the water treatment processes—i.e., their concentrations at the WTP intake were not statistically different from those at its discharge. The one exception was sulfadimethoxine, with inconsistent concentrations at all sampling locations leading to inconclusive removal efficiency. The concentrations of some substances were in the vicinity of their LoDs, making it difficult to determine removal efficiencies. However, a general trend suggested that the water treatment processes – including ozonation – were incapable of removing or transforming very low concentrations of these substances.

Table 3 | PhACs and EDCs grouped by removal efficiencies in WWTP-1, WWTP-2, and WTP

Undetected	No/ − ve removal (≤0%)	0–50% Low	50 ± 75% Moderate	75 ± 95% High	95 + % Excellent	Inconclusive
WWTP-1						
Equilin PFOA PFOS	Carbamazepine Chlorotetra- cycline Diclofenac Enrofloxacin Erythromycin Monensin sodium	19-Norethisterone Clofibric acid Diethylstilbestrol Gemfibrozil Lasalocid A Oxytetracycline	17-α-Estradiol 17-β-Estradiol Bezafibrate Ciprofloxacin Sulfamerazine Sulfa-methoxazole Trimethoprim	Bisphenol A Progesterone	Acetaminophen Estriol Estrone Ibuprofen Naproxen Sulfathiazole Sulfamethazine Sulfamethizole Tetracycline Warfarin	17-α-Ethynyl Estradiol Carbadox Chloramphenicol Doxycycline Indomethacin Ketoprofen Lincomycin Meclocycline Norfloxacin Roxithromycin Sulfachloropyridazine Sulfadiazine Sulfa-dimethoxine
WTP						
17-β-Estradiol Carbadox Chloramphenicol Equilin Estrone Indomethacin PFOA Sulfachloro-pyridazine Sulfadiazine	Enrofloxacin Ketoprofen Sulfamethizole Sulfamerazine Sulfathiazole Warfarin	17-α-Estradiol Bezafibrate Chlorotetracycline Diethylstilbestrol Doxycycline Estriol Gemfibrozil Lasalocid A Norfloxacin Oxytetracycline Tetracycline	Acetaminophen	Carbamazepine Ibuprofen	 PFOS Progesterone Roxithromycin Sulfadimethoxine Sulfamethazine Sulfa-methoxazole Trimethoprim	17-α-Ethynyl Estradiol 19-Norethisterone Bisphenol A Ciprofloxacin Clofibric acid Diclofenac Erythromycin Lincomycin Meclocycline Monensin sodium Naproxen

(*Continued.*)

Table 3 | Continued

Undetected	No/ − ve removal (≤0%)	0–50% Low	50 ± 75% Moderate	75 ± 95% High	95 + % Excellent	Inconclusive
WWTP-2						
Diethylstilbestrol	17-α-Estradiol	17-β-Estradiol	Ciprofloxacin	Bisphenol A	Acetaminophen	17-α-Ethynyl Estradiol
Monensin sodium	19-Norethsterone	Bezafibrate	Ketoprofen Naproxen	Estriol		Carbadox
PFOA	Carbamazepine	Chlorotetracycline	Oxytetracycline	Ibuprofen		Chloramphenicol
PFOS	Diclofenac	Clofibric acid				Lincomycin
Sulfamerazine	Doxycycline	Enrofloxacin				Meclocycline
Sulfathiazole	Erythromycin	Equilin Estrone				Progesterone
	Sulfadimethoxine	Gemfibrozil				Roxithromycin
	Sulfamethoxazole	Indomethacin				Sulfachloropyridazine
		Lasalocid A				Sulfamethazine
		Norfloxacin				Sulfamethizole
		Sulfadiazine				Tetracycline
						Trimethoprim
						Warfarin

doi: 10.2166/wpt.2016.035

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Table 4 | The ten commonest PhACs/EDCs at different sampling locations

Substance	LoD (ng/L)	Detection frequency	Min[1] (ng/L)	Max (ng/L)	Median (ng/L)	Mean (ng/L) ± Standard Error	% Removal Efficiency
WWTP-1 Influent							
Acetaminophen	2	4/4	42,264	226,250	180,000	157,000 ± 41,000	100 ± 0
Ibuprofen	0.5	4/4	4,828	16,625	13,625	12,000 ± 3,000	99 ± 0
Naproxen	2	3/4	ND/8,038	9,650	8,100	8,600 ± 500	99 ± 0
Sulfamethoxazole	2	4/4	744	2,188	1,725	1,600 ± 400	55 ± 11
Trimethoprim	1	2/4	ND/901	1,988	1,444	1,400 ± 500	55 ± 8
Bisphenol A	2	4/4	363	2,400	574	1,000 ± 500	82 ± 5
Ciprofloxacin	0.5	4/4	134	1,288	932	800 ± 300	57 ± 27
Norfloxacin	10	3/4	ND/84	1,300	855	750 ± 350	49 ± 34
Carbamazepine	1	4/4	377	533	454	450 ± 40	20 ± 30
Bezafibrate	0.5	4/4	163	600	466	420 ± 90	53 ± 13
WWTP-1 Effluent							
Trimethoprim	1	25/25	134	791	448	460 ± 40	55 ± 8
Carbamazepine	1	23/25	ND/196	838	409	440 ± 30	–7 ± 20
Diclofenac	1	23/25	ND/194	749	451	425 ± 25	–21 ± 17
Sulfamethoxazole	2	25/25	116	841	403	420 ± 30	55 ± 11
Bisphenol A	2	23/25	ND/10	782	318	350 ± 50	82 ± 5
Ciprofloxacin	0.5	25/25	80	343	158	170 ± 20	57 ± 27
Norfloxacin	10	25/25	70	235	161	150 ± 10	49 ± 34
Bezafibrate	0.5	23/25	ND/49	258	140	150 ± 10	53 ± 13
Clofibric acid	1	21/25	ND/3	360	134	130 ± 20	19 ± 9
Enrofloxacin	5	23/25	ND/85	143	115	115± 5	0 ± 18
WTP Intake							
Ciprofloxacin	0.5	2/4	ND/134	238	119	230 ± 160	0 ± 71
Enrofloxacin	5	3/4	ND/111	119	114	90 ± 30	−1 ± 18
Acetaminophen	2	3/4	ND/5	209	11	60 ± 50	72 ± 14
Norfloxacin	10	3/4	ND/39	80	43	40 ± 20	4 ± 2
17-α-Estradiol	5	4/4	9	39	36	30 ± 10	10 ± 8
Chlorotetracycline	10	3/4	ND/17	65	24	30 ± 10	2 ± 1
Meclocycline	10	1/4	ND/101	101	ND	30 ± 20	0 ± NA
Tetracycline	10	3/4	ND/20	57	21	30 ± 10	1 ± 1
Erythromycin	10	2/4	ND/22	50	14	20 ± 10	34 ± 40
Doxycycline	5	3/4	ND/13	38	13	20 ± 10	1 ± 0
WTP Finished Drinking Water							
Ciprofloxacin	0.5	3/4	ND/9.5	476	13	130 ± 120	0 ± 71
Enrofloxacin	5	4/4	110	128	120	120 ± 4	−1 ± 18
Norfloxacin	10	3/4	ND/37	80	41	40 ± 20	4 ± 2
Acetaminophen	2	1/4	ND/124	124	<LoD	30 ± 30	72 ± 14
Meclocycline	10	1/4	ND/101	101	<LoD	30 ± 20	0 ± NA
Chlorotetracycline	10	3/4	ND/16	65	23	30 ± 10	2 ± 1
17-α-Estradiol	5	4/4	6	38	34	30 ± 10	10 ± 8
Tetracycline	10	3/4	ND/19	58	20	30 ± 10	1 ± 1
Indomethacin	5	1/4	ND/94	94	<LoD	30 ± 20	NA
Sulfadimethoxine	1	1/4	ND/75	75	<LoD	20 ± 20	NA

(*Continued.*)

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Table 4 | Continued

Substance	LoD (ng/L)	Detection frequency	Min[1] (ng/L)	Max (ng/L)	Median (ng/L)	Mean (ng/L) ± Standard Error	% Removal Efficiency
WWTP-2 Influent							
Acetaminophen	2	4/4	83,500	178,750	150,625	140,000 ± 20,000	100 ± 0
Ibuprofen	0.5	4/4	14,250	56,500	22,125	29,000 ± 9,000	88 ± 4
Bisphenol A	2	4/4	2,950	43,125	12,150	18,000 ± 9,000	92 ± 4
Naproxen	2	4/4	4,775	7,763	5,400	6,000 ± 700	58 ± 8
Sulfamethoxazole	2	4/4	673	961	755	800 ± 60	−29 ± 10
Trimethoprim	1	4/4	135	1,031	706	600 ± 200	−16 ± 47
Ciprofloxacin	0.5	4/4	186	576	462	420 ± 90	52 ± 8
Diclofenac	1	4/4	243	340	313	300 ± 20	−9 ± 10
Carbamazepine	1	4/4	179	323	269	260 ± 30	−12 ± 5
Bezafibrate	0.5	4/4	226	291	243	250 ± 10	40 ± 12
WWTP-2 Effluent							
Ibuprofen	0.5	4/4	1,030	5,488	2,881	3,000 ± 1,000	88 ± 4
Naproxen	2	4/4	951	3,288	2,881	2,500 ± 500	58 ± 8
Sulfamethoxazole	2	4/4	741	1,325	993	1,000 ± 100	–29 ± 10
Bisphenol A	2	4/4	401	916	599	600 ± 100	92 ± 4
Trimethoprim	1	4/4	330	843	396	500 ± 100	−16 ± 47
Diclofenac	1	4/4	259	399	324	330 ± 30	−9 ± 10
Acetaminophen	2	3/4	ND/129	733	273	300 ± 200	100 ± 0
Carbamazepine	1	4/4	188	394	298	290 ± 50	−12 ± 5
Ciprofloxacin	0.5	4/4	117	323	176	200 ± 50	52 ± 8
Bezafibrate	0.5	4/4	72	265	143	150 ± 40	40 ± 12

[1]If one or more values were non-detect both ND and the minimum detected values are reported.

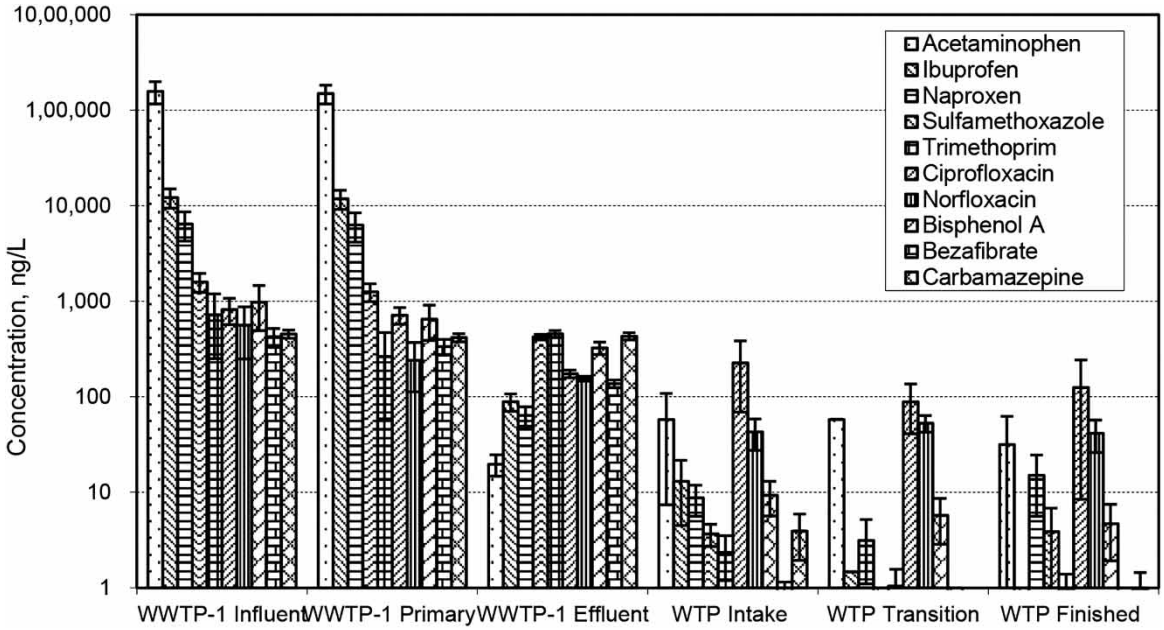

Figure 2 | Variation in concentrations of the ten commonest PPCPs/EDCs from the influent of WWTP-1 through the sampling locations to the drinking water discharge from the WTP.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

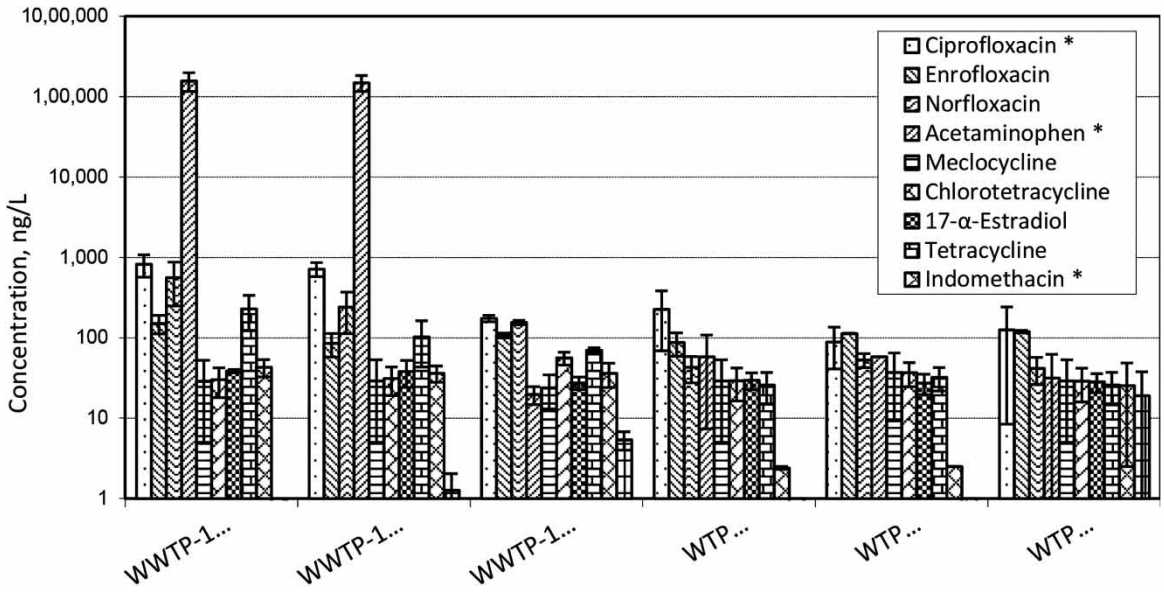

Figure 3 | History of the concentrations of the ten commonest substances detected in the finished drinking water traced back to the influent of WWTP-1.

Of the ten substances, four persisted through both wastewater and water treatment processes, with their average concentrations remaining statistically the same from the influent to the effluent of the WWTP-1 and then from the intake to the finished water in WTP. These four included enrofloxacin, chlortetracycline, 17α-estradiol, and meclocycline. The latter had concentrations in the vicinity of its LoD. The performance of the plants in relation to these substances underlined the relative inefficiency of the treatment processes in removing or transforming certain substances at very low concentrations.

The concentrations of the ten commonest substances in the influent and effluent of WWTP-2 are shown in Figure 4. Comparison of Figures 2 and 4 indicates that nine out of ten substances were common in the influents of both WWTPs. The exceptions are norfloxacin in WWTP-1 which is replaced by diclofenac in WWTP-2. The high concentration of bisphenol A in the influent of

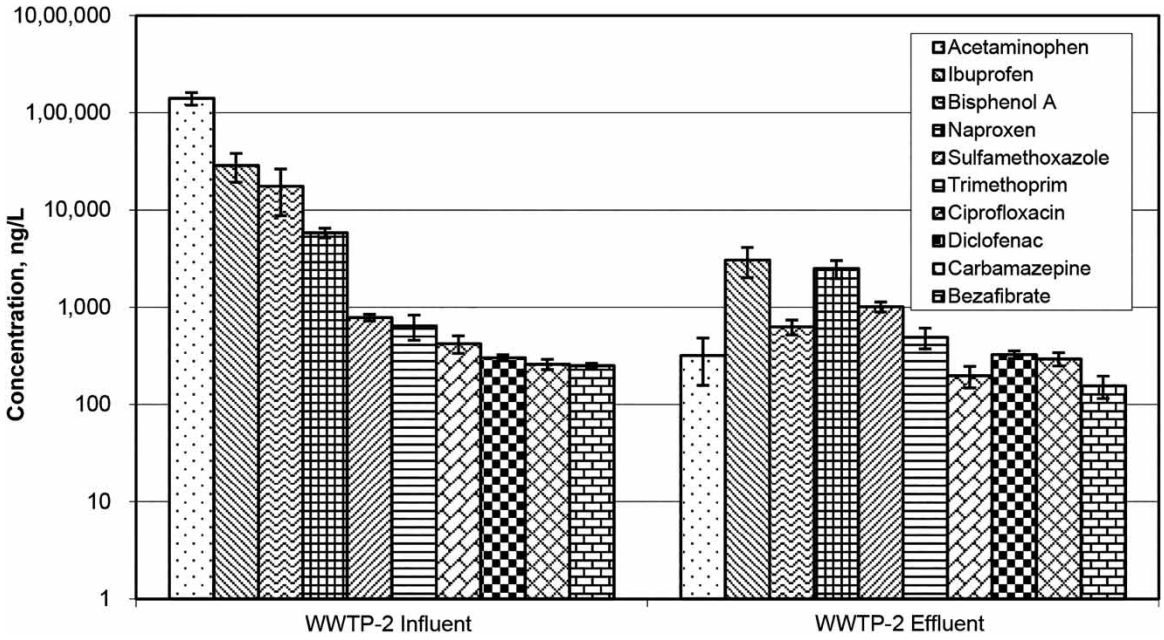

Figure 4 | Concentrations of high occurrence substances in WWTP-2.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

WWTP-2 is probably due to the industrial wastewater influent to this plant. Four of the ten substances – sulfamethoxazole, trimethoprim, diclofenac, and carbamazepine – persisted through the treatment processes, with influent and effluent concentrations statistically the same.

PBDEs

Some 17 PBDE congeners were analyzed. The samples were collected monthly for 3 months. The sub-ng/L to ng/L LoDs enabled detection of all target PBDEs in all samples. Most of the PBDE congeners were present at sub-ng/L levels, much lower than the concentrations of PhACs/EDCs. The results for those with mean concentrations of 1 ng/L or above in the WWTP influents are summarized in Table 5, and Figures 5 and 6.

Table 5 also shows the Canadian Federal Environmental Quality Guideline (FEQGs) levels for the two WWTP effluents (CEPA 2013). FEQGs have been developed in Canada for certain PBDE congeners in water, fish tissue, sediments, wildlife (including birds' eggs), to assess the ecological impacts of PBDEs in the environment. Use of FEQGs is voluntary unless prescribed in permits or other regulatory tools.

Table 5 | Concentrations and removal efficiencies of the top five PBDE congeners in the WWTP influents compared with FEQG recommended levels

Congener	Influent ng/L	Primary ng/L	Effluent ng/L	Removal %	FEQG ng/L
WWTP-1					
PBDE-209	112 ± 22	42 ± 13	5 ± 1	61 ± 12	–
PBDE-99	43 ± 9	26 ± 8	2.8 ± 0.7	42 ± 12	4
PBDE-47	39 ± 8	26 ± 8	4 ± 1	36 ± 13	24
PBDE-100	8 ± 2	5 ± 1	0.7 ± 0.2	38 ± 14	0.2
PBDE-153	4 ± 1	2.4 ± 0.6	0.16 ± 0.04	40 ± 12	120
WWTP-2					
PBDE-209	63 ± 3		9 ± 4	86 ± 5	–
PBDE-99	33 ± 4		3.5 ± 0.1	89 ± 1	4
PBDE-47	31 ± 4		3.3 ± 0.4	89 ± 3	24
PBDE-100	6.5 ± 0.8		0.86 ± 0.09	86 ± 2	0.2
PBDE-153	2.7 ± 0.4		0.15 ± 0.03	94 ± 2	120

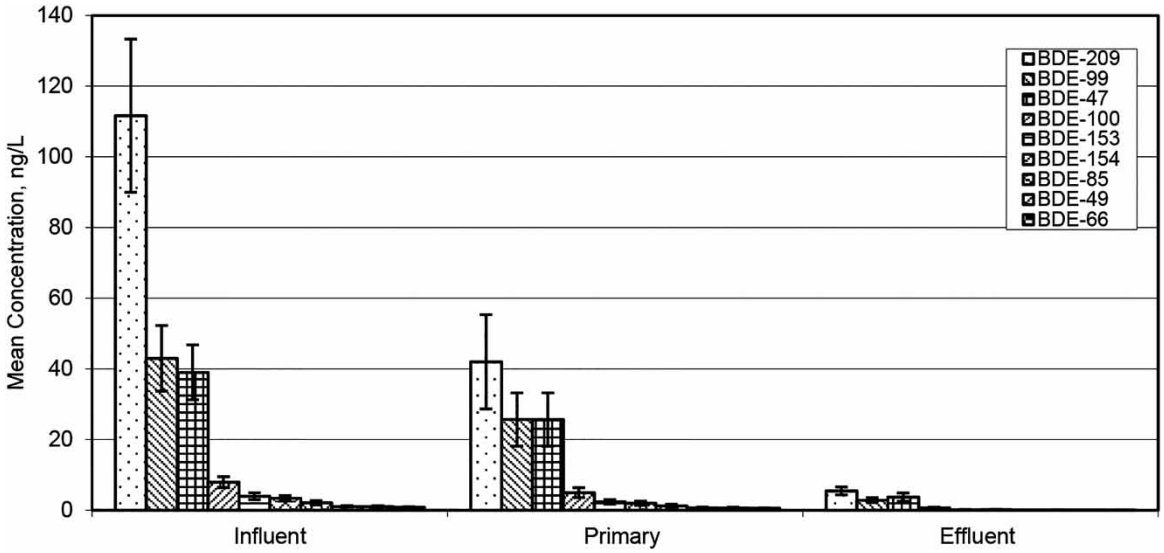

Figure 5 | Occurrence of PBDE congeners at 1 ng/L or more in the influent, and primary and final effluents of WWTP-1.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

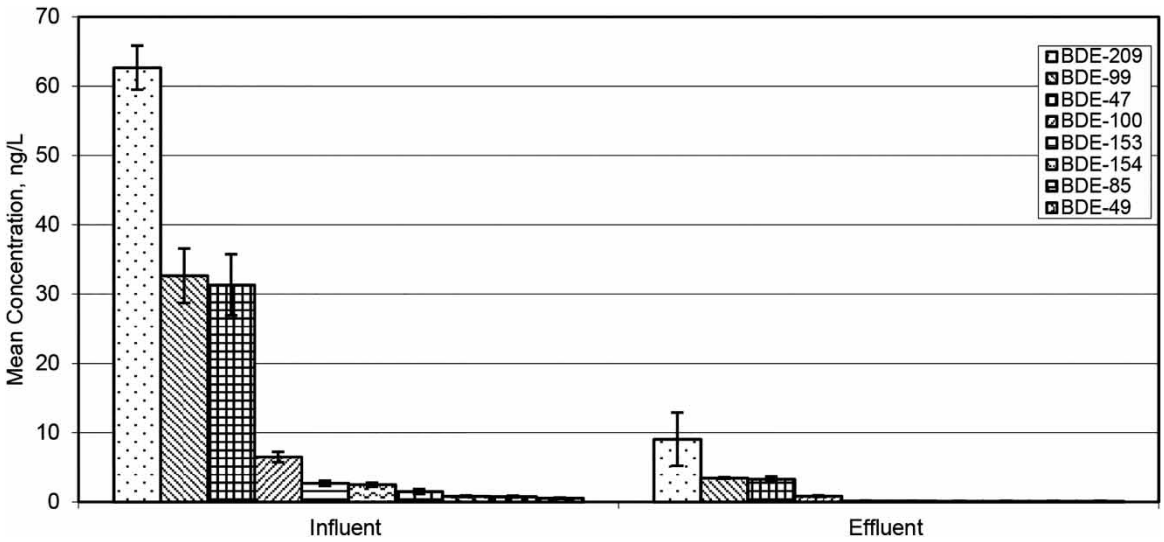

Figure 6 | Occurrence of PBDE congeners at 1 ng/L or more in the influent and final effluent of WWTP-2.

PBDE-209 (deca-brominated diphenyl ether) alone contributed ~50% to the total concentration of PBDEs in the influents of both plants, and, together with PBDE-99 and PBDE-47, comprised ~90% of all PBDEs. The primary treatment at WWTP-1 removed almost half of all influent PBDEs, while the secondary treatment effectively reduced the concentration to ~7% of the influent. The relatively high removal efficiency of the primary treatment could arise from the hydrophobic nature of these substances and their high-log K_{OW}, which increased their tendency to adsorb onto and be removed with suspended solids. PBDE-209 showed the highest removal efficiency from the primary effluent at 61%, with others in the vicinity of 40%.

The final concentrations of the target congeners in the plant effluents were in the range of sub- and a few ng/L. PBDE-100 exceeded the FEQGs values in both plants and PBDE-99 at WWTP-1. However, dilution in the Detroit River is expected to bring both concentrations below the guidelines.

Table 6 groups the target congeners according to the WWTPs' removal efficiencies. They removed approximately three quarters of the congeners at high or excellent efficiencies.

Table 6 | Summary of removal efficiencies of PBDEs in WWTP-1 and WWTP-2

No Detection	No/ − ve removal (≤ 0%)	0–50% Low	50 ± 75% Moderate	75 + %–95% High	95 + % Excellent	Inconcl-usive
WWTP-1						
		PBDE-17	PBDE-126	PBDE-28	PBDE-85	
		PBDE-71		PBDE-47	PBDE-153	
		PBDE-77		PBDE-49		
				PBDE-66	PBDE-119	PBDE-183
				PBDE-99	PBDE-138	PBDE-209
				PBDE-100	PBDE-154	
WWTP-2						
		PBDE-77	PBDE-17	PBDE-47		
			PBDE-28	PBDE-49		
			PBDE-71	PBDE-66		
			PBDE-126	PBDE-85	PBDE-119	PBDE-154
				PBDE-99	PBDE-138	PBDE-183
				PBDE-100	PBDE-153	PBDE-209

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Table 7 | Concentrations and LoDs of NP, NPEs, and OP at sampling point S1-2

	OP, ng/L		4-nonlyphenol, ng/L		4-nonylphenol mono-ethoxylates, ng/L		4-nonylphenol diethoxylates, ng/L		
Sampling Event	LoD	Conc.	LoD	Conc.	LoD	Conc.	LoD	Conc.	Surrogate recovery
1	1.3	ND	5.36	282	4.67	51.9	10.2	60.3	76.4%
2	1.77	ND	7.97	268	7.18	72.2	8.86	110	73.8%
3	1.82	16.1	5.92	225	8.27	28.5	15.2	74.0	77.0%
Mean ± SE	NA		258 ± 17		51 ± 13		81 ± 15		

Alkylphenols and alkylphenol ethoxylates

The group included OP, 4-nonylphenol, 4-nonylphenol mono-ethoxylates, and 4-nonylphenol diethoxylates. The two ethoxylates include different isomers. Also, $^{13}C_6$-4-n-nonylphenol was used as an isotope-labelled surrogate.

Three sets of monthly samples, collected at S1-2, were analyzed for these substances, and the results are reported in Table 7. The most prevalent substance was 4-nonylphenol, contributing approximately 2/3 of the total content of NPEs. Because samples were not collected at S1-0, the plant's removal efficiency for NPEs is unknown.

SUMMARY AND CONCLUSIONS

TrOC occurrences were studied over 4 months at two WWTPs and one WTP in Windsor, Ontario, Canada. The concentration reduction efficiencies of the existing treatment processes in reducing TrOC concentrations were estimated.

Three analgesics – acetaminophen, ibuprofen, and naproxen – were predominant among the 47 PhACs/EDCs studied. Bisphenol A was also detected at quite high concentrations in WWTP-2, which treats mixed industrial and residential wastewaters. Large proportions of these four chemical species were removed in treatment. The removal efficiencies for most other PhACs/EDCs were low.

Thus, although the WWTPs are not designed to remove PhACs/EDCs, a number of them are removed together with other contaminants.

The concentrations of PhACs/EDCs at the WTP intake were low and, sometimes, close to their LoDs. This made calculation of plant removal efficiencies inaccurate.

Three pharmaceuticals – enrofloxacin, chlorotetracycline, and 17-α estradiol – persisted through both the water and wastewater treatment processes. That is, their concentrations at the influent of the WWTP-1 were statistically similar to that at the effluent, and the concentrations at the intake of the WTP were statistically similar to those in the finished drinking water.

REFERENCES

Andreozzi, R., Raffaele, M. & Nicklas, P. 2003 Pharmaceuticals in WWTP effluents and their solar photodegradation in aquatic environment. *Chemosphere* **50**, 1319–1330.

Boxall, A. B. A., Kolpin, D. W., Halling-Sorensen, B. & Tolls, J. 2003 Are veterinary medicines causing environmental risks? *Environ Sci. Technol* **37** (15), 286a–294a.

CEPA 2013 *Federal Environmental Quality Guidelines (FEQGs) for Polybrominated Diphenyl Ethers (PBDEs).* Environment Canada. http://www.ec.gc.ca/ese-ees/05DF7A37-60FF-403F-BB37-OCC697DBD9A3/FEQG_PBDE_EN.pdf.

Galus, M., Jeyaranjaan, J., Smith, E., Li, H., Metcalfe, C. & Wilson, J. Y. 2013 Chronic effects of exposure to a pharmaceutical mixture and municipal wastewater in zebrafish. *Aquat. Toxicol.* **132–133**, 212–222.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Hao, C., Zhao, X., Tabe, S. & Yang, P. 2008 Optimization of a multi-residual method for the determination of waterborne emerging organic pollutants using solid phase extraction and liquid chromatography/tandem mass spectrometry and isotope dilution mass spectrometry. *Environ. Sci. Technol.* **42**, 4068–4075.

Harley, K., Marks, A., Chevrier, J., Bradman, A., Sjödin, A. & Eskenazi, B. 2010 PBDE concentrations in women's serum and fecundability. *Environ. Health Perspect.* **118** (5), 699–704.

Heberer, T. 2002 Tracking pharmaceutical residues from municipal sewage to drinking water. *J. Hydrol.*, **266** (3–4), 175–189.

Heberer, T., Redderson, K. & Mechlinski, A. 2002 From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas. *Water Sci. Technol.* **46** (3), 81–88.

Helsel, D. R. 2012 *Statistics for Censored Environmental Data Using Minitab and R*. 2nd edn. John Wiley and Sons, New York.

Hua, W. Y., Bennett, E. R. & Letcher, R. J. 2006 Ozone treatment and the depletion of detectable pharmaceuticals and atrazine herbicide in drinking water sourced from the upper Detroit River, Ontario, Canada. *Water Res.* **40** (12), 2259–2266.

Jobling, S., Nolan, M., Tyler, C. R., Brighty, G. & Sumpter, J. P. 1998 Widespread sexual disruption in wild fish. *Environ. Sci. Technol.* **32**, 2498–2506.

Jobling, S., Burn, R. W., Thorpe, K., Williams, R. & Tyler, C. 2009 Statistical modeling suggests that antiandrogens in effluents from wastewater treatment works contribute to widespread sexual disruption in fish living in English rivers. *Environ. Health Perspect.* **117** (5), 797–802.

Jones, O. A. H., Voulvoulis, N. & Lester, J. N. 2004 Potential ecological and human health risks associated with the presence of pharmaceutically active compounds in the aquatic environment. *Crit. Rev. Toxicol.* **34** (4), 335–350.

Kleywegt, S., Pileggi, V., Yang, P., Hao, C., Zhao, X., Rocks, C., Thach, S., Cheung, P. & Whitehead, B. 2011 Pharmaceutical substances, hormones and bisphenol A in untreated source and finished drinking water in Ontario, Canada–occurrence and treatment efficiency. *Sci. Total Environ.* **409**, 1481–1488.

Kochukov, Y., Jeng, J. & Watson, S. 2009 Alkylphenol xenoestrogens with varying carbon chain lengths differentially and potently activate signaling and functional responses in GH3/B6/F10 somatomammotropes. *Environ. Health Perspect.* **117** (5), 723–730.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B. & Buxton, H. T. 2002 Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: a national reconnaissance. *Environ. Sci. Technol.* **36** (6), 1202–1211.

Laville, N., Aït-Aïssa, S., Gomez, E., Casellas, C. & Porcher, J. M. 2004 Effects of human pharmaceuticals on cytotoxicity, EROD activity and ROS production in fish hepatocytes. *Toxicology* **196**, 41–55.

Lishman, L., Smyth, S. A., Sarafin, K., Kleywegt, S., Toito, J., Peart, T., Lee, B., Servos, M., Bland, M. & Seto, P. 2006 Occurrence and reduction of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada. *Sci. Total Environ.* **367**, 544–558.

Metcalfe, C. D., Miao, X.-S., Koenig, B. G. & Struger, J. 2003 Distribution of acidic and neutral drugs in surface waters near sewage treatment plants in the Lower Great Lakes, Canada. *Environ Toxicol. Chem.* **22**, 2881–2889.

Richardson, S. D. 2003 Disinfection by-products and other emerging contaminants in drinking water. *Trends Analyt. Chem.* **22**, 666–684.

Sanderson, H., Johnson, D. J., Reitsma, T., Brain, R. A., Wilson, C. J. & Solomon, K. R. 2004 Ranking and prioritization of environmental risks of pharmaceuticals in surface waters. *Regul. Toxicol. Pharmacol.* **39**, 158–183.

Sedlak, D., Pinkston, K. & Huang, C.-H. 2005 Occurrence survey of pharmaceutically active compounds. Water Research Foundation (formerly American Water Works Association Research Foundation) Report #91051.

Singh, S., Seth, R. & Tabe, S. 2015 Oxidation of emerging contaminants during pilot-scale ozonation of municipal effluent. *Ozone Sci. Eng.* **37**, 1–7.

Snyder, S., Vanderford, B., Pearson, R. & Rexing, D. 2002 Analytical methods for measuring endocrine disruptors in water. In *Presented at the AWWA Water Quality Technology Conference*, Seattle, WA, November 10–14.

Snyder, S., Wert, E. C., Lei, H., Westerhoff, P. & Yoon, Y. 2007 Removal of EDCs and pharmaceuticals in drinking and reuse treatment processes. Water Research Foundation (formerly American Water Works Association Research Foundation) Report #91188.

Stackelberg, P. E., Furlong, E. T., Meyer, M. T., Zaugg, S. D., Henderson, A. K. & Reissman, D. B. 2004 Persistence of pharmaceutical compounds and other organic wastewater contaminants in a conventional drinking water treatment plant. *Sci. Total Environ.*, **329** (1–3), 99–113.

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 Report #3071.

Tabe, S., Yang, P., Zhao, X., Hao, C., Seth, R., Schweitzer, L. & Jamal, T. 2010 Occurrence and removal of PPCPs and EDCs in the Detroit River watershed. *J. Water Pract. Technol.* **5** (1), 1–8.

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

Tetreault, G. R., Bennett, C. J., Shires, K., Knight, B., Servos, M. R. & McMaster, M. E. 2011 Intersex and reproductive impairment of wild fish exposed to multiple municipal wastewater discharges. *Aquat. Toxicol.* **104**, 278–290.

USEPA 2010 http://www.epa.gov/oppt/existingchemicals/pubs/actionplans/RIN2070-ZA09_NP-NPEs%20Action%20Plan_Final_2010-08-09.pdf, last visited June 2015.

Uslu, M., Seth, R., Jasim, S., Tabe, S. & Biswas, N. 2015 Reaction kinetics of ozone with pharmaceutical products in the Great Lakes basin and their potential removal from wastewater effluents. *Ozone Sci. Eng.* **37**, 36–44.

Water Practice & Technology Vol 11 No 2
doi: 10.2166/wpt.2016.035

Vanderford, B. J., Drewes, J. E., Hoppe-Jones, C., Eaton, A., Haghani, A., Guo, Y., Snyder, S., Ternes, T. & Schluesener, M. 2012 Evaluation of analytical methods for EDCs and PPCPs via interlaboratory comparison. Water Research Foundation (formerly American Water Works Association Research Foundation) Report #4167.

Westergaard, K., Muller, A. K., Christensen, S., Bloem, J. & Sorensen, S. J. 2001 Effects of tylosin as a disturbance on the soil microbial community. *Soil Biol. Biochem.* **33** (15), 2061–2071.

Weyer, P. & Riley, D. 2001 *Endocrine disruptors and pharmaceuticals in drinking water*. American Waterworks Association Research Foundation Report, Denver, Colorado, 2001.

Yang, P., Hao, C., Zhao, X. & Tabe, S. 2008 Optimization of a multi-residual method for the determination of waterborne emerging organic pollutants using solid phase extraction and liquid chromatography/tandem mass spectrometry and isotope dilution mass spectrometry. *Environ. Sci. Technol.* **42**, 4068–4075.

Young, W. F., Whitehouse, P., Johnson, I. & Sorokin, N. 2002 Proposed no-effect-concentrations (PNECs) for natural and synthetic steroid oestrogens in surface waters. R&D Technical Report P2-TO4/1'; Bristol UK: Environment Agency.