



Removal of selected pharmaceuticals, personal care products and artificial sweetener in an aerated sewage lagoon



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HIGHLIGHTS

- Removals of PPCPs and an artificial sweetener in a sewage lagoon are presented.
- Predicted values obtained from lagoon modeling generally agreed well with measured concentrations.
- Lagoon was as effective at removing target compounds as many conventional WWTPs.
- Seasonal variations were observed, and optimal removals occurred during summer.

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ABSTRACT

A sewage lagoon serving the small municipality of Lakefield in Ontario, Canada was monitored in the summer, fall and winter to determine removals of carbamazepine, trimethoprim, sulfamethoxazole, ibuprofen, gemfibrozil, triclosan, sucralose, HHCb and AHTN. Concentrations of these compounds in untreated and treated wastewater were estimated by deploying POCIS and SPMD passive samplers in the sewage lagoon. Passive samplers were also deployed at several points upstream and downstream of the point of discharge from the lagoon into the Otonabee River. LC–MS/MS and GC–MS were utilized to determine the concentrations of pharmaceuticals and personal care products (PPCPs) and sucralose, an artificial sweetener. Among PPCPs sampled by POCIS, the highest estimated concentration in untreated wastewater was ibuprofen sampled during the fall, at an estimated concentration of 60.3 ng/L. The estimated average concentration of sucralose was 13.6 ng/L in the untreated wastewaters. Triclosan, HHCb and AHTN in SPMDs were highest during fall season, at 30, 1677 and 109 ng/L, respectively. For all compounds except gemfibrozil, carbamazepine and sucralose, removals were highest in the summer (83.0 to 98.8%) relative to removals in the fall (48.4 to 91.4%) and winter (14.0 to 78.3%). Finally, the estimated concentrations of carbamazepine, sulfamethoxazole, triclosan and HHCb were compared with predicted values obtained through application of the WEST® modeling tool, with a new model based on the River Water Quality Model No. 1 and extended with dynamic mass balances describing the fate of chemicals of emerging concern subject to a variety of removal pathways. The model was able to adequately predict the fate of these four compounds in the lagoon in summer and winter, but the model overestimated removals of three of the four test compounds in the fall sampling period. This lagoon was as effective at removing PPCPs as many conventional WWTPs, but removals were better during the summer.

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1. Introduction

Municipal wastewater treatment plants (WWTPs) are point sources for the discharge of contaminants of emerging concern into surface waters. The literature indicates that conventional wastewater treatment processes remove some pharmaceuticals, personal care products and endocrine disrupting chemicals, but other compounds from these classes of “down the drain” chemicals are not effectively removed

(Carballa et al., 2004; Jones et al., 2005; Miège et al., 2009; Monteiro and Boxall, 2010; Verlicchi et al., 2012). Advanced oxidation processes, especially ozonation and UV photolysis are effective at degrading a number of the contaminants of emerging concern that are in wastewater (Zwiener and Frimmel, 2000; Androozzi et al., 2003; Ternes et al., 2003; Huber et al., 2005; McDowell et al., 2005; Nakada et al., 2007; Rodayan et al., 2010; Nasuhoglu et al., 2011). However, small municipalities in North America usually do not have the resources to install and operate advanced oxidation technologies, or even conventional wastewater treatments systems. Many of these small municipalities use sewage lagoons as treatment systems for municipal wastewater.

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According to a report published in 2004, there were 868 sewage lagoons located in Canadian municipalities (Federation of Canadian Municipalities, 2004), but these numbers may have changed substantially in the past 10 years.

Lagoon-based sewage treatment systems are pond-like water bodies or basins that receive, hold and treat the wastewater. These systems are widely used in small communities because of their simplicity and because they are inexpensive to install, operate and maintain. Treatment processes in the basin are complex, involving a combination of physical, chemical and biological processes that include sedimentation, bioflocculation, precipitation, biochemical oxidation, photolysis, volatilization, fermentation and disinfection. The design parameters for a lagoon are dependent on the lagoon type. For example, in aerated lagoons, sewage retention times are typically 7–20 days (Federation of Canadian Municipalities, 2004).

There is some evidence that sewage lagoons are effective at removing contaminants of emerging concern from wastewater (Camacho-Muñoz et al., 2012; Carlson et al., 2013; Conkle et al., 2008; Li et al., 2013; MacLeod and Wong, 2010; Metcalfe et al., 2003; Ying et al., 2009). However, there have been no studies conducted to date to fully evaluate the removals of microcontaminants by lagoons; especially in the winter months when microbial activity may be low and the duration and intensity of sunlight is reduced. Also, there have been few attempts to predict the fate of microcontaminants in lagoons using predictive models.

The objective of this study was to determine the removals of selected pharmaceuticals and personal care products (PPCPs) and an artificial sweetener, sucralose in a sewage lagoon serving the municipality of Lakefield, Ontario, Canada during 3 different seasons, summer, fall and winter, and observe their presence and persistence in the receiving waters of the Otonabee River upstream and downstream of the lagoon discharge. Also, modeling studies were performed, and model predictions were compared with the measured concentrations of PPCPs and sucralose.

Most of the previous studies on removal of PPCPs in sewage lagoons were conducted using either grab or composite samples (Camacho-Muñoz et al., 2012; Carlson et al., 2013; Conkle et al., 2008; Li et al., 2013; Ying et al., 2009). Because of the rapid temporal changes in the concentrations of PPCPs in wastewater, it is difficult to estimate removals of chemicals using data from “grab” samples or even composite samples (Ort et al., 2010). These sampling methods provide information on the instantaneous concentrations of the target analytes, which may be misleading if there are spikes in concentrations throughout the day, week or month. Therefore, passive samplers, the Polar Organic Chemical Integrated Sampler (POCIS) for polar contaminants and the Semipermeable Membrane Device (SPMD) for non-polar contaminants were used to estimate time weighted average concentrations of the target compounds over a 2 week deployment period. The disadvantages of passive sampling include the requirement for data on chemical sampling rates (R_S) to estimate the concentration of analytes in water. In addition, sampling rates are influenced by temperature, flow and biofouling. To date, there are sampling rates in the literature for only a limited number of compounds. R_S values for the analytes were determined in laboratory experiments and were calculated according to the relationship shown in Eq. (1),

$$R_S = [(C_0 - C_t) / C_0] \times (V/d) \quad (1)$$

where, C_0 , C_t , V and d are initial (spiked with analyte) concentration in water, measured (remaining) concentration after POCIS or SPMD exposure, volume of water (L) and exposure time in day (d).

Passive samplers are usually deployed to accumulate contaminants of emerging concern to high ng or low μg amounts over the deployment period. Then, data on the R_S (L/day) for the target compounds in POCIS (Li et al., 2010) and in SPMDs (Helm et al., 2012) are used to estimate concentrations in wastewater (i.e., ng/L) integrated over the deployment

period. In this study, the estimates of time weighted average concentrations were used to determine how effective the sewage lagoon was at removing PPCPs and sucralose at different seasons, and to evaluate whether these compounds persist in the river downstream of the discharge. Later, measured values were compared with modeling data.

A large number of PPCPs have been detected in both untreated and treated wastewater and could be considered for this research. However, in order to minimize analytical effort and cost, while monitoring a series of compounds that will provide valuable information on the various mechanisms of removal, we analyzed nine “indicator compounds” that are typically detected in wastewater and for which the processes governing their fate in the aquatic environment are reasonably well understood, including five pharmaceuticals, carbamazepine, sulfamethoxazole, trimethoprim, gemfibrozil and ibuprofen, an artificial sweetener, sucralose and the personal care product, triclosan and two synthetic musk compounds, HHCB (Galaxolide, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- γ -2-benzopyran) and AHTN (Tonalide, 6-Acetyl-1,1,2,4,4,7-hexamethyltetraline). Several of these indicator compounds were selected according to the criteria identified by (Dickenson et al., 2011) in a study that illustrated the value of monitoring a small number of PPCPs in wastewater treatment facilities in the U.S. Sucralose is widely used artificial sweetener in North America and has been detected in drinking water systems in the USA and wastewaters in Europe and because of its persistence and ubiquitous presence, has been proposed as a tracer of wastewater contaminants in drinking water samples and surface waters (Lange et al., 2012; Mawhinney et al., 2011; Oppenheimer et al., 2011). The advantage of using these indicator compounds is that they are almost always detected in untreated and treated wastewater, and they show variations in removals by microbial, oxidative and photolytic processes, as well as by partitioning to sediments or air that provide an indication of the most important removal processes within the lagoon.

2. Materials and methods

2.1. Chemicals and materials

The pharmaceuticals, sucralose and their labeled surrogates were purchased from Sigma-Aldrich (St. Louis, MO, USA) and C/D/N Isotopes (Pointe-Claire, QC, Canada). HHCB and AHTN were purchased from LGC Promochem GmbH (Wesel, Germany) and triclosan was purchased from Sigma-Aldrich. Triclosan- $^{13}\text{C}_{12}$ was obtained from Cambridge Isotopes (Andover, MA, USA) and AHTN-d7 was purchased from C/D/N Isotopes. All stock solutions were made in methanol and stored in the refrigerator (4 °C) until required. Working standard solutions were prepared from stock solutions through serial dilution.

High purity acetic acid, methanol and acetone were obtained from Fisher Scientific (Ottawa, Ontario, Canada). The POCIS samplers were purchased from Environmental Sampling Technologies (St. Joseph, MO, USA). The SPMDs were prepared from layflat polyethylene tubing containing triolein, as described previously (Helm et al., 2012). The triolein in the SPMDs was spiked with performance reference compounds (PRCs) that were used to refine the R_S that varies according to the temperature and flow rates in the water and biofouling (Huckins et al., 2002). The PRCs included fluorene-d10, PCB congener 14 (3,5-dichlorobiphenyl) and PCB congener 32 (2,4',6-trichlorobiphenyl).

2.2. Sampling sites

The passive samplers were placed in stainless steel sampling cages with capacity to accommodate three POCIS and three SPMD passive samplers; so each cage gave triplicate measurements. The sampling cages were deployed in the sewage lagoon and in the river in July (summer) and October (fall) of 2010 and in March (winter) of 2011. Sampling was done at the sewage lagoon serving the village of Lakefield (population approximately 2600) in Ontario, Canada by deploying the passive samplers for 2 weeks at three locations. The Lakefield sewage

lagoon, located at latitude 44.0° received about 15.2–14.5 h of sunlight in July and 10.2–9.7 h of sunlight in late October. Raw sewage is collected at the sewage pump house where alum is added to the flow and then, sewage is pumped (around 1 km) to the aerated lagoon.

The sewage lagoon is split into south and north ponds that operate in series. The south pond has an approximate area of 52,000 m², an approximate depth of 3 m and retention time of about 8 weeks, and it is aerated for treatment of the sewage. The north pond, which is a settling pond that operates only under ice-free condition has an approximate area of 55,000 m², an approximate depth of 2 m and retention time of about 6 weeks. When the north pond is frozen over, the wastewater is taken directly from the distal end of the south pond and is disinfected by UV-irradiation before discharge into the river.

PPCPs were monitored at various locations in the sewage lagoon and in the river. As shown in Figs. 1 and 2, for the summer and fall samples, one sampling cage was placed in the south pond next to the raw sewage influent pipe (i.e., L1) to measure the initial concentrations of chemicals entering the sewage lagoon. Another cage was placed at the other end of the south pond, at the cross over point to the north pond (L2). The last sampling cage was placed at the outflow box in the north pond (L3), which leads to the discharge point in the river. In the winter, samplers were placed at L1, and at points before UV-disinfection (i.e., pre-UV) and after UV-disinfection (post-UV).

Treated sewage enters the Otonabee River through a diffusion grate located on the riverbed in the middle of the river. A reference site (R1) was located upstream of the sewage outflow grate, above the Lakefield

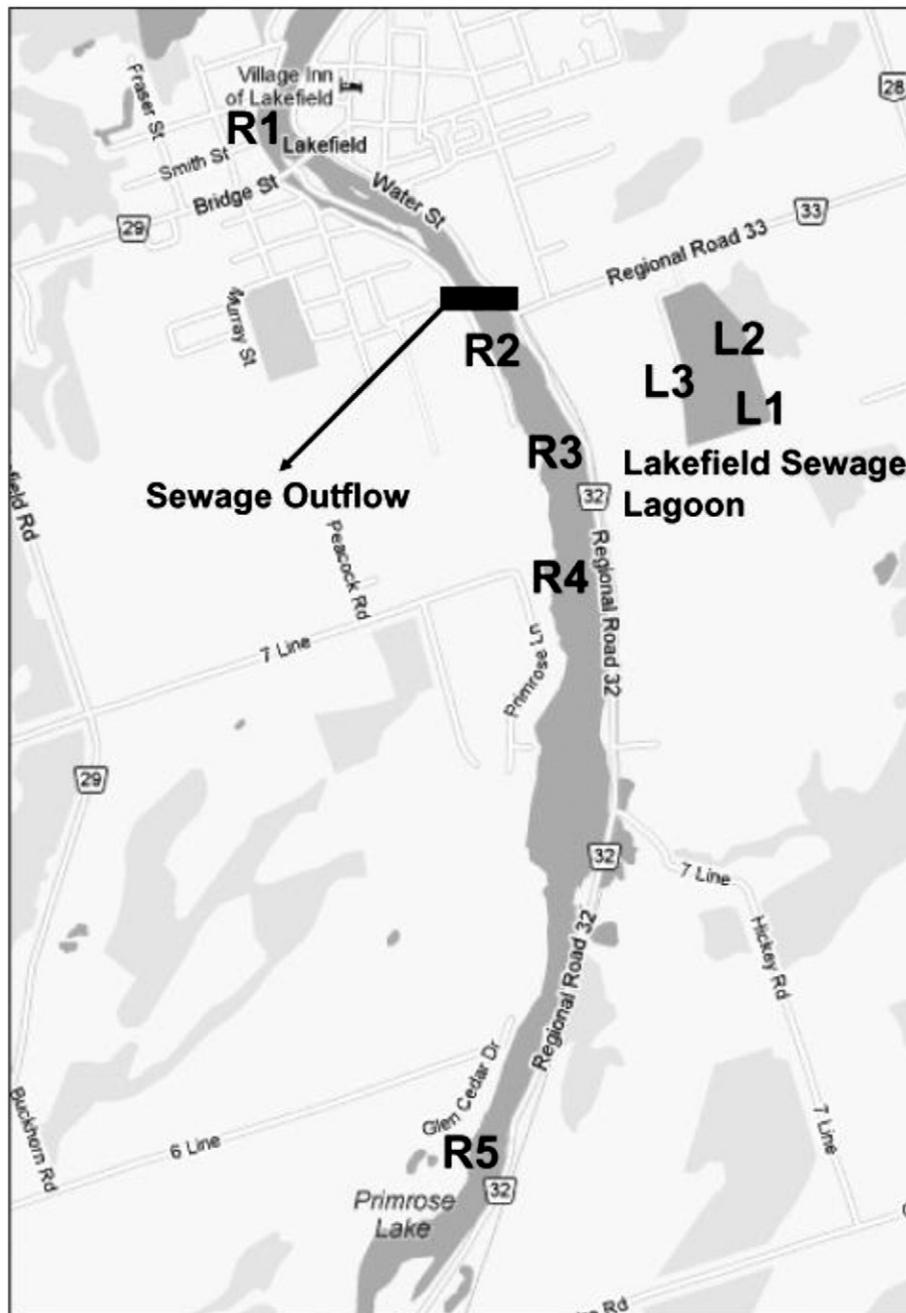


Fig. 1. Map showing the sampling sites at the Lakefield sewage lagoon and the Otonabee River in Ontario, Canada (source: Google Map). L1, L2 and L3 sites at raw sewage inflow (influent), aerated sewage and treated sewage outflow pipe (final effluent), respectively. R1 at Otonabee River reference site upstream of the sewage outflow grate. R2, R3, R4 and R5 sampling sites at increasing distances downstream of outflow grate.

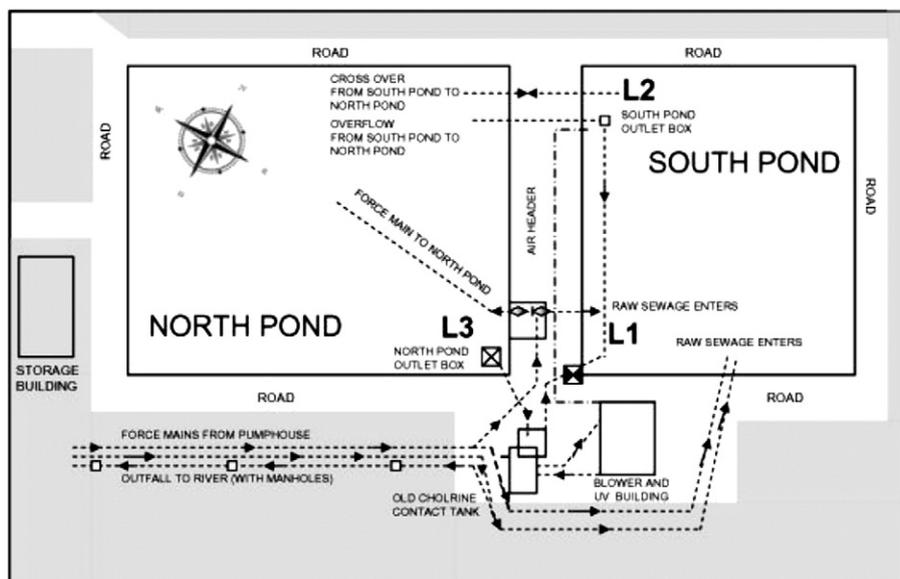


Fig. 2. Schematic of Lakefield sewage lagoon (source: Lakefield Water and Wastewater, Lakefield, Ontario, Canada). L1, L2 and L3 sites at raw sewage inflow (influent), aerated sewage and treated sewage outflow pipe (final effluent), respectively.

dam. Four downstream sampling points (R2, R3, R4 and R5) at increasing distances from the discharge (approximately 30, 173, 308 and 1760 m, respectively) were monitored in the summer (Fig. 1), and three downstream sampling points (R2, R3 and R4) were monitored in the fall. The sampling points were located in the middle of the river at depths roughly 0.5 m below the surface. The passive samplers were set up for 4 weeks in the Otonabee River, as compared to 2 weeks in the Lakefield sewage lagoon. During retrieval of samplers, the POCIS were removed from the cages and wrapped in aluminum foil, and the SPMDs were removed and stored in amber glass jars. Samplers collected in the field were placed in a cooler with ice packs. Upon returning to the lab, all samples were frozen for storage. POCIS and SPMD field blanks were exposed to the air during deployment and collection.

2.3. Sample preparation

Extraction from POCIS samplers was performed in the lab according to the procedures described elsewhere (Li et al., 2010). Briefly, frozen samplers were removed from storage and allowed to thaw, then rinsed with water to remove debris and biofouling materials. Using a spatula, the sorbent in the POCIS was transferred to a glass chromatography column (1 cm ID \times 30 cm length) packed to 1/3 full with solvent-washed granular Na_2SO_4 . A 0.1 mL mixture of an internal standard (500 ng/mL) containing the stable isotope labeled surrogates of the analytes was then added to the column. Elution from the column was performed with 100 mL methanol. The eluate was collected and then evaporated in a rotary evaporator to a volume of \sim 1 mL. Final evaporation to 0.1 mL was conducted using a vacuum centrifuge evaporator, and then the samples were made up to their final volume (0.4 mL) with methanol.

SPMD samples were prepared according to the procedure published elsewhere by (O'Toole and Metcalfe, 2006; Helm et al., 2012). Briefly, the SPMD was cleaned and then dialyzed into hexane for total of 24 h (i.e., first dialysis for 18 h and second dialysis for 6 h). Labeled surrogates were added to the extract at this point. Co-extractives in the hexane extract were then removed by gel permeation chromatography (GPC) using BioBeads S-X3 (BioRad Laboratories, Mississauga, Ontario, Canada) with a mobile phase of hexane and ethyl acetate (1:1, v/v). The eluate was split into two aliquots. One aliquot was solvent exchanged into hexane for analysis of the synthetic musks and PRCs

(i.e., Aliquot A) and the other aliquot was exchanged into methanol for analysis of triclosan (i.e., Aliquot B). Aliquot A was further fractionated by silica gel column chromatography as described by O'Toole and Metcalfe (2006) to yield Fraction 1 containing the PCB congeners 14 and 32 (i.e., PRCs) and Fraction 2 containing fluorene-d10 (i.e., PRC) and the synthetic musks, HHCB and AHTN. These fractions were solvent exchanged into iso-octane (0.150 mL final volume) prior to analysis by GC-MS.

2.4. LC-MS and GC-MS analysis

The pharmaceuticals and triclosan were analyzed by liquid chromatography and tandem mass spectrometry (LC-MS/MS) with an electrospray ionization (ESI) source using an API 3000 instrument purchased from Applied Biosystems Sciex (Concord, Ontario, Canada). This system was equipped with a Series 200 autosampler from Perkin Elmer (Waltham, MA, USA), and pumps (LC-10AD), degasser (DGU-14A) and system controller (SCL-10A) from Shimadzu (Columbia, MD, USA). For the analysis of the pharmaceuticals accumulated in the POCIS (carbamazepine, sulfamethoxazole, trimethoprim, gemfibrozil and ibuprofen), the LC-MS/MS was run in double polarity mode by positive and negative voltage switching, similar to the method described elsewhere (Miao and Metcalfe, 2003). For analysis of triclosan accumulated in the SPMDs, LC-MS/MS analysis was conducted separately in negative ion mode. Sucralose was analyzed in negative ion mode using an AB Sciex Q-Trap 5500 instrument with a turbospray ionization source. This system was equipped with an Agilent 1100 series (Mississauga, ON, Canada) LC systems. Analytes were separated chromatographically using a Genesis C18 column of 150 mm long, 2.1 mm ID and 4 μm particle size (Chromatography Specialties Inc., Brockville, Ontario, Canada) with a guard column (Genesis C18, 10 \times 2.1 mm and 4 μm). The LC mobile phases in gradient elution were (A) water (100%) with 0.1% acetic acid and (B) acetonitrile (100%) with 0.1% acetic acid. MS detection was performed using multiple reaction monitoring. The mass transitions for analytes and corresponding labeled analytes are listed in Table 1. For quantification, an internal standard method with a five-point calibration graph covering the range of anticipated analyte concentration in the samples, using a weighted (1/concentration) linear regression. The purpose of using internal standards (labeled compounds) for calculation was to correct analyte recovery and matrix

Table 1

Ions monitored for analysis of target compounds and their stable isotope surrogates by LC–MS/MS (Multiple Reaction Monitoring) and GC–MS (Selected Ion Monitoring).

Compounds LC–MS/MS	Mass transition (m/z)
Carbamazepine	237.1/194.0
Carbamazepine-d10	247.0/204.1
Sulfamethoxazole	254.1/156.0
Sulfamethoxazole- ¹³ C ₆	260.0/162.0
Trimethoprim	291.1/123.2
Trimethoprim- ¹³ C ₃	294.1/126.2
Gemfibrozil	249.1/121.0
Gemfibrozil-d6	255.0/121.0
Ibuprofen	205.0/161.0
Ibuprofen- ¹³ C ₃	208.0/163.0
Sucralose	395.0/35.0
Sucralose-d6	403.0/35.0
Triclosan	287.0/35.0
Triclosan- ¹³ C ₁₂	299.0/35.0
GC–MS	
HHCB	243
AHTN	243
AHTN-d3	246
PCB-32	256
PCB-14	222
Fluorene-d10	176

LODs and LOQs for PPCPs and sucralose were between 0.1 to 2 and 0.3 to 5 ng/L, respectively, and for AHTN and HHCB, were 1.5 and 4, and 1 and 3 ng/L, respectively.

effects. The limits of detection (LOD) and limits of quantitation (LOQ) were calculated as the analyte concentrations that produced peaks with signal-to-noise ratio of 3 and 10, respectively (Table 1).

The synthetic musks (HHCB, AHTN and AHTN-d3) and the PRC compounds were analyzed with a GC–MS purchased from Agilent Technologies (Mississauga, Ontario, Canada) consisting of a Model 3800 GC and a Model 4000 Ion Trap MS. The GC–MS method using electron impact (EI) ionization was similar to the method described by Yang and Metcalfe (2006). MS detection was performed using selected ion monitoring (SIM) for the ions listed in Table 1. Chromatographic separation was performed using a 30 m VF5 capillary column (0.25 mm ID). The injector, transfer line and ion trap temperatures were 275 °C, 250 °C and 200 °C, respectively. The temperature program for the column oven consisted of an initial hold for 1.5 min. at 50 °C, then an increase to 150 °C at 10 °C/min, then to 190 °C at 2 °C/min, and finally to 290 °C at 100 °C/min, where the temperature was held for 4 min.

2.5. Estimation of concentrations in water and wastewater

The estimated concentrations of the pharmaceuticals accumulated in POCIS were calculated using the R_S previously determined in laboratory experiments at 5, 15 and 25 °C (Li et al., 2010). The R_S for POCIS appears to vary relatively little with temperature, as less than a 2 fold change in R_S was previously observed over a temperature range from 5 °C to 25 °C (Li et al., 2010). The R_S of sucralose (i.e., 0.156 L/day at 25 °C) was determined following static exposure technique previously described by Li et al. (2010). The concentrations of the personal care products accumulated in SPMDs were calculated using the R_S determined in laboratory experiments at 5, 15 and 25 °C (Helm et al., 2012) and adjusted according to the loss of PRCs from the SPMDs over the time of deployment. PRCs were used to adjust the SPMD data because this passive sampling device is particularly susceptible to variations in R_S as a result of variations in temperature, flow rates and biofouling (Huckins et al., 2002).

Rates of elimination of the PRCs (i.e., h^{-1}) from the SPMDs were determined in laboratory experiments at 25 °C (i.e., $k_{ePRC-cal}$) as -0.0053 , -0.0019 and -0.0003 for fluorine-d10, PCB14 and PCB32, respectively. As described by Huckins et al. (2002) the exposure adjustment factor (EAF) was calculated for each PRC by comparing the rate of elimination

determined in the field ($k_{ePRC-field}$) with the rate of elimination determined in the laboratory, according to Eq. (2).

$$EAF = k_{ePRC-field} / k_{ePRC-cal} \quad (2)$$

Then, the concentrations of the analytes in water (ng/L) were estimated for each target compound using Eq. (3),

$$\frac{\text{Amount of analyte in SPMD (ng)} \times EAF}{R_S \times d} \quad (3)$$

where, ng, R_S , d and EAF are extracted amount of analyte from SPMD, sampling rate in L/day, total deployment days of SPMD and exposure adjustment factor, respectively. The EAF was calculated for the PRC that showed elimination over the time of deployment of between 40 and 70%, and in all cases, this was PCB32.

The non-parametric Mann–Whitney U test (two-tailed) was used to test for the significance of differences in the concentrations of each of the analytes between raw influent and final effluent of Lakefield sewage lagoon. Statistical analyses were conducted at a level of significance of 0.001 using SYSTAT (2004) version 11 software for Windows (Richmond, CA, USA).

2.6. Lagoon modeling

Modeling and fate simulations were done using the modeling and simulation software, WEST® (www.mikebydhi.com) which allows the user to represent the dynamics and fate of pollution in different wastewater unit processes (Vanhooen et al., 2003). Using this tool, a lagoon model was developed to assess the efficacy of removals of emerging contaminants within existing treatment trains, with a particular emphasis on the effects of Canadian cold climate and seasonal conditions. Dynamic mass balances for the different pollutants and organisms were derived from the River Water Quality Model No. 1 (RWQM1) and its extension for pesticides, called RWQM1GC (De Schepper et al., 2012). Also included are dynamic mass balances for algae, as described in the original RWQM1 (Reichert et al., 2000).

The lagoon was modeled as a series of four continuously stirred tank reactors (CSTRs), with two representing the aerated south pond and the other two representing the stabilization north pond. In each reactor two homogenous compartments were included: the bulk water and the sediment. Diffusion, sedimentation and resuspension occur between the two compartments, depending on the conditions of the lagoons. For instance, it was predicted for the aeration lagoon that no sedimentation occurs while it is being mechanically aerated, and resuspension is driven by the mechanical aeration and the sheer stress at the bottom of the lagoon. For simplicity the lagoons were assumed to be rectangular and the volume constant. A UV disinfection unit was added to replace the north pond during the winter months. It was assumed that the UV unit was operational from December 1 to April 30, which corresponds to the last day of the simulation.

In both compartments the fate of traditional wastewater pollutants and of four of the emerging contaminants was modeled. Volatilization and photolysis were only modeled in the bulk water, while sorption and biodegradation were modeled in both water and sediment compartments. Four compounds (i.e., carbamazepine, sulfamethoxazole, triclosan and HHCB) were studied with the lagoon model, based on the availability of the physicochemical parameters required to run the model. Traditional pollutants were first calibrated as sorption, biodegradation and photolysis are all affected by their behavior. Then, physicochemical properties of the compounds (i.e., aerobic, anoxic and photolytic half-lives, partition coefficient, Henry's constant) were collected from the literature and used as initial estimates for model calibration. Table 2 shows the calibrated property values used for each contaminant (Carballa et al., 2008; Ternes et al., 2004; US-EPA, 2008).

Table 2
Calibrated physicochemical properties of the selected emerging contaminants.

	Log (K_{OC})	Aerobic	Anoxic	Molecular weight	Henry's constant	Photolysis half-life
		half-life	half-life			
		Days	Days	g/mol	$\text{Pa} \cdot \text{m}^3/\text{mol}$	Days
Carbamazepine	3.48	>100	>100	236.27	1.094 E-5	82
Sulfamethoxazole	3.47	>100	>100	253.28	6.515 E-8	0.392
Triclosan	3.96	18	>100	289.54	1.520 E-2	0.0285
HHCB	4.20	8.7	>100	258.40	36.9	8.6

K_{OC} = Octanol–carbon partition co-efficient.

To create the dynamic input to the model of the lagoon it was important to come up with a realistic dynamic evolution of its pollutants over a whole year. Since no actual data were available, the input file was based on days 215 to 609 of the Benchmark Simulation Model 2 influent file, where components are based on the Activated Sludge Model No. 1 (Nopens et al., 2010). Those data were converted to a RWQM1GC format and rescaled so that the monthly average biological oxygen demand (BOD), total suspended solids (TSS), total Kjeldahl nitrogen (TKN), phosphorus, flow rate and temperature were similar to the values measured at the Lakefield sewage lagoon. The irradiance from the sun was modeled as a sinusoidal function, with a mean value of 200 W/m^2 and amplitude of 150 W/m^2 . The aeration was controlled so that the dissolved oxygen concentration remained close to 2 mg/L in the two units representing the south (i.e. aeration) pond. The initial concentrations of the state variables were determined by running a steady-state simulation under summer conditions, such that the dynamic simulation started on June 1st.

3. Results and discussion

3.1. LC–MS and GC–MS method

The purpose of using double polarity mode in LC–MS/MS was to simultaneously analyze the pharmaceuticals extracted from POCIS in a single run. Carbamazepine, sulfamethoxazole and trimethoprim eluted during the first monitoring interval in positive mode, and gemfibrozil and ibuprofen eluted during the second monitoring interval in negative mode. The total LC run time was 16 min, with the first 9 min run in positive mode and the latter 7 min run in negative mode. Sucralose was analyzed separately in negative polarity LC–MS/MS with an LC run time of 19 min. Triclosan accumulated in the SPMDs was analyzed by LC–MS/MS with a chromatographic retention time of 9 min and MS/MS monitoring in negative mode. For the GC–MS analysis of musks (i.e., HHCB and AHTN), the total run time was 37 min.

3.2. Sampling rates

Li et al. (2010) studied the effect of water temperature on R_S of POCIS between 5 and 25 °C and found an increase of R_S (L/day) with

temperature (Li et al., 2010). However, the increase in R_S with temperature was found to be less than 2 fold over this wide temperature range. Similarly, it was reported that R_S in POCIS varied only slightly over a wide range of hydrological flow rates (Li et al., 2010).

Wastewater entering the Lakefield sewage lagoon generally has temperature of 15 to 25 °C. The treated wastewater exiting the north pond of the lagoon has a temperature of 0 to 5 °C in the winter months, 15 to 27 °C in the summer months and 4 to 20 °C in the fall (Lakefield Sewage Lagoon Report, 2011). The average temperature in the Otonabee River in the fall is generally around 10 to 15 °C, and in the summer, it is generally 20 to 25 °C (Peterborough Utility Commission Report, 2008). Using higher R_S (i.e., at 25 °C) or lower R_S (i.e., at 5 °C) to calculate the estimated concentration had only a modest effect on the estimated concentrations of the target compounds.

In this study, the R_S values for PPCPs used to estimate the concentrations were all based on laboratory experiments at three different temperatures (5, 15 and 15 °C). For the summer and fall, R_S at 25 °C and 15 °C was used for the influent and effluent, respectively, and for the winter, rates at 15 °C and 5 °C were used for the influent and effluent, respectively. For sucralose, a R_S value at 25 °C was utilized for calculation. In contrast, R_S in SPMDs can vary by several orders of magnitude under varying conditions of temperature, flow and biofouling (Huckins et al., 2002). Therefore, PRCs were used to adjust the R_S (i.e., R_S at 15 °C) to compensate for variations in conditions.

3.3. Indicator compounds in the sewage lagoon and river

In the Lakefield sewage lagoon, all target compounds were detected at L1, L2 and L3 during the sampling periods. The mean estimated concentrations of pharmaceuticals and sucralose accumulated in POCIS of the sewage lagoon are listed in Table 3 and the mean estimated concentrations of personal care products accumulated in SPMDs of the lagoon are listed in Table 4. Among the pharmaceuticals accumulated in the POCIS, carbamazepine and ibuprofen were detected at the highest estimated concentrations of 22.6 ng/L and 60.3 ng/L, respectively in the influent (L1) during the fall sampling period (Table 3). Ibuprofen levels may have spiked in the fall as a result of increased use for treatment of the common cold. Sucralose was consistently present at all sites within the Lakefield sewage lagoon over all three seasons. The estimated

Table 3
Estimated mean concentrations of indicator compounds (POCIS) in Lakefield sewage lagoon during the summer, fall and winter sampling periods. Final effluents that show statistically significant (Mann Whitney U test; $p = 0.001$) differences in mean concentrations from the raw influent are indicated by an asterisk (*).

Compounds	Summer			Fall			Winter		
	L1 (raw influent) (ng/L)	L2 (aerated sewage) (ng/L)	L3 (final effluent) (ng/L)	L1 (raw influent) (ng/L)	L2 (aerated sewage) (ng/L)	L3 (final effluent) (ng/L)	L1 (raw influent) (ng/L)	Pre-UV (ng/L)	Post-UV (ng/L)
Carbamazepine	4.15 ± 0.90	4.85 ± 1.23	4.54 ± 0.51	22.6 ± 19.1	13.2 ± 0.21	12.3 ± 0.46*	7.37 ± 0.30	10.5 ± 0.17	11.4 ± 0.19*
Sulfamethoxazole	3.53 ± 0.03	0.58 ± 0.23	0.04 ± 0.01*	3.35 ± 0.14	1.81 ± 0.11	0.74 ± 0.11*	3.91 ± 0.87	0.73 ± 0.25	1.19 ± 0.28*
Trimethoprim	3.66 ± 0.70	1.11 ± 1.05	1.07 ± 0.25*	5.21 ± 1.19	10.5 ± 2.07	2.69 ± 0.34	9.72 ± 0.40	9.81 ± 1.27	8.36 ± 0.46
Gemfibrozil	0.06 ± 0.01	0.16 ± 0.00	0.08 ± 0.02	0.10 ± 0.01	0.14 ± 0.00	0.14 ± 0.00	0.02 ± 0.00	0.05 ± 0.00	0.04 ± 0.00
Ibuprofen	7.54 ± 0.48	1.62 ± 0.40	0.64 ± 0.05*	60.3 ± 8.05	51.3 ± 5.07	11.4 ± 0.40*	4.38 ± 0.61	0.44 ± 0.02	0.95 ± 0.03*
Sucralose	18.2 ± 0.85	30.8 ± 5.02	35.2 ± 4.47*	11.5 ± 1.05	29.5 ± 1.78	47.8 ± 5.36*	11.1 ± 5.76	18.3 ± 0.07	18.2 ± 2.90

L1, L2 and L3 sites at raw sewage inflow (influent), aerated sewage and treated sewage outflow pipe (final effluent). Pre-UV = Before UV treatment. Post-UV = After UV treatment. For mean concentrations, $n = 3$; ±SD.

effluent concentrations for sucralose varied from 18.2 to 47.8 ng/L (Table 3). Estimated concentrations in the final effluents for carbamazepine in summer, trimethoprim in fall and winter, gemfibrozil in summer, fall and winter, and sucralose in winter were not significantly different from the mean concentrations of these compounds in raw influents (Table 3). This indicates that these compounds were not removed efficiently by lagoon treatment, as discussed in Section 3.4.

Among the personal care products accumulated in the SPMDs, triclosan, HHCB and AHTN were detected in all samples collected during the summer, fall and winter (Table 4). The lowest and highest estimated concentrations of triclosan at L1 were 0.83 ng/L in the winter and 30.1 ng/L in the fall, respectively. HHCB and AHTN concentrations at L1 ranged from a low in winter of 492 and 32.9 ng/L, respectively and a high in the fall of 1677 ng/L and 109 ng/L, respectively. Except for AHTN in the fall and triclosan in winter, there were statistically significantly lower mean estimated concentrations of the target analytes in the treated effluent relative to mean estimated concentrations in the raw influents (Table 4). The ratios of the concentrations of HHCB and AHTN ranged from 5 to 32, and the highest ratio (i.e., 32) was found in the effluent (L3) during the winter sampling period. In a previous study of these compounds in wastewater in a conventional WWTP in Peterborough, Ontario, Canada, the ratios of HHCB to AHTN varied from 2.7 to 5.6 in samples collected at various stages of treatment (Yang and Metcalfe, 2006). The reported ratios of HHCB to AHTN in untreated and treated wastewater from several WWTPs in Ontario, Canada were always <3 (Lee et al., 2003).

In the Otonabee River, only carbamazepine was detected in the POCIS at all sites during both summer and fall sampling periods (Table 5). The estimated mean concentration of carbamazepine was lowest at the R1 site, upstream of the sewage discharge. These data indicate that there is a source of this persistent pharmaceutical compound that is upstream of the lagoon discharge. The Otonabee River at Lakefield is located downstream of a number of recreational lakes. The areas around these lakes are heavily populated with seasonal and year round homes with septic tanks. It is possible that these septic systems are the source of the compounds detected in the river at the site upstream of the lagoon discharge (i.e., R1). Sucralose was not monitored in the Otonabee River. However, a recent study conducted in US drinking water treatment plants showed that sucralose was present in source waters known to be impacted by wastewater discharges at concentrations ranging from 47 to 2900 ng/L (Mawhinney et al., 2011).

No triclosan was detected in the SPMDs deployed in the river over both summer and fall sampling periods. However, HHCB and AHTN

were detected in SPMDs placed in the river, yielding estimated mean concentrations ranging from 0.09 to 0.99 ng/L and 0.01 to 0.18 ng/L, respectively (Table 6). The presence of carbamazepine, HHCB and AHTN in passive samplers at distances as much as ~2 km downstream of the discharge point was probably due to the relative persistence of these compounds. During the sampling periods, the Otonabee River received approximately 1,314,000 L/day (July 2010), 867,000 L/day (October 2010) and 1,720,000 L/day (March 2011) of effluent (i.e., effluent flow rate) from the Lakefield sewage lagoon (Lakefield Sewage Lagoon Report, 2011). The daily average water flow rate in Otonabee River (i.e., river flow rate) at Lakefield over these periods were 6.0×10^9 L/day (July 2010), 7.0×10^9 L/day (October 2010) and 1.0×10^{10} L/day (March 2011) (Trent Severn Waterway Report, 2011). Using these flow rates, it was calculated that the dilution factors (i.e., river flow rate/effluent flow rate) for effluent in the river were between 4400 and 7800. Therefore, the lagoon effluent makes up a minor part of the Otonabee River flow. This could be a reason why the concentrations of the target compounds were either low or these compounds not detected (Al Aukidy et al., 2012). Dispersion of effluent in the river is likely, but it should be noted that temperature differences may cause a density gradient that could keep the plume intact for a considerable distance from the discharge point. In some rivers, WWTP effluents contribute a high percentage to the total river flow. For example, the flow of the Hoje River located in Sweden decreases significantly in the summer months, and during this time, WWTP effluents frequently composed of >75% of the river flow (Bendz et al., 2005).

3.4. Removals in the Lakefield sewage lagoon

In Ontario, Canada, there are large seasonal differences in air and water temperature and the duration and intensity of sunlight that could affect the rates of removal of contaminants from wastewater. Table 7 shows the percent removal of the PPCPs monitored in this study, and the statistical significance of the differences in mean estimated concentrations between raw influent and final effluents. For carbamazepine in the summer sampling period, the estimated concentration of that anti-epileptic drug did not change consistently between the sewage influent and the final effluent sampling site (Table 7). Also, there was a negative removal of carbamazepine observed during the winter season, as the estimated influent concentration was 7.37 ng/L and the estimated effluent concentration was higher, at 11.4 ng/L. In a previous study of three conventional activated sludge wastewater treatment plants (WWTPs), the average removal of

Table 4

Adjusted estimated mean concentrations^a of indicator compounds accumulated in SPMDs deployed in the Lakefield sewage lagoon during the summer, fall and winter sampling periods. Final effluents that show statistically significant (Mann Whitney *U* test; $p = 0.001$) differences in adjusted mean concentrations from the raw influent are indicated by an asterisk (*).

Compounds	L1 (raw influent)	L2 (aerated sewage)	L3 (final effluent)
<i>Summer</i>			
EAF (PCB-32)	2.39	3.23	3.37
Triclosan (ng/L) _{Corrected}	10.3 ± 0.98	6.17 ± 0.32	0.29 ± 0.15*
HHCB (ng/L) _{Corrected}	1068 ± 64.06	133.4 ± 17.11	43.1 ± 5.71*
AHTN (ng/L) _{Corrected}	46.7 ± 2.99	21.1 ± 1.62	7.96 ± 0.38*
<i>Fall</i>			
EAF (PCB-32)	7.53	8.42	9.50
Triclosan (ng/L) _{Corrected}	30.1 ± 5.49	11.1 ± 3.36	2.58 ± 0.65*
HHCB (ng/L) _{Corrected}	1677 ± 216.2	365.6 ± 27.55	209.0 ± 226.8*
AHTN (ng/L) _{Corrected}	109 ± 46.6	40.4 ± 24.5	29.1 ± 39.9
<i>Winter</i>			
EAF (PCB-32)	2.62	3.20	2.70
Triclosan (ng/L) _{Corrected}	0.83 ± 0.39	2.45 ± 1.70	0.48 ± 0.44
HHCB (ng/L) _{Corrected}	492.2 ± 56.84	157.3 ± 24.12	291.4 ± 26.39*
AHTN (ng/L) _{Corrected}	32.9 ± 0.63	16.7 ± 6.47	9.19 ± 1.75*

EAF was used to adjust for variations in R_s as a result of temperature, flows and biofouling. L1, L2 and L3 sites at raw sewage inflow (influent), aerated sewage and treated sewage outflow pipe (final effluent).

^a Corrected by EAF (based on PCB-32); $n = 3$; ±SD. Corrected concentration = concentration × EAF.

Table 5

Estimated mean concentrations of indicator compounds accumulated in POCIS deployed in the Otonabee River during the summer and fall sampling periods.

Compounds	Summer					Fall			
	R1 (ng/L)	R2 (ng/L)	R3 (ng/L)	R4 (ng/L)	R5 (ng/L)	R1 (ng/L)	R2 (ng/L)	R3 (ng/L)	R4 (ng/L)
Carbamazepine	0.11 ± 0.01	0.15 ± 0.02	0.17 ± 0.01	0.12 ± 0.00	0.12 ± 0.01	0.18 ± 0.06	0.23 ± 0.13	0.31 ± 0.01	0.31 ± 0.07
Sulfamethoxazole	ND								
Trimethoprim	ND								
Gemfibrozil	ND								
Ibuprofen	ND								
Sucralose	NM								

R1 = Otonabee River reference site upstream of the sewage outflow grate. R2, R3, R4 and R5 sampling sites at increasing distances downstream of outflow gate. R5 was not sampled in the fall. ND = not detected. NM = not monitored. For mean concentrations, n = 3; ± SD.

carbamazepine was found to be less than 25% (Jelic et al., 2011), while Bendz et al. (2005) measured a 30% reduction in a WWTP that also used activated sludge (Bendz et al., 2005). Essentially no removal of carbamazepine was observed in a WWTP, although there were changes in the relative amounts of the metabolites of carbamazepine throughout the treatment stream (Miao et al., 2005). Kasprzyk-Hordern et al. (2009) reported that the concentration of carbamazepine was higher in the effluent than that of the influent of an activated sludge WWTP due to poor biodegradability and hydrolysis of carbamazepine from a glucuronide conjugate. The studied sewage lagoon reduced the estimated concentration of carbamazepine by 43.6% in the fall sampling period (Table 7), but it is difficult to speculate on the reason for the more effective removal at this time. Adsorption onto sludge (i.e., biosolid) is not an important removal process for carbamazepine, which is consistent with its low sorption coefficient, K_d of 1.2 L/kg_{ss} (Ternes et al., 2004; Miao et al., 2005; Zhang et al., 2008). Photocatalytic degradation could be a pathway for removal of carbamazepine (Dai et al., 2012).

The removal efficiencies for ibuprofen in the summer, fall and winter sampling periods were 91.5%, 81.1% and 78.3%, respectively (Table 7). A review of 6 articles documented an average removal rate of 90% for ibuprofen (Bendz et al., 2005). Another review found that out of 44 studies at WWTPs, the average removal for ibuprofen was 69% (Oulton et al., 2010). Thus, the removals of ibuprofen in the Lakefield lagoon are similar to removals of this compound reported for conventional WWTPs. The seasonal trend for ibuprofen in the Lakefield lagoon is consistent with the trend for all PPCPs in the lagoon, showing removals declining in the order of summer > fall > winter (Table 7). No seasonal trends for removals of a number of pharmaceuticals, including ibuprofen at a WWTP in Windsor, Ontario, Canada were found (Hua et al., 2006). However, for the study by Hua et al. (2006) the fall sampling period was performed in September, while the fall sampling in the present study was done in late October when the weather would be expected to be colder and the days shorter. It was reported that removals of ibuprofen at a WWTP reduce during the winter, and

it was speculated that this was due to lower temperatures reducing the microbial degradation rates (Vieno et al., 2005).

Removals of sulfamethoxazole were 98.8%, 78.1% and 69.6% in the summer, fall and winter season, respectively (Table 7). Trimethoprim underwent a significant 70.8% reduction in the summer. While removals of trimethoprim were calculated as 48.4% and 14.0% in the fall and winter, respectively (Table 7), the estimated mean concentrations were not significantly different. Sulfamethoxazole estimated concentrations in raw influents were significantly higher than estimated concentrations in the effluents. The antibiotics, sulfamethoxazole and trimethoprim are both considered to be moderately persistent in wastewater treatment plants (Bendz et al., 2005). However, 91% reductions in the concentration of sulfamethoxazole was observed in a non-conventional lagoon and wetland treatment system in Louisiana, USA (Conkle et al., 2008). Sulfamethoxazole is known to be susceptible to photodegradation, which could explain the reduced removals of sulfamethoxazole in winter because of shorter and less intense exposure to sunlight (Andreozzi et al., 2003; Ryan et al., 2011). The rates may also have been affected by the closure of the north settling pond in winter. The other antibiotic, trimethoprim might also be affected by photodegradation. It was reported that direct and indirect photolysis contributed to the degradation of trimethoprim in wastewater treatment ponds and allowing wastewater to undergo photolysis in settling lagoons helped to reduce the concentrations of some pharmaceuticals (Ryan et al., 2011). In contrast, it was observed that trimethoprim was relatively persistent in a conventional WWTP, with less than a 30% reduction in concentration (Jelic et al., 2011).

During the three sampling periods, the mean concentrations of gemfibrozil in treated wastewater were not significantly different from the untreated wastewater entering the Lakefield sewage lagoon. It was suggested that glucuronide conjugates formed during human metabolism of drugs might be cleaved as these conjugates pass through wastewater treatments, thereby increasing the concentration of the parent compound in the treated wastewater (Ternes, 1998). It has

Table 6Adjusted estimated mean concentrations^a of indicator compounds accumulated in SPMDs deployed in the Otonabee River during the summer and fall sampling periods.

Compounds	Summer				
	R1	R2	R3	R4	R5
EAF (PCB-32)	2.50	3.54	2.33	4.43	3.99
HHCB (ng/L) _{Corrected}	0.20 ± 0.02	0.53 ± 0.15	0.33 ± 0.15	0.67 ± 0.41	0.47 ± 0.04
AHTN (ng/L) _{Corrected}	0.04 ± 0.02	0.09 ± 0.06	0.03 ± 0.01	0.05 ± 0.03	0.05 ± 0.01
<i>Fall</i>					
EAF (PCB-32)	^b	3.15	3.99	1.10	^c
HHCB (ng/L) _{Corrected}	NA	0.87 ± 0.49	0.99 ± 0.48	0.09 ± 0.05	^c
AHTN (ng/L) _{Corrected}	NA	0.09 ± 0.04	0.18 ± 0.07	0.01 ± 0.00	^c

EAF was used to adjust for variations in R_5 as a result of temperature, flows and biofouling. However, EAF values were not available for the fall sampling.

^a Corrected by EAF (based on PCB-32); n = 3; ± SD. Corrected concentration = concentration × EAF. R1 = Otonabee River control (site at upstream of the sewage outflow grate). R2, R3, R4 and R5 sampling sites at increasing distances of downstream outflow gate.

^b EAF value not determined.

^c R5 not sampled in the fall. NA = not applicable.

Table 7

Removal of the indicator compounds and conventional wastewater quality parameters. Removals that show statistically significant differences between raw influent and final effluent are indicated with an asterisk (*).

Compounds/parameters	Summer	Fall	Winter
	% Removal	% Removal	% Removal
BOD ^a	98.8	99.2	96.4
SS ^a	98.7	97.3	87.5
P ^a	98.3	98.9	92.8
N ^a	96.5	98.9	58.9
Carbamazepine	-9.28	45.8*	-54.1*
Sulfamethoxazole	98.9*	78.1*	69.5*
Trimethoprim	70.8*	48.5	14.0
Gemfibrozil	-23.9	-45.7	-99.8
Ibuprofen	91.5*	81.1*	78.3*
Sucralose	-103*	-330*	-83
Triclosan	97.2*	91.4*	42.5
HHCB	96.0*	87.5*	40.8*
AHTN	83.0*	73.4*	72.1*

% Removal = (influent - effluent) / influent × 100.

^a Data provided by Village of Lakefield, Lakefield, ON, Canada.

been reported that 50% of gemfibrozil is excreted as the glucuronide conjugate, so it is possible that de-conjugation released significant amounts into the treated sewage (Ternes, 1998). However, 55% removal of gemfibrozil was observed in a conventional WWTP (Paxéus, 2004). More work is required to determine the mechanisms for the negative removals of gemfibrozil in the sewage lagoon.

For sucralose, estimated mean concentrations were found to be highest in the final effluents for samples collected in all seasons (Table 3). This indicates that this compound was not removed during lagoon-based treatment processes (Table 7). Literature data support this finding. Sucralose was detected in the range of 800 to 1800 ng/L in WWTP influents and effluents in Sweden, Switzerland, Germany, Austria, Israel and Canada (Lange et al., 2012). Sucralose is a very hydrophilic compound, with a log K_{ow} = -0.50 and it is not biodegradable (Pasquini et al., 2013). A fate study conducted by Soh et al. (2011) indicated that sucralose is a persistent compound that is resistant to microbial degradation, hydrolysis, soil sorption, chlorination, ozonation and UV-photolysis. Further study needs to be conducted to determine the cause of the increase in the estimated concentration (2 to 3 fold) in the lagoon effluent relative to the raw influent.

For triclosan, there was also a significant seasonal trend in removals, with percent removals in the range of 42.6–97.1% (Table 7). In a WWTP in Dortmund, Germany serving 350,000 inhabitants with influent triclosan concentrations of 1200 ng/L, removals were 95% (Bester, 2003). Triclosan is relatively hydrophobic, and most of the triclosan is likely to be removed through partitioning onto sewage sludge and biodegradation by microorganism (Hua et al., 2005; Lee et al., 2012).

For the synthetic musks, HHCB and AHTN removals in the summer were also higher than in the fall and winter, but were still in the range of 40.8–96.0% (Table 7). A previous study at a conventional WWTP in Ontario, Canada showed 73% and 67% (annual average) removals for HHCB and AHTN, respectively (Yang and Metcalfe, 2006). Another study performed in WWTPs in Ontario, Canada showed removals of HHCB and AHTN in the range of 80% (Lee et al., 2003). Once again, it appears that the Lakefield lagoon is equally as effective at removing PPCPs as conventional WWTPs. Both synthetic musk compounds would be expected to have a similar tendency to partition between aqueous and non-polar matrices (e.g., sludge) because of their similar log K_{ow} values of 5.9 and 5.7, respectively. The measured K_d values (i.e., sorption potential on sludge) for sorption of AHTN and HHCB on sludge reported by Smyth et al. (2007) were 4920 and 5300 L/kg (primary treatment) and 20,800 and 25,300 L/kg (secondary treatment), respectively (Smyth et al., 2007). These values confirm that a major mechanism for removal of HHCB and AHTN is through partitioning onto sludge. Buerge et al. (2003) suggested that photochemical degradation is another significant elimination process for AHTN. This may explain why AHTN was not removed very efficiently in winter (Table 7) when photodegradation would be expected to be minimized because of reduced sunlight and closure of the settling pond. Volatilization from water to the atmosphere is also an important fate process for both musk compounds (Buerge et al., 2003), due to the relatively high Henry's law constants (K_H) for these compounds (Yang and Metcalfe, 2006).

As mentioned before, in the winter season, the wastewater bypassed the stabilization pond and so samplers were placed at points before and after UV-disinfection at the outlet of the lagoon. Pre-UV and post-UV concentrations (Tables 3 and 4) of all monitored compounds (carbamazepine, sulfamethoxazole, trimethoprim, gemfibrozil, ibuprofen, sucralose, triclosan, HHCB and AHTN) in the winter samples from the lagoon were found to be similar. Hence, removals were minimal from UV-treatment at the fluences used for wastewater disinfection.

Table 7 also lists the removal data for various conventional wastewater quality parameters in the Lakefield sewage lagoon, including the biological oxygen demand (BOD), suspended solids (SS), total phosphorus (P) and total nitrogen (N). The removals of these conventional parameters ranged from 58.9 to 99.2% and showed a trend to lower removals in the winter. The removal data for BOD, SS, P and N are comparable to the removals of several indicator compounds in this study; especially during the summer months.

The concentrations of PPCPs measured in this study were generally lower in comparison to the data in the literature for conventional wastewater treatment plants. This may be due to the small size of the population served by the lagoon. Consumption amounts of PPCPs are dependent on the population size. The population of the village of Lakefield is about 2600, whereas other studies on conventional WWTPs focus on larger

Table 8

Loading of indicator compounds into Otonabee River during summer, fall and winter sampling period.

Compounds	Summer ^a		Fall ^b		Winter ^c	
	Mass loading (mg/day)	Mass loading (mg/1000 inhabitants/day)	Mass loading (mg/day)	Mass loading (mg/1000 inhabitants/day)	Mass loading (mg/day)	Mass loading (mg/1000 inhabitants/day)
Carbamazepine	5963	2293	11,072	4258	19,521	7508
Sulfamethoxazole	53	20	637	245	2047	787
Trimethoprim	1406	541	2332	897	14,379	5530
Gemfibrozil	101	39	125	48	65	25
Ibuprofen	838	322	9879	3800	1637	630
Sucralose	4.6E + 07	1.8E + 07	4.1E + 07	1.6E + 07	3.1E + 07	1.2E + 07
Triclosan	381	147	2237	860	824	317
HHCB	5.7E + 04	2.2E + 04	1.8E + 05	7.0E + 04	5.0E + 05	1.9E + 05
AHTN	10,459	4023	25,264	9717	15,807	6080

Daily average effluent discharge volume: ^a1,314,000 L for July 2010, ^b867,000 L for October 2010 and ^c1,720,000 L for March 2011 (data provided by Village of Lakefield, Lakefield, ON, Canada). Mass loading = (concentration in final effluent) × (daily average effluent discharge volume) and = [(concentration in final effluent × daily average effluent discharge volume) / served population] × 1000.

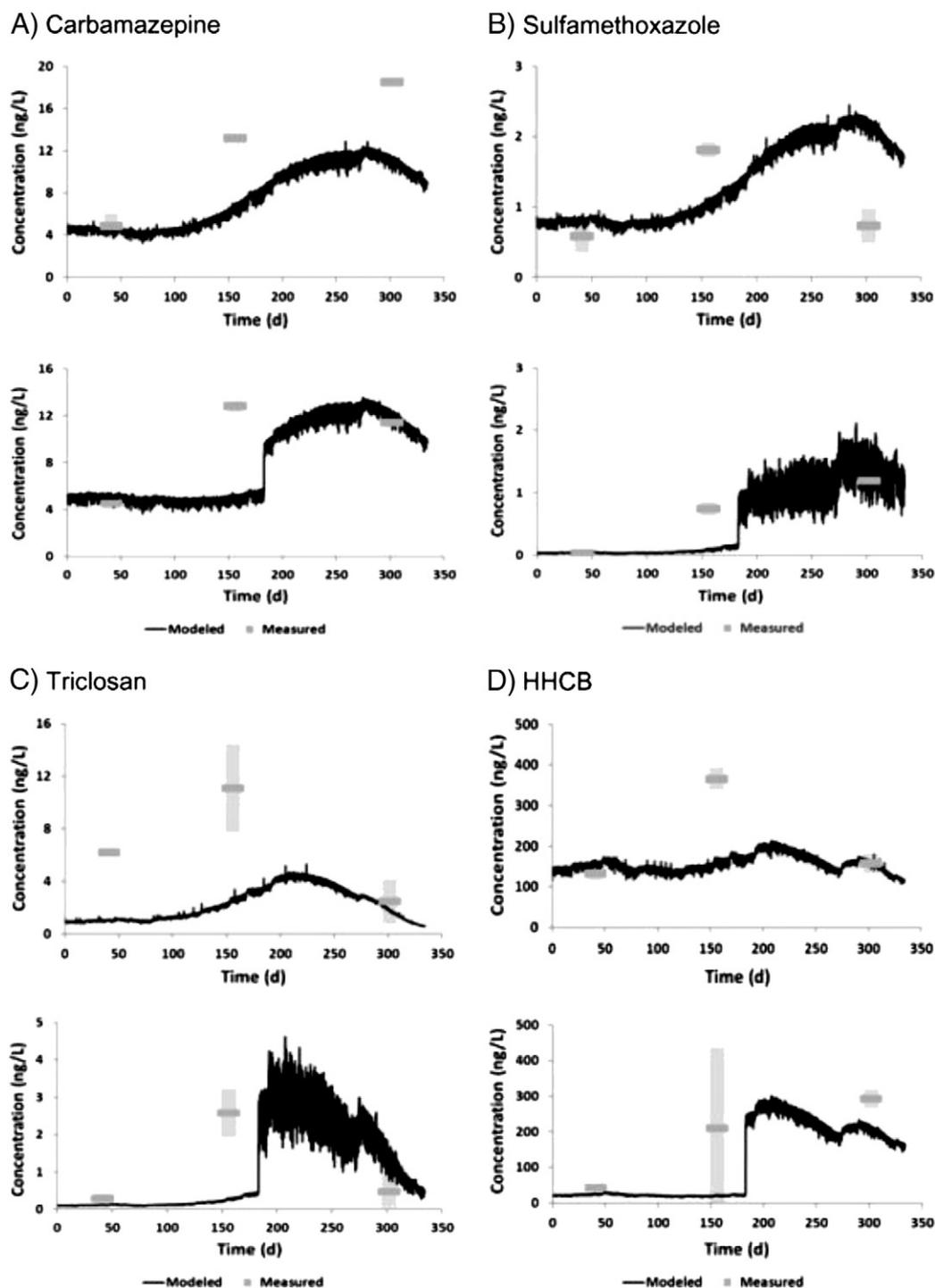


Fig. 3. Modeled and measured concentrations of (A) carbamazepine, (B) sulfamethoxazole, (C) triclosan and (D) HHCB after the aerated lagoon (top) and at the effluent (bottom).

urban centers with larger population. However, there is also some treatment of the wastewater before it is pumped from a collection sump in the village of Lakefield to the lagoon. Alum is added as a flocculant prior to discharge of sewage into the lagoon and this may precipitate some of the PPCPs out with suspended solids. Also, precipitation may have resulted in dilution of the wastewater in the lagoon.

3.5. Loading of indicator compounds

The estimated daily loadings (mg/day) of PPCPs and sucralose into the Otonabee River from the Lakefield sewage lagoon are presented in Table 8. The loadings for PPCPs ranged from 53 to $5.0E + 05$ mg/day,

with the highest loadings generally occurring in the winter season and for sucralose $3.1E + 07$ to $4.6E + 07$ mg/day. A study reported that the sum loadings for several commonly used pharmaceuticals from two urban wastewater treatment plants (population of 250,000 and 750,000) in Alberta, Canada were three orders of magnitude greater than the loadings from a rural lagoon (>4000 population) at 4000 mg/day (MacLeod and Wong, 2010), but the per capita loadings for all plants were found to be similar. The loading amount should be dependent on population size, consumption patterns of the sites and effluent discharge rate (L/day). In Table 8, mass loading data is also presented as mg/1000 inhabitant/day. The mass loading data of urban WWTPs presented in a review article by Verlicchi et al. (2012) was in

the range of 90 to 364 mg/1000 inhabitant/day for carbamazepine, ibuprofen, gemfibrozil, triclosan and sulfamethoxazole. Mass loading values are dependent on daily effluent discharge flow (L/day) and population size. For the community of 2600 people in Lakefield Village, the effluent flow rate was high (867,000 to 1,720,000 L/day). This could be the reason for the higher mass loading in compare to the literature values.

3.6. Lagoon modeling results

Fig. 3 shows the results of the simulations for carbamazepine, sulfamethoxazole, triclosan and HHCB, in comparison to the estimated average concentrations. For all compounds, we observe an important bump on day 183 (December 1st) that is caused by the redirection of the effluent of the south pond in the photolysis unit. Results for carbamazepine show that the model overestimates removal of this compound in the fall (Fig. 3A). For sulfamethoxazole, the model was able to describe the dynamics of the contaminant consistent with the observations for all seasons (Fig. 3B). The removals of triclosan as shown by the model were higher than what was determined from the estimated concentrations in the summer and fall (Fig. 3C). Modeling results for HHCB were predictive of the estimated concentrations in summer and winter (Fig. 3D). However, the predictions for HHCB in the fall did not match the estimated concentrations, although there was high variability in the estimated values from that sampling period.

Overall, it appears that the model was able to adequately describe the fate of these four emerging contaminants in the summer and winter. These compounds are affected differentially by environmental fate processes (Table 2), so it is encouraging that the model was able to make reasonable predictions of removals during the summer and winter sampling periods. However, the fall measurements were not well represented by the model. A temperature effect that is not well described by the model, inhibition of biological or physicochemical processes during this season, or application of inappropriate R_s to estimate concentrations from the amounts accumulated in the passive samplers are all possible reasons for the lack of correlation between predicted and estimated concentrations. Further analysis on the lagoon would be required to resolve this issue.

3.7. Potential biological impacts

In the Otonabee River, the detected indicator compounds were carbamazepine, HHCB and AHTN, and their concentrations were low (<1 ng/L) during summer and fall sampling periods. At this concentration, carbamazepine would not be expected to be a toxic hazard to organisms in the Otonabee River, since EC_{50} values for this compound have been reported as >100 mg/L (48 h) for immobilization of *Daphnia magna* and 25.5 mg/L (7 day) for reduced growth rates of *Lemna minor* (Cleuvers, 2003). HHCB and AHTN are toxic to aquatic invertebrates at ppb ($\mu\text{g/L}$) to low ppm (mg/L) levels (Brausch and Rand, 2011). Toxicology tests using multiple chemicals were found to have a greater toxic effect than from exposures to a single chemical. Specific combinations that were found to have increased toxicity were clofibrac acid and carbamazepine and diclofenac and ibuprofen (Cleuvers, 2003). It is important to consider the cumulative effects of all the drugs present when assessing risk to aquatic organisms. However, it is possible that the synthetic musks and triclosan could bioaccumulate in aquatic organisms to higher concentrations (Gatermann et al., 2002; Orvos et al., 2002; O'Toole and Metcalfe, 2006).

4. Conclusions

Removal rates of the PPCPs in the lagoon were generally consistent with removals of these indicator compounds reported in the literature for conventional WWTPs. Compounds that are susceptible to photodegradation (i.e., sulfamethoxazole and trimethoprim) showed greater removals in

the lagoon in the summer, and also ibuprofen, which is susceptible to microbial degradation showed greater removals in the summer. Carbamazepine, which is considered recalcitrant in wastewater treatment systems showed inconsistent results for removals in the summer, fall and winter. Also, sucralose was found to be resistant to treatment processes in all seasons. For triclosan, HHCB and AHTN, higher removals were also observed during the summer season. Estimated concentrations of carbamazepine, HHCB and AHTN were very low (<1 ng/L) in the Otonabee River at downstream of the sewage lagoon discharge, and they are unlikely to pose a threat to the ecosystem. Also, a new lagoon model was able to adequately predict the fate of carbamazepine, sulfamethoxazole, triclosan and HHCB in the lagoon in the summer and winter season. The predicted values obtained from lagoon modeling generally agreed well with measured concentrations. POCIS and SPMD passive samplers were shown to be an effective monitoring tool for PPCPs in wastewater and receiving waters.

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