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Monitoring for contaminants of emerging concern in drinking water using POCIS passive samplers

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Contaminants of emerging concern (CEC) have been detected in drinking water world-wide. The source of most of these compounds is generally attributed to contamination from municipal wastewater. Traditional water sampling methods (grab or composite) often require the concentration of large amounts of water in order to detect trace levels of these contaminants. The Polar Organic Compounds Integrative Sampler (POCIS) is a passive sampling technology that has been developed to concentrate trace levels of CEC to provide time-weighted average concentrations for individual compounds in water. However, few studies to date have evaluated whether POCIS is suitable for monitoring contaminants in drinking water. In this study, the POCIS was evaluated as a monitoring tool for CEC in drinking water over a period of 2 and 4 weeks with comparisons to typical grab samples. Seven "indicator compounds" which included carbamazepine, trimethoprim, sulfamethoxazole, ibuprofen, gemfibrozil, estrone and sucralose, were monitored in five drinking water treatment plants (DWTPs) in Ontario. All indicator compounds were detected in raw water samples from the POCIS in comparison to six from grab samples. Similarly, four compounds were detected in grab samples of treated drinking water, whereas six were detected in the POCIS. Sucralose was the only compound that was detected consistently at all five plants. The POCIS technique provided integrative exposures of CECs in drinking water at lower detection limits, while episodic events were captured *via* traditional sampling methods. There was evidence that the accumulation of target compounds by POCIS is a dynamic process, with adsorption and desorption on the sorbent occurring in response to ambient levels of the target compounds in water. CECs in treated drinking water were present at low ng L^{-1} concentrations, which are not considered to be a threat to human health.

Environmental impact

In this study, the polar organic contaminant integrative sampler (POCIS) was evaluated as a monitoring tool for contaminants of emerging concern (CECs) in drinking water, with comparisons to monitoring with typical grab samples. Seven "indicator compounds" were monitored in five drinking water treatment plants (DWTPs) in Ontario, Canada. The POCIS technique provided integrative exposures of CECs in drinking water at lower detection limits. Concentrations of contaminants were several orders of magnitude lower than concentrations that have been predicted to be a concern for human health. No environmental impacts are expected from this study.

Introduction

Contaminants of emerging concern (CEC) include pharmaceuticals and personal care products (PPCPs), flame retardants, surface active chemicals such as stain protectors and detergents, endocrine disrupting chemicals (EDCs) and new and replacement chemicals entering the marketplace. Many studies conducted world-wide have reported CECs in drinking water,[1–5] and concerns regarding the presence of these compounds in drinking water have captured the attention of government agencies and the public. The World Health Organization recently released a report on pharmaceuticals in drinking water, which concluded that "adverse health impacts to humans are very unlikely from exposure to the trace concentrations of pharmaceuticals".[6] While routine monitoring for pharmaceuticals in drinking water sources was not recommended in the WHO report, it was noted that it is a challenge to obtain occurrence data for a diverse group of CECs. The authors of the report acknowledge that there is a need for "standardized sampling and analysis protocols to support monitoring studies".[6]

To date, most studies that report the occurrence of CECs in drinking water were conducted using traditional sampling

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methods with grab or composite samples. These methods often require enrichment of large amounts of water to detect trace levels of an increasing number of CECs, and they only offer a single "snap-shot" in time of what is present in the water. The Polar Organic Compound Integrative Sampler (POCIS) is a passive sampling technology developed to measure time-weighted average exposures to trace concentrations of PPCPs, EDCs, and pesticides over several weeks of deployment. The POCIS contains a solid-phase sorbent sandwiched between two porous polymer membranes and these devices are typically deployed in water in stainless steel cages. Sampling rates determined in the laboratory for individual chemicals are integrated into uptake models to provide estimates of water concentrations. As summarized in recent reviews,[7,8] POCIS have been used in a number of monitoring studies in surface waters, including in the Laurentian Great Lakes[9] and in rivers in the USA.[10–12]

The purpose of this study was to evaluate the use of POCIS as a monitoring tool within drinking water treatment plants (DWTPs) in Ontario, Canada. Five DWTPs were monitored over deployment periods of two and four weeks for seven "indicator compounds" that included a non-prescription pharmaceutical (Ibuprofen), two prescription pharmaceuticals (carbamazepine, gemfibrozil), two antibiotics (sulfamethoxazole, trimethoprim), an estrogen (estrone), and an artificial sweetener (sucralose) in both raw and treated drinking water. These target compounds were selected according to the criteria identified in a recent study that illustrated the value of monitoring a small number of PPCPs in wastewater treatment facilities in the U.S.[13] Sucralose has been widely detected in drinking water systems in the USA and, because of its persistence and ubiquitous presence, has been proposed as a tracer of wastewater contaminants in drinking water samples.[14] In addition to the POCIS samples, grab samples were also taken at the DWTPs at 0, 2 and 4 weeks and extracted by solid phase extraction (SPE) techniques to compare the results to those obtained by the POCIS.

Methods and materials

Chemicals and materials

The pharmaceutical analytes and estrone were purchased from Sigma-Aldrich Canada (Oakville, ON, Canada) and their stable isotope surrogates were purchased from C/D/N Isotopes (Pointe-Claire, QC, Canada), respectively. Sucralose and its deuterated surrogate were purchased from Sigma-Aldrich Canada and Toronto Research Chemicals (Toronto, ON, Canada) respectively. All stock solutions were made up in methanol and working standard solutions. High purity acetic acid, methanol and acetone were obtained from Fisher Scientific (Ottawa, ON, Canada). The POCIS samplers were purchased from Environmental Sampling Technologies (St. Joseph, MO, USA). SPE cartridges (Oasis MCX, Oasis MAX) were purchased from Waters (Milford, MA, USA).

Sampling sites

The POCIS samplers were deployed in DWTPs that serve five municipalities in southern, Ontario, Canada. The populations

Table 1 Operational data and sampling information at the DWTPs monitored. NA = data not available. * Population served at DWTP 5 includes estimates of people with direct connections, but does not include people who truck water or fill water containers at the plant

DWTP	Pop served/$\times 10^3$	Water source	Treatment technology	Capacity/ $L \times 10^6$ per day	Sampling dates 0–2 weeks, 2–4 weeks	Range of water flows/ $L \times 10^6$ per day	Range of water temp./°C
1	750	Ottawa R	1 Coagulation, 2 flocculation, 3 sedimentation, 4 filtration, 5 pre-chlorination, 6 pH correction, 7 chloramination, 8 fluoridation	360	29/09/2011, 10/10/2011, 10/10/2011, 27/10/2011	136–197, 128–222	16.1–20.0, 11.5–16.1
2	124	L Ontario	1 Mussel control, 2 pre-chlorination, 3 screening, 4 coagulation/flocculation, 5 sedimentation, 6 filtration, 7 post-chlorination	150	28/09/2011, 09/10/2011, 09/10/2011, 26/10/2011	49.5–59.9, 49.3–62.1	13.6–15.0, 12.6–14.9
3	98.5	Grand R	1 Screening, 2 coagulation, 3 flocculation, 4 sedimentation, 5 pre-chlorination, 6 filtration, 7 post-chlorination, 8 fluoridation	100	30/05/2012, 13/06/2012, 14/06/2012, 27/06/2012	33.9–53.3, 42.4–54.4	16.0–21.5, 21.5–26.8
4	5.7	L Erie	1 Coagulation, 2 flocculation, 3 sedimentation, 4 filtration, 5 chlorination	14.5	30/05/2012, 13/06/2012, 14/06/2012, 27/06/2012	9.5–10.4, 7.3–10.9	10.5–16.0, 14.0–18.0
5	1.8*	Grand R	1 Coagulation, 2 flocculation, 3 sedimentation, 4 filtration, 5 chlorination	1.5	30/05/2012, 13/06/2012, 14/06/2012, 27/06/2012	NA	NA

served, the source of the water, the flows and the temperatures of raw water, as well as a basic description of the treatment technologies used at each plant are summarized in Table 1. The passive samplers were deployed in stainless steel sampling cages with capacity to accommodate three POCIS, so each cage gave triplicate measurements.

Monitoring in DWTPs 1 and 2 occurred in the fall of 2011 and monitoring in DWTPs 3, 4 and 5 occurred in the spring of 2012 (Table 1). At each DWTP, two sampling cages were placed in the flow of raw water to measure the initial concentrations of chemicals entering the DWTPs, and another two cages were placed in the flow of treated drinking water to measure the concentrations of chemicals after treatment. The first set of POCIS ($n = 3$ in each of raw and treated water) was removed after two weeks of deployment and the second set of POCIS ($n = 3$) was removed after 4 weeks of deployment. At the start of deployment and when POCIS were retrieved at weeks 2 and 4, grab samples (1 L) of raw and treated drinking water were collected at each DWTP for extraction using solid phase extraction (SPE) cartridges. After retrieval, the POCIS were transported on ice and frozen at −20 °C until processed for analysis. The water samples were transported on ice and extracted by SPE within 48 h of collection.

Sample preparation

Extraction of POCIS samplers was performed according to the procedures described previously.[9] Briefly, frozen samplers were removed from storage and allowed to thaw, then rinsed with water to remove debris and biofouling material. The sorbent in the POCIS was transferred to a glass chromatography column (1 cm ID × 30 cm length) previously packed to 1/3 full with solvent-washed granular Na_2SO_4. A 100 μL volume of a mixture of stable isotope labelled surrogates (500 ng mL^{-1}) was then added to the column. Elution from the column was performed with 100 mL methanol. The eluate was collected and then reduced in volume by rotary evaporation to a volume of ~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.

SPE extraction of all analytes except sucralose was conducted as described previously.[9] Briefly, 300 mL subsamples of water were enriched using Oasis mixed-mode anion exchange (MAX) cartridges, which were pre-conditioned with methanol, 0.1 M NaOH and water (pH 8.0). Water samples were adjusted to pH 8 with 1.0% ammonium hydroxide and then loaded onto the cartridges after addition of 300 μL of the standard containing stable isotope surrogates. The cartridges were eluted sequentially with 2 mL methanol and then 3 × 3 mL of 2% formic acid in methanol. The extracts were evaporated to near dryness and then reconstituted in 0.4 mL methanol.

For sucralose, Oasis MCX mixed mode cation exchange cartridges (MCX; 6 cm^3, 500 mg) were used. The cartridges were preconditioned with sequential additions of 6 mL of acetone, 6 mL of methanol and 6 mL of Milli Q water (pH 1.5). Subsamples of drinking water (300 mL) were acidified to pH 1.5 prior to spiking with an internal standard (Sucralose-D6, 100 μl of 500 ppb stock solution). After loading the water samples along with rinses, the cartridges were washed with 2 mL of Milli Q water and then aspirated to dryness for 10 min under vacuum. The analytes were eluted from the SPE cartridges with 3 × 3 mL of 5% ammonium hydroxide in methanol. The extracts were evaporated and reconstituted in 0.4 mL methanol for analysis. In extracts prepared from deionized water spiked with varying concentrations of sucralose, extraction efficiencies were all >77%.

Analysis

The pharmaceuticals 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 AB Sciex (Concord, ON, 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). Analytes were separated chromatographically using a Genesis C18 column (150 mm × 2.1 mm ID; 4 μm particle size) and a guard column (Genesis C18, 10 mm × 2.1 mm ID; 4 μm); both purchased from Chromatography Specialities (Brockville, ON, Canada). 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. For the pharmaceutical analytes, carbamazepine, sulfamethoxazole, trimethoprim, gemfibrozil and ibuprofen, the LC-MS/MS was run in double polarity mode by switching from positive to negative voltage, as described previously.[15] The precursor and product ion transitions for multiple reaction monitoring (MRM) of the pharmaceutical analytes and their corresponding labelled surrogates are listed in Table 2. For quantification, an external standard method with a five-point calibration curve was used, and the data were adjusted according to the response for the surrogate internal standards in order to compensate for matrix effects.

For determination of estrone and sucralose, LC-MS/MS analysis in negative ion mode was conducted separately using an AB Sciex Q-Trap 5500 instrument with a turbospray ionization source, equipped with an Agilent 1100 series (Mississauga, ON, Canada) separation system. In addition, samples from the sorption/desorption experiment were analyzed with the AB Sciex instrument. The analytes were separated chromatographically using a Genesis C-18 column and a guard column of the same stationary phase (Chromatographic Specialties). The LC mobile phases for gradient elution were the same as described above. MRM detection was performed using the precursor and product ion transitions and their labelled surrogates listed in Table 2. An external standard method was used for quantification, adjusted using the surrogate internal standards.

Quality assurance

The Limits of Detection (LODs) and Limits of Quantitation (LOQs) listed in Table 2 were previously reported for all target analytes, except for sucralose.[9] The LOD and LOQ values for sucralose were determined as the analyte concentration that

Table 2 Multiple reaction monitoring (MRM) ion transitions for the target compounds and their stable isotope surrogates using LC-MS/MS analysis in negative or positive ion mode. Limits of Detection (LODs) and Limits of Quantitation (LOQs) for SPE extracts are also listed

Compound	MRM Transition	Polarity	Instrument	LOD, LOQ ng per L
Carbamazepine (CBZ)	237 → 194	+	API 3000	0.3, 1
Trimethoprim (TPM)	291 → 123	+	API 3000	0.6, 2
Sulfamethoxazole (SMX)	254 → 156	+	API 3000	0.3, 1
Ibuprofen	205 → 161	−	API 3000	0.6, 2
Gemfibrozil	249 → 121	−	API 3000	2, 5
Estrone	269 → 145	−	QTrap 5500	0.2, 0.7
Sucralose	395 → 35	−	QTrap 5500	0.1, 0.3
Carbamazepine-d10	2472 → 204	+	API 3000	
Trimethoprim-13C3	294 → 126	+	API 3000	
Sulfamethoxazole-13C6	260 → 162	+	API 3000	
Ibuprofen-13C3	208 → 163	−	API 3000	
Gemfibrozil-d6	255 → 121	−	API 3000	
Estrone-13C2	271 → 147	−	QTrap 5500	
Sucralose-d6	403 → 35	−	QTrap 5500	

produced a peak with a signal-to-noise ratio of 3 and 10, respectively, determined by analysis of serial dilutions of the analytical standard. For the SPE extractions, laboratory blanks with deionized water were prepared for every 7–8 field samples.

Field blank POCIS accompanied the samplers during deployment, retrieval and transportation. The field blanks were processed and analysed as described for the deployed samples.

Estimates of CEC concentrations

Time weighted average concentrations in raw and treated drinking water were estimated according to the model:

$$C_W = N/R_S \times t \quad (1)$$

where: N is the amount accumulated in POCIS (ng), t is the deployment duration (day), and R_S is the sampling rate (L day^{-1}).

The R_S for the pharmaceuticals and estrone were determined previously in laboratory experiments at 15 °C.[9] The R_S for sucralose (0.16 L per day) was measured using the same static exposure technique previously described.[9] Briefly, the static experiments were conducted in triplicate in containers with 3 L of water placed in a temperature controlled environmental chamber at 15 °C. For each replicate, the water was spiked with sucralose at a nominal concentration of 3 μg L^{-1}, and a single POCIS was placed in the water for a period of 8 days. A magnetic stirrer was used to gently mix the water. Aliquots of the exposure water (40 mL) were removed from the bottles every 24 h to monitor the decrease in water concentration over time. The water was extracted by SPE according to the methods describe above. A positive control containing only spiked water without the POCIS was run along with the calibration to correct for sorption, volatilization or degradation during exposure. As a negative control, one POCIS was exposed to 3 L of water without spiking of pharmaceuticals.

The R_S of the POCIS was calculated as:

$$R_S = k_U V_T \quad (2)$$

where: V_T is the total volume of water in the tank (3 L).

The value of k is estimated from the slope of the decrease of water concentration ($\ln[C_W(t)/C_W(0)]$) over the exposure time. Analysis of the POCIS collected at the end of the experiment confirmed that the mass of sucralose collected in the sorbent corresponded (±10%) to the amount of sucralose removed from the test solution over time.

Sorption and desorption experiment

A sorption/desorption experiment with POCIS conducted over 18 days was divided into a sorption phase (days 0–7) followed by a desorption phase (days 8–18). The experiment were conducted in a controlled environment chamber set at an average temperature of 15 °C and 16 h light:8 h darkness. During the sorption phase, a static experiment was conducted in 9 separate glass jars as described previously.[9] Briefly, one POCIS was suspended vertically in each jar in deionized water spiked with a mixture of carbamazepine, ibuprofen, gemfibrozil, trimethoprim, sulfamethoxazole and sucralose, each at a concentration of 2 μg L^{-1}. The POCIS were maintained in this solution for 7 days to achieve sorption of the target analytes. On the 8th day of the experiment, 3 POCIS were removed from the water at the end of sorption study and frozen for later extraction. These POCIS represented Day 1 of the desorption experiment. The remaining six POCIS were removed and suspended together in a glass aquarium through which there was a continuous flow of municipal drinking water at a flow rate of approximately 3L min^{-1}. The flow was monitored and adjusted every day. At Day 5 and Day 10 of the desorption experiment, 3 replicate POCIS were removed from the aquarium for extraction. The POCIS were extracted and analyzed by LC-MS/MS for the target compounds, as previously described.

Results and discussion

Grab sample results for raw and treated drinking water

The monitoring results for indicator compounds in raw and treated drinking water in grab samples from the five DWTPs are presented in Table 3. Analysis of contaminants of emerging

Table 3 Average (ng L^{-1} ± SD) concentrations in SPE extracts of grab samples of raw and treated drinking water ($n = 3$) collected at 0, 2 and 4 weeks of the monitoring period in 5 DWTPs

DWTP	Source	Week	Gemfibrozil	Ibuprofen	SMX	CBZ	TPM	Estrone	Sucralose
1	Raw	0	<LOD	<LOD	4.0 ± 0.3	<LOQ	<LOD	<LOD	13.2 ± 0.8
		2	<LOD	<LOD	<LOD	1.2 ± 0.1	<LOD	<LOD	19.5 ± 3.1
		4	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	19.1 ± 1.1
	Treated	0	<LOD	<LOD	1.3 ± 0.2	<LOD	<LOD	<LOD	<LOD
		2	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	5.2 ± 0.7
		4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3.7 ± 1.1
2	Raw	0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
		2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
		4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Treated	0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
		2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
		4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
3	Raw	0	<LOQ	<LOQ	<LOD	22.8 ± 0.4	3.4 ± 0.1	1.9 ± 0.4	243.6 ± 12.7
		2	<LOD	<LOQ	<LOD	5.4 ± 0.8	<LOD	<LOD	30.7 ± 7.0
		4	<LOD	2.7 ± 0.4	<LOD	3.9 ± 1.0	3.8 ± 0.6	<LOD	165.5 ± 14.9
	Treated	0	<LOD	<LOD	<LOD	<LOD	<LOD	1.0 ± 0.1	253.7 ± 6.9
		2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	50.1 ± 14.6
		4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	90.4 ± 16.8
4	Raw	0	<LOQ	<LOD	<LOD	<LOQ	<LOD	1.9 ± 0.2	19.3 ± 1.6
		2	<LOD	<LOD	<LOD	<LOQ	<LOD	<LOD	13.9 ± 1.2
		4	<LOD	<LOD	2.1 ± 0.7	<LOQ	<LOD	<LOD	14.5 ± 1.5
	Treated	0	<LOD	<LOD	<LOD	<LOD	<LOD	1.5 ± 0.5	15.1 ± 0.4
		2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	9.5 ± 1.7
		4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	6.2 ± 0.3
5	Raw	0	<LOQ	<LOQ	3.6 ± 0.8	21.7 ± 1.0	3.6 ± 0.4	1.6 ± 0.4	226.0 ± 34.8
		2	<LOD	1.4 ± 0.5	4.0 ± 0.5	12.9 ± 1.7	6.6 ± 1.2	<LOD	108.4 ± 14.7
		4	<LOQ	4.6 ± 1.9	1.6 ± 0.3	28.7 ± 4.8	4.7 ± 0.8	<LOD	156.6 ± 11.2
	Treated	0	<LOD	<LOD	<LOD	<LOD	<LOD	<LOQ	238.9 ± 11.3
		2	<LOD	<LOD	<LOD	7.7 ± 0.7	<LOD	<LOD	156.2 ± 10.8
		4	<LOD	<LOD	<LOD	2.9 ± 2.5	<LOD	<LOD	85.2 ± 11.7

concern in drinking water using conventional monitoring methods with grab or composite samples often generate data with values below LODs or LOQs. Analysis of the grab samples generated data that were frequently below the LOQs or LODs (Table 3). This was especially the case in samples collected from DWTPs 1 and 2, both of which take surface water from source waters that have lesser degrees of influence from municipal wastewater than for DWTPs 3, 4, and 5. Of the seven compounds analyzed, six were detected in grab samples of raw drinking water, indicating that these analytes were appropriate indicator compounds. The detection of indicator compounds varied by analyte and among plants for the grab samples of both raw and treated water. Sucralose was detected at four of the five DWTPs at concentrations up to 279 ng L^{-1}. The widespread detection of this artificial sweetener supports previous suggestions that this compound can be used as a tracer of contaminants in drinking water originating from wastewater sources.[14]

Four of the seven compounds were detected in the treated drinking water, while gemfibrozil, ibuprofen and trimethoprim were not detected in any grab samples of treated drinking water (Table 3). In some cases, the concentrations in grab samples varied widely over the 4 week monitoring period, indicating that there was considerable temporal variation in concentrations. As was the case for untreated water, the most frequently detected compound in grab samples of treated drinking water was sucralose, which was present at similar concentrations to those reported previously.[14] Although some reduction in concentrations was apparent from raw to treated drinking water, sucralose was not removed by conventional drinking water treatment processes. Similar results were observed for estrone, which was detected in some of the samples at Plants 3 and 4, but was not reduced in treated water relative to raw water. However, the timing for collections of grab samples of raw and treated water were not paired to account for retention times in the plants and therefore, quantitative assessment of removal efficiencies was not possible. Gemfibrozil was the only compound not detected at concentrations greater than the LOQ of 5 ng L^{-1}, although it was detected in four samples of raw water at concentrations greater than the LOD of 2 ng L^{-1} (Table 3). Gemfibrozil was detected in a previous study of Ontario DWTPs at frequencies of 33 and 15% in raw and treated waters, respectively.[5]

The observed concentrations of gemfibrozil, ibuprofen, sulfamethoxazole, trimethoprim, and carbamazepine in drinking water were lower than those reported previously for DWTPs in Ontario, Canada,[1,5] and in source waters.[3,9]

POCIS results and comparison to grab sampling

The time-weighted average concentrations of target analytes collected in POCIS over 2 and 4 weeks are listed in Table 4, along

Table 4 Time-weighted average concentrations (ng L^{-1} ± SD) estimated from amounts accumulated in POCIS ($n = 3$) over 2 and 4 weeks of deployment in raw and treated drinking water in 5 DWTPs. R_s = POCIS sampling rates in L per day at 15 °C

			Gemfibrozil	Ibuprofen	SMX	CBZ	TPM	Estrone	Sucralose
DWTP	Source	Week	$R_s = 0.31$	$R_s = 0.25$	$R_s = 0.35$	$R_s = 0.40$	$R_s = 0.41$	$R_s = 0.64$	$R_s = 0.16$
1	Raw	2	0.12 ± 0.03	2.19 ± 0.13	0.06 ± 0.02	0.74 ± 0.06	<LOD	<LOD	7.28 ± 0.14
		4	0.11 ± 0.01	6.10 ± 0.07	<LOD	0.58 ± 0.05	<LOD	<LOD	1.95 ± 0.16
	Treated	2	<LOQ	<LOD	<LOD	0.35 ± 0.03	<LOD	<LOD	6.51 ± 0.42
		4	<LOQ	<LOD	<LOD	0.22 ± 0.02	<LOD	<LOD	1.56 ± 0.18
2	Raw	2	<LOD	2.11 ± 4.47	<LOD	0.20 ± 0.02	<LOD	<LOD	0.30 ± 0.09
		4	<LOD	1.41 ± 0.16	<LOD	0.10 ± 0.01	<LOD	<LOD	<LOD
	Treated	2	<LOD	0.19 ± 0.03	<LOD	0.16 ± 0.02	<LOD	<LOD	<LOD
		4	<LOD	<LOQ	<LOD	0.08 ± 0.01	<LOD	<LOD	<LOD
3	Raw	2	<LOD	0.19 ± 0.03	<LOD	6.75 ± 0.33	<LOD	0.07 ± 0.01	13.92 ± 1.59
		4	0.02 ± 0.01	0.12 ± 0.01	<LOD	3.57 ± 0.35	1.75 ± 0.47	0.16 ± 0.08	19.60 ± 1.20
	Treated	2	<LOD	<LOD	<LOD	4.29 ± 0.63	<LOD	0.03 ± 0.00	11.68 ± 1.20
		4	0.02 ± 0.01	0.08 ± 0.01	<LOD	3.40 ± 0.54	1.08 ± 0.17	0.09 ± 0.02	12.78 ± 0.17
4	Raw	2	0.04 ± 0.01	0.68 ± 0.19	<LOD	0.39 ± 0.03	<LOD	0.10 ± 0.01	9.38 ± 0.51
		4	0.02 ± 0.01	0.34 ± 0.06	<LOD	0.32 ± 0.01	<LOD	0.48 ± 0.09	6.45 ± 0.06
	Treated	2	<LOD	<LOD	<LOD	0.04 ± 0.00	<LOD	0.05 ± 0.01	3.14 ± 0.61
		4	<LOD	<LOD	<LOD	0.05 ± 0.01	<LOD	0.11 ± 0.01	2.14 ± 0.31
5	Raw	2	0.04 ± 0.01	0.48 ± 0.06	0.17 ± 0.02	4.73 ± 0.18	2.92 ± 0.94	0.11 ± 0.01	29.83 ± 6.03
		4	0.02 ± 0.01	0.23 ± 0.02	0.27 ± 0.02	2.60 ± 0.19	1.56 ± 0.13	0.46 ± 0.10	17.03 ± 2.23
	Treated	2	<LOD	<LOD	<LOD	1.25 ± 0.20	<LOD	0.08 ± 0.01	16.36 ± 4.79
		4	<LOD	<LOD	<LOD	0.61 ± 0.02	<LOD	0.10 ± 0.01	6.99 ± 1.58

with the sampling rates (R_S) that were used to estimate these concentrations. All indicator compounds were detected in raw water samples and only sulfamethoxazole was not detected by POCIS in treated drinking water. Target compounds were detected more frequently and consistently in POCIS samplers deployed in the raw and treated drinking water than in the grab samples from the same media. Comparisons between the amounts of the target analytes accumulated in POCIS deployed for 2 and 4 weeks (Table 6) indicate that, while some compounds at some plants continued to accumulate in POCIS to higher amounts at four weeks when compared POCIS deployed for two weeks, others had similar amounts accumulated among samplers deployed for two and four weeks. There were some cases where the amounts accumulated in POCIS at 2 weeks were higher than the amounts in POCIS at 4 weeks, but this was not consistent at all plants. For example, at DWTP 5, sucralose accumulated to approximately twice the amount of this compound in POCIS after 2 weeks compared to 4 weeks, whereas at DWTP 3, the amounts were essentially the same among the POCIS deployed for 2 and 4 weeks. At DWTPs 3 and 5, grab sample concentrations were high during the first sampling (Day 0) but declined in subsequent samples. The amounts of ibuprofen in POCIS also declined in the samplers deployed for 4 weeks relative to the 2 week deployment in DWTP 1 and 2. The lower levels at 4 week deployments indicate that sorption to the POCIS sorbent phase is a dynamic process, with some target compounds moving into and out of the POCIS in response to changes in ambient levels in water. This has been observed in other lab and field-based studies.[15,16]

To test the hypothesis that sorption in POCIS may be a dynamic process, we conducted a sorption/desorption study where POCIS that had accumulated target compounds in the sorption phase were placed in flowing drinking water and monitored in the desorption phase at 5 and 10 days. The analytical data (Table 5) indicate that the amounts of the target compounds sorbed to the POCIS declined with time during the desorption phase, except for sucralose. The rates of loss varied, depending on the compound, with the highest rates of loss observed for trimethoprim and sulfamathoxazole (Table 5). These data are consistent with a dynamic process by which there is desorption of these compounds from the solid phase of the POCIS back into the flowing water. However, it cannot be ruled out that there was transformation over time of the compounds that had accumulated on the sorbent. In either case, more work is required to evaluate the kinetics of accumulation of compounds on POCIS.[17]

In addition to capturing differences among plants, the POCIS samplers also detected differences within the plants, since the POCIS afforded greater detection frequencies. Since the POCIS accumulates compounds of interest over a longer time period,

Table 5 Mean amounts (ng ± SD) of selected pharmaceuticals and the artificial sweetener, sucralose in POCIS ($n = 3$) sampled in the desorption phase of the experiment at days 1, 5 and 10. * = day 10 mean amounts significantly different from Day 1 mean amounts (Mann Whitney U test, $P < 0.01$)

Compound	Day 1	Day 5	Day 10
CBZ	1205.3 ± 106.8	968.03 ± 188.7	894.7 ± 37.2
Ibuprofen	617.3 ± 54.5	368.5 ± 103.8	262.4 ± 80.1*
Gemfibrozil	213.2 ± 49.8	166.5 ± 53.5	144.5 ± 31.3*
TPM	425.7 ± 83.7	39.1 ± 17.1	23.8 ± 5.9*
SMX	391.3 ± 59.6	15.1 ± 2.1	8.7 ± 2.2*
Sucralose	191.8 ± 11.5	197.2 ± 28.5	186.1 ± 15.0

Table 6 Amounts (ng ± SD) accumulated in POCIS ($n = 3$) over 2 and 4 weeks of deployment in raw and treated drinking water in 5 DWTPs

DWTP	Source	Week	Gemfibrozil	Ibuprofen	SMX	CBZ	TPM	Estrone	Sucralose
1	Raw	2	1.0 ± 0.1	42.7 ± 0.5	0.3 ± 0.1	4.2 ± 0.3	<LOD	<LOD	15.6 ± 0.4
		4	0.9 ± 0.0	34.9 ± 5.5	<LOD	6.5 ± 0.6	<LOD	<LOD	8.4 ± 1.1
	Treated	2	<LOQ	<LOD	<LOD	1.9 ± 0.2	<LOD	<LOD	13.9 ± 1.3
		4	<LOQ	<LOD	<LOD	2.5 ± 0.2	<LOD	<LOD	6.7 ± 1.2
2	Raw	2	<LOD	42.4 ± 15.6	<LOD	1.1 ± 0.1	<LOD	<LOD	0.7 ± 0.3
		4	<LOD	9.9 ± 1.1	<LOD	1.1 ± 0.1	<LOD	<LOD	<LOD
	Treated	2	<LOD	0.7 ± 0.0	<LOD	0.9 ± 0.1	<LOD	<LOD	<LOD
		4	<LOD	<LOQ	<LOD	0.9 ± 0.1	<LOD	<LOD	<LOD
3	Raw	2	<LOD	0.7 ± 0.1	<LOD	37.8 ± 1.8	<LOD	0.6 ± 0.1	30.4 ± 3.5
		4	0.1 ± 0.0	0.9 ± 0.1	<LOD	40.0 ± 3.9	20.2 ± 5.4	2.9 ± 1.4	85.6 ± 5.2
	Treated	2	<LOD	<LOD	<LOD	24.0 ± 3.5	<LOD	0.3 ± 0.0	25.5 ± 2.6
		4	0.2 ± 0.0	0.6 ± 0.1	<LOD	38.0 ± 6.1	12.4 ± 1.9	1.6 ± 0.4	55.8 ± 0.7
4	Raw	2	0.2 ± 0.0	2.4 ± 0.7	<LOD	2.2 ± 0.2	<LOD	0.9 ± 0.1	20.5 ± 1.1
		4	0.2 ± 0.0	2.4 ± 0.4	<LOD	3.6 ± 0.1	<LOD	8.1 ± 1.6	28.2 ± 0.3
	Treated	2	<LOD	<LOD	<LOD	0.2 ± 0.0	<LOD	0.4 ± 0.1	6.5 ± 1.3
		4	<LOD	<LOD	<LOD	0.5 ± 0.1	<LOD	1.9 ± 0.3	9.4 ± 1.3
5	Raw	2	0.2 ± 0.0	1.7 ± 0.2	0.9 ± 0.1	26.5 ± 1.0	16.8 ± 5.4	0.9 ± 0.1	63.4 ± 13.2
		4	0.2 ± 0.0	1.6 ± 0.1	1.7 ± 0.2	29.1 ± 2.1	17.9 ± 1.5	8.3 ± 1.9	74.4 ± 9.8
	Treated	2	<LOD	<LOD	<LOD	7.0 ± 1.1	<LOD	0.7 ± 0.1	35.7 ± 10.5
		4	<LOD	<LOD	<LOD	6.8 ± 0.3	<LOD	1.8 ± 0.2	30.5 ± 6.9

the issue of timing the grab samples to account for hydraulic retention times within the plants is avoided. For POCIS monitoring, most of the compounds showed a reduction in the amounts (ng/POCIS) accumulated from treated water relative to the amounts accumulated from raw water in each of the DWTPs, with examples highlighted in Fig. 2. Reductions were observed in treated water in both the two and four week deployments. The POCIS is likely to provide a better indicator of removal efficiency than grab sampling. For example, the most consistently detected compounds were carbamazepine, ibuprofen and sucralose, with detection frequencies of 100, 65 and 85%, respectively in POCIS, compared to 50, 20, and 77%, respectively in grab samples. Gemfibrozil (50% detects in POCIS; 13% in grabs) and estrone (60% in POCIS; 20% in grabs) were detected more frequently in POCIS, while sulfamethoxazole and trimethoprim were detected at similar frequencies using both monitoring approaches.

Time-weighted average concentrations estimated from POCIS data were generally consistent with data on the concentrations detected in SPE extracts from grab samples (Fig. 1). Based on the estimated concentrations, it is not surprising that many of the target compounds were present in SPE extracts at concentrations <LOQs or <LODs, as several of the compounds were estimated to be present at average concentrations below the LODs (Table 4). For sucralose and carbamazepine, which were the compounds most frequently detected in both the samples, the POCIS captured concentration differences among DWTPs. Plants which had higher concentrations of these compounds in the grab samples also had higher concentrations in the POCIS in both the 2 and 4 week samples (Fig. 1). The results for DWTPs 3 and 5 showed that the time-weighted average concentrations for sucralose estimated from POCIS were lower than the concentrations in grab samples by a factor of up to 10. However, for sucralose in DWTPs 1 and 4, grab sample concentrations and time-weighted estimates from POCIS were within a factor of 1–2 of each other (Tables 3 and 4). These comparisons between grab samples and POCIS must be interpreted with caution, since grab samples were only collected at 3 discrete points during the monitoring period and these samples may not reflect the exposure history over the entire deployment period.

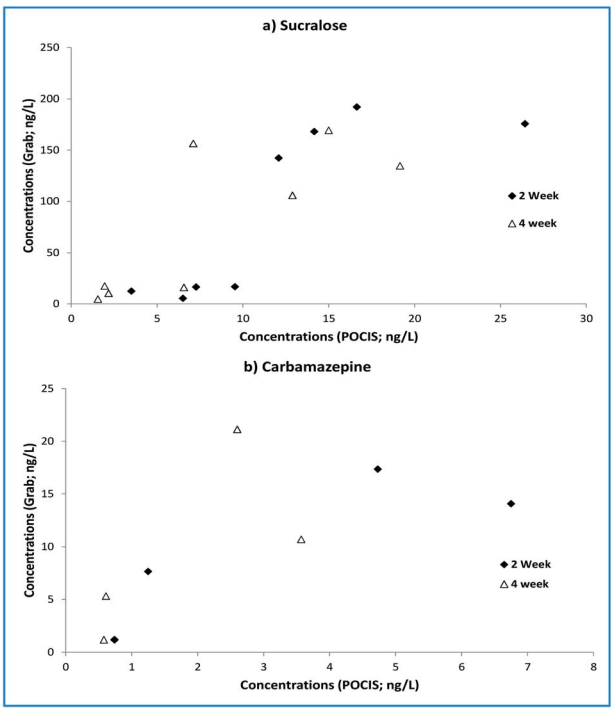

Fig. 1 Comparison of POCIS and grab sample concentrations in raw and treated drinking water in the 5 DWTPs for (a) sucralose and (b) carbamazepine.

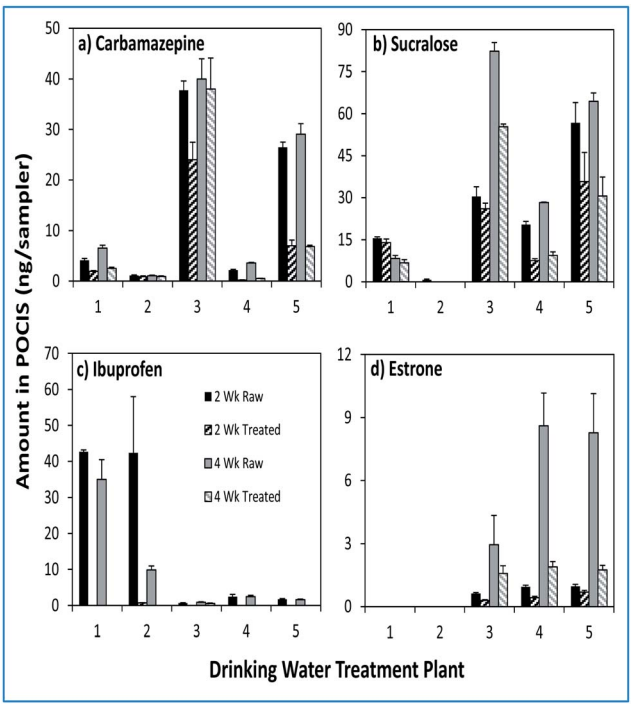

Fig. 2 Mean amounts of compounds in POCIS illustrating changes from raw to treated water in each of the DWTPs for (a) carbamazepine, (b) sucralose, (c) ibuprofen, and (d) estrone. All concentrations in treated water were significantly lower than in raw water, except for carbamazepine in DWTP 3 in week 4, and in DWTP 2 in weeks 2 and 4, and for sucralose in DWTPs 3 and 5 in week 2 (Mann Whitney *U* test, $P < 0.01$).

Risk considerations

The low ng L^{-1} concentrations of target compounds estimated using POCIS monitoring are consistent with other studies of CECs in drinking water. A variety of approaches have been used to evaluate whether contaminants of emerging concern detected in drinking water are a risk to human health, and these studies have generally shown that daily intakes of pharmaceuticals consumed in contaminated drinking water is several orders of magnitude below the therapeutic dose.[18,19] The World Health Organization recently published a report that concluded that the risk to human health was minimal as a result of exposure to pharmaceuticals in drinking water.[6]

Conclusions

The deployment of POCIS was found to be a useful technique for monitoring for CECs of wastewater origin. Pharmaceutical, hormone and artificial sweetener compounds were present in raw and treated drinking water from 5 DWTPs in Ontario, Canada. The concentrations in grab samples were typically below detection limits. However, POCIS samplers deployed in drinking water typically concentrated the contaminants to detectable levels, allowing for assessments of the differences in removal efficiencies between and within DWTPs. Concentrations estimated from POCIS were generally comparable to concentrations in grab samples. More work is required to understand the dynamic nature of the flux of PPCPs and EDCs between the POCIS sorbent and the surrounding aqueous matrix. Concentrations of the pharmaceuticals were several orders of magnitude lower than the concentrations that have been predicted to be a hazard to human health.

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References

1 M. R. Servos, M. Smith, R. McInnis, K. Burnison, B.-H. Lee, P. Seto and S. Backus, The presence of selected pharmaceuticals and the antimicrobial triclosan in drinking water in Ontario, Canada, *Water Qual. Res. J. Can.*, 2007, **42**, 130–137.
2 M. J. Focazio, D. W. Kolpin, K. K. Barnes, E. T. Furlong, M. T. Meyer, S. D. Zaugg, L. B. Barber and M. E. Thurman, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States – II untreated drinking water sources, *Sci. Total Environ.*, 2008, **402**, 201–216.
3 A. Garcia-Ac, P. A. Segura, L. Viglino, A. Furtos, C. Gagnon, M. Prevost and S. Sauve, On-line solid phase extraction of large-volume injections coupled to liquid chromatography-tandem mass spectrometry for the quantitation and confirmation of 14 selected trace organic contaminants in drinking and surface water, *J Chromatogr A*, 2009, **1216**, 8518–8527.
4 M. Benotti, R. Trenholm, B. Vanderford, J. Holady, B. Stanford and S. Snyder, Pharmaceuticals and endocrine disrupting compounds in US drinking water, *Environ. Sci. Technol.*, 2009, **43**, 597–603.
5 S. Kleywegt, V. Pileggi, P. Yang, C. Hao, X. Zhao, C. Rocks, S. Thach, P. Cheung and B. Whitehead, Pharmaceuticals, hormones and bisphenol A in untreated source and finished drinking water in Ontario, Canada – Occurrence and treatment efficiency, *Sci. Total Environ.*, 2011, **409**, 1481–1488.
6 WHO, *Pharmaceuticals in drinking water*, World Health Organization, Geneva, WHO/HSE/WSH/11.05, 2012, p. 35.
7 C. Harman, I. J. Allan and E. L. M. Vermeirssen, Calibration and use of the Polar Organic Chemical Integrative Sampler – A critical review, *Environ. Toxicol. Chem.*, 2012, **31**, 2724–2738.
8 N. Morin, C. Miege, J. Randon and M. Coquery, Chemical calibration, performance, validation, and applications of the polar organic chemical integrative sampler (POCIS) in aquatic environments, *Trends Anal. Chem.*, 2012, **36**, 144–175.

9 H. Li, P. Helm and C. Metcalfe, Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine disrupting substances using the passive polar organic chemical integrative sampler, *Environ. Toxicol. Chem.*, 2010, **29**, 751–762.

10 K. A. McCarthy, D. Alvarez, C. W. Anderson, W. L. Cranor, S. D. Perkins and V. Schroeder, *Evaluation of passive samplers for long-term monitoring of organic compounds in the untreated drinking water supply for the city of Eugene, Oregon, September-October 2007*, U.S. Geological Survey Scientific Investigations Report, 2009, vol. 5178, p. 20.

11 K. A. McCarthy, D. A. Alvarez and J. H. Goldman, *Water quality data from semipermeable membrane devices and polar organic chemical integrative samplers deployed in the McKenzie River Basin*, Oregon: U.S. Geological Survey Data Series, 2012, vol. 692, p. 6.

12 T. L. Jones-Lepp, C. Sanchez, D. A. Alvarez, D. C. Wilson and R.-L. Taniguchi-Fu, Point sources of emerging contaminants along the Colorado River Basin: Source water for the arid southwestern United States, *Sci. Total Environ.*, 2012, **430**, 237–245.

13 R. V. Dickenson, S. A. Snyder, D. Sedlak and J. E. Drewes, Indicator compounds for assessment of wastewater effluent contributions to flow and water quality, *Water Res.*, 2011, **45**, 1199–1212.

14 D. B. Mawhinney, R. B. Young, B. J. Vanderford, T. Borch and S. A. Snyder, Artificial sweetener sucralose in U.S. drinking water systems, *Environ. Sci. Technol.*, 2011, **45**, 8716–8722.

15 (*a*) C. Harman, O. Boyum, K. V. Thomas and M. Grung, Small but different effect of fouling on the uptake rates of semi-permeable membrane devices and polar organic chemical integrative samplers, *Environ. Toxicol. Chem.*, 2009, **28**, 2324–2332; (*b*) X. Miao and C. D. Metcalfe, Pharmaceutical analysis in aqueous samples usingpositive and negative voltage switching microbore LC-ESI-MS/MS, *J. Mass Spectrom.*, 2003, **38**, 27–34.

16 C. Harman, M. Reid and K. V. Thomas, In situ calibration of a passive sampling device for selected illicit drugs and their metabolites in wastewater, and subsequent year-long assessment of community drug usage, *Environ. Sci. Technol.*, 2011, **45**, 5676–5682.

17 N. Morin, J. Camilleri, C. Cren-Olivé, M. Coquery and C. Miège, Determination of uptake kinetics for 56 organic micropollutants using "pharmaceutical" POCIS, *Talanta*, 2013, **109**, 61–73.

18 O. A. Jones, J. N. Lester and N. Voulvoulis, Pharmaceuticals: a threat to drinking water?, *Trends Biotechnol.*, 2005, **23**, 163–167.

19 D. S. Bachman and A. Sapkota, Presence of pharmaceuticals and personal care products in the environment – A concern for human health?, in *Contaminants of Emerging Concern in the Environment: Ecological and Human Health Considerations*, ed. R. U. Halden, ACS Symposium Series1048, American Chemical Society, Washington, DC, USA, 2010, pp. 345–365.