Fate and mass balances of triclosan (TCS), tetrabromobisphenol A (TBBPA) and tribromobisphenol A (tri-BBPA) during the municipal wastewater treatment process
Kerry McPhedran, Rajesh Seth, Min Song, Shaogang Chu and Robert J. Letcher

ABSTRACT
Municipal wastewater treatment plants (MWTPs) are impacted by down-the-drain influents of anthropogenic chemicals. These chemicals are in consumer products and include the flame retardant tetrabromobisphenol A (TBBPA) and antimicrobial triclosan (TCS). Characterization of the distribution of TBBPA, TCS and the TBBPA product tribromobisphenol A (tri-BBPA) was determined at five stages along the treatment process of a typical Canadian MWTP facility. Overall, the TCS concentrations for both liquid (influents, primary effluents and final effluents (FEs)) and solid samples (primary and waste activated sludges) were similar to reported ranges in the literature. In contrast to TCS, both TBBPA and tri-BBPA concentrations were scarcely available in the literature. The TBBPA concentrations were within literature ranges for both influents and sludges, while the tri-BBPA sludge concentrations were markedly higher than a single available previous study. Mass balances for TCS, TBBPA and tri-BBPA indicated 7, 9 and 42%, respectively, of each chemical remaining in the FEs. The resultant annual mass loadings into the Detroit River were estimated to be 3.3 kg, 6.57 g, and 21.5 g for TCS, TBBPA and tri-BBPA, respectively.

INTRODUCTION
For over half a century organic contaminants have progressed into municipal sewer systems through down-the-drain anthropogenic products (Lee & Peart 2002). In the past 25 years research has been developed in the fate and transport and identification of these contaminants in municipal wastewater treatment plants (MWTPs) within Canada and worldwide (Lee et al. 2005). Generally, chemicals are added to products with the goal of mediating human-health concerns and include chemical classes such as personal care products (PPCPs) which may include endocrine disrupting compounds (EDCs). The PPCPs and EDCs are two groups of organic contaminants of interest over the last decade due to their potential environmental risk following human use, release into sewer systems and transport via influents to MWTPs. These influents are subsequently discharged carrying both the parent compounds and metabolites into the environment via final effluents (FEs) and land-applied biosolids (Langdon et al. 2011). Recently, it was reported that 78% of the Canadian population wastewaters are treated with secondary and tertiary (advanced treatment) in 1999 (Environment Canada 2001). These MWTPs include a primary treatment process, which removes particles via settling, followed by a secondary treatment process, which degrades organic chemicals biologically using activated sludge (AS) (Lee & Peart 2002). However, hydrophobic or lipophilic chemicals such as triclosan (TCS) and
tetrabromobisphenol A (TBBPA) may sorb to solids, thus avoiding degradation and accumulating in sludges.

One of the most commonly used PPCPs worldwide is TCS which is an antimicrobial additive widely used as a preservative and disinfectant in personal care (e.g. soaps, toothpaste) and consumer products (e.g. footwear, plastic products) (Daughton & Ternes 1999; Lindstrom et al. 2002). Recently, TCS has been included in a list of 90 chemicals that are suspected risks to human or environmental health in the European Union REACH regulation of chemicals (ECHA 2012) and has been frequently detected in US streams with MWTP effluent discharges being recognized as the predominant input sources (Kolpin et al. 2002). In Canada, TCS has recently been assessed for human and environmental health effects with the goal to develop policies for the reduction of TCS use in PPCPs (Environment Canada 2012). TCS is hydrophobic with a log$K_{OW}$ of 4.8 making bioaccumulation possible in human and wildlife tissues (McAvoy et al. 2002). TCS has been found in human samples including breast milk (Adolfsson-Erici et al. 2002; Dayan 2007) and can degrade to chlorinated dibenzodioxins, which are carcinogenic (Lores et al. 2005). TCS may be acutely toxic to various aquatic species including algae, invertebrates and fish (Orvos et al. 2002; Ishibashi et al. 2004; Dussault et al. 2008). Several worldwide studies have examined TCS concentrations in various streams (influent, effluent, sludges) of a MWTP (Tables 1 and 2). However, few studies have reported measurements for all streams to allow better understanding of the fate and transport of TCS during the MWTP process (McAvoy et al. 2002; Bester 2003; Heidler & Halden 2007; Stasinakis et al. 2008). Despite the general reporting of TCS MWTP concentrations for Canadian MWTPs, a detailed examination of TCS fate during the MWTP process has not been considered previously (Table 1).

A chemical suite in the EDC group are the brominated flame retardants including TBBPA. TBBPA is the most abundantly produced flame retardant worldwide with over 170,000 tonnes produced in 2004 accounting for 59% of the brominated flame retardant production (Law et al. 2006; George & Häggblom 2008). TBBPA is a reactive flame retardant that is found in polymers and acrylonitrile butadiene styrene (ABS) plastics (WHO 1995) that is hydrophobic (log$K_{OW} = 4.5$) resulting in the potential for bioaccumulation (Sellström & Jansson 1995). Also, a moiety of TBBPA structure is similar to the thyroid hormone thyroxine and has been found to bind to trans-thyretin in vitro (Meerts et al. 2000; de Wit 2002; Danerud 2003). Historically, TBBPA and many other flame retardants are assumed safe in the environment so no regulations have been imposed upon TBBPA production

### Table 1 | Concentration ranges of triclosan (TCS), tetrabromobisphenol A (TBBPA) and tribromobisphenol A (tri-BBPA) from municipal wastewater treatment plants in Canada

<table>
<thead>
<tr>
<th>Compound</th>
<th>Study</th>
<th>Sites</th>
<th>TCS</th>
<th>TBBPA</th>
<th>tri-BBPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Influent (μg L⁻¹)</td>
<td>Lee et al. (2005)</td>
<td>9 sites</td>
<td>0.38–3.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lee et al. (2005)</td>
<td>8 sites</td>
<td>0.87–1.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lishman et al. (2006)</td>
<td>12 sites</td>
<td>1.95c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Effluent (μg L⁻¹)</td>
<td>Lee et al. (2005)</td>
<td>9 sites</td>
<td>0.05–0.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hua et al. (2005)</td>
<td>1 site</td>
<td>0.06–0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lee et al. (2005)</td>
<td>8 sites</td>
<td>0.05–0.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lishman et al. (2006)</td>
<td>12 sites</td>
<td>0.108c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludges (TCS: μg g⁻¹; TBBPA and tri-BBPA: ng g⁻¹)</td>
<td>Lee &amp; Peart (2002)</td>
<td>12 sites (PS)a</td>
<td>3.4–17.9</td>
<td>&lt;1.0–46.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>21 sites (AS)b</td>
<td>0.9–28.2</td>
<td>3.8–27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Chu et al. (2005)</td>
<td>2 sites (AS)b</td>
<td>0.62–1.45</td>
<td>2.1–28.3</td>
<td>0.11–0.26</td>
</tr>
<tr>
<td></td>
<td>Chu &amp; Metcalfe (2007)</td>
<td>2 sites (AS)b</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a*: primary sludge;  
*b*: activated sludge;  
*c*: mean: individual values not reported.
In contrast to TCS, TBBPA concentrations in MWTPs have not been reported extensively (Tables 1 and 2) and no previous study includes all MWTP streams, which may be used in determination of fate and transport processes. TBBPA is resistant to biodegradation and would not be expected to degrade during the MWTP process based on EPISUITE™ BIOWIN model predictions (US EPA 2012). A possible degradation pathway of TBBPA via dehalogenation to tribromobisphenol A (tri-BBPA) with the final product of bisphenol A has been suggested (Ronen & Abeliovich 2000, Chu et al. 2005) and Guerra et al. (2010) have reported the product tri-BBPA in wastewater sludge. However, detailed examination of tri-BBPA concentrations during the MWTP process has not been conducted.

Despite the potential of human and environmental health risks for TCS, TBBPA and tri-BBPA, there have been few reported Canadian studies of their MWTP concentrations (Table 1). In Canadian MWTPs TCS concentrations in influents (0.38–5.24 μg L⁻¹) generally decrease over 90% via sorption and degradation processes with resulting discharge in effluents of 0.03–0.74 μg L⁻¹. The sorption process results in TCS sludge concentrations of 0.26 ng g⁻¹. The concentrations of TBBPA in Canadian MWTP processes have only been reported in sludges ranging from <1.0 to 330 ng g⁻¹ (Table 1). Similarly, tri-BBPA concentrations of 0.11–0.26 ng g⁻¹ have been reported in a single Canadian MWTP study (Table 1). In the present study, we carried out a detailed examination of the concentrations of TCS, TBBPA and tri-BBPA in the influent, effluent and primary/secondary sludges of the MWTP process in Little River Pollution Control Plant (LRPCP) located in Windsor, Ontario, Canada. The monitored concentrations and resultant mass flows are determined with the goal of elucidating factors affecting chemical fate and transport processes.

**Table 2** Concentration ranges of triclosan (TCS), tetrabromobisphenol A (TBBPA) and tribromobisphenol A (tri-BBPA) from municipal wastewater treatment plants worldwide

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample</th>
<th>Site</th>
<th>Range</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCS</td>
<td>Influent (μg L⁻¹)</td>
<td>Canada</td>
<td>0.38–3.24</td>
<td>1–3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>USA</td>
<td>0.25–86.2</td>
<td>4–9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Europe</td>
<td>0.23–21.9</td>
<td>10–16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>China</td>
<td>0.14–2.30</td>
<td>17–19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Japan</td>
<td>0.06–1.00</td>
<td>20–21</td>
</tr>
<tr>
<td></td>
<td>Effluent (μg L⁻¹)</td>
<td>Canada</td>
<td>0.03–0.74</td>
<td>1–3, 22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>USA</td>
<td>0.01–5.37</td>
<td>4–7, 9, 23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Europe</td>
<td>0.01–2.21</td>
<td>10–13, 15–16, 24–25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>China</td>
<td>0.02–1.02</td>
<td>17, 28–29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Japan</td>
<td>0.03–0.36</td>
<td>20, 30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Australia</td>
<td>0.02–0.43</td>
<td>31–32</td>
</tr>
<tr>
<td></td>
<td>Sludges (μg g⁻¹; dw⁻¹)</td>
<td>Canada</td>
<td>0.90–28.2</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>USA</td>
<td>0.52–12.6</td>
<td>7–9, 34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Europe</td>
<td>0.46–1.49</td>
<td>13, 15, 35</td>
</tr>
<tr>
<td>TBBPA</td>
<td>Influent (ng L⁻¹)</td>
<td>Europe</td>
<td>2.6–85</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>Sludges (ng g⁻¹; dw⁻¹)</td>
<td>Canada</td>
<td>&lt;1–330</td>
<td>33, 37–38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Europe</td>
<td>&lt;0.3–1.330</td>
<td>36, 39–41</td>
</tr>
<tr>
<td>tri-BBPA</td>
<td>Sludges (ng g⁻¹; dw⁻¹)</td>
<td>Canada</td>
<td>0.11–0.26</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Europe</td>
<td>nd³–640</td>
<td>41</td>
</tr>
</tbody>
</table>

³dw: dry weight basis.
²nd: not detected.

1) Lee et al. (2005); 2) Lee et al. (2003); 3) Listman et al. (2006); 4) Waltman et al. (2006); 5) Thomas & Foster (2005); 6) Halden & Paull (2005); 7) McAvoy et al. (2010); 8) Kumar et al. (2010); 9) Yu & Chu (2009); 10) Thompson et al. (2005); 11) Sabalkunas et al. (2003); 12) Bester (2003); 13) Bester (2005); 14) Weigelt et al. (2004); 15) Pothiou & Voutsas (2008); 16) Kantianl et al. (2008); 17) Wu et al. (2010); 18) Guo et al. (2009); 19) Yu et al. (2011); 20) Nakada et al. (2006); 21) Nishi et al. (2008); 22) Hua et al. (2005); 23) Boyd et al. (2003); 24) Singer et al. (2002); 25) Lindstrom et al. (2002); 26) Aguera et al. (2003); 27) Pageus (1996); 28) Zhao et al. (2010); 29) Peng et al. (2008); 30) Harada et al. (2008); 31) Ying & Kookana (2007); 32) Kookana et al. (2011); 33) Lee & Peart (2002); 34) McClellan & Halden (2010); 35) Nieto et al. (2009); 36) Morris et al. (2004); 37) Saint-Louis & Pelletier (2004); 38) Chu et al. (2005); 39) Selßström & Jansson (1995); 40) Öberg et al. (2002); 41) Guerra et al. (2010).
EXPERIMENTAL METHODS

Sampling

LRPCP is located in Windsor, Ontario, Canada. The plant serves the eastern portion of the City of Windsor and the surrounding municipalities of Tecumseh, St Clair Beach and Sandwich South, and has two parallel and similar AS-type secondary wastewater treatment systems with a combined design capacity of 60,000 m$^3$ d$^{-1}$. The actual flow rates on three sampling dates ranged from 24,480 to 33,600 m$^3$ d$^{-1}$. The volumes of the primary settling tank, aeration tank and secondary settling tank at LRPCP are 6,314, 6,620 and 5,399 m$^3$, respectively.

Three sets of samples were collected on separate days between 9:00 AM and 12:00 PM under normal dry weather conditions over a 6-week period (March–May 2004). On each sampling occasion grab samples were collected in pre-cleaned glass bottles or jars at different stages of the treatment process including (Figure 1): influent to primary sedimentation tanks (IN), primary sedimentation tank effluent (PE), primary sludge (PS), waste AS and FE. The three liquid samples (IN, PE and FE) were collected in 4 L glass bottles each, whereas the two sludge samples were collected in two 1.5 L glass jars each. Samples were transported to the laboratory within 2 hours of collection and stored at 4 $^\circ$C prior to chemical analysis.

Liquid samples (IN, PE and FE) were filtered through glass fiber filters (1.6 $\mu$m prefilter followed by 1.0 $\mu$m filter, Fisher Scientific, Canada) to separate into dissolved and solid fractions. A 50 mL sample of each of the two sludges (PS, AS) was centrifuged at 12,000 g for 20 minutes at 4 $^\circ$C. The supernatant was filtered through a glass fiber filter (1.0 $\mu$m filter, Fisher Scientific) to obtain the dissolved fraction.

Sample extraction and polycyclic aromatic hydrocarbon analysis

Chemicals

TBBPA and TCS were obtained from Aldrich Chemical Co. (WI, USA) and were of minimum 97% purity. 2'-HO-CB72 was kindly supplied by Dr Göran Marsh (Department of Environmental Chemistry, Stockholm University, Sweden). tri-BBPA was a kind gift from Drs Göran Marsh and Åke Bergman (Department of Environmental Chemistry, Stockholm University, Sweden). TBBPA-$^{13}$C$_{12}$ and TCS-$^{13}$C$_{12}$ were obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Anhydrous sodium sulfate was purchased from VWR international Inc. (ON, Canada) and pretreated in a muffle furnace at 650 $^\circ$C for 12 hours to destroy all possible organic contamination. N-nitroso-N-methylurea was obtained from Aldrich Chemical Co. (WI, USA). All other solvents used (hexane, dichloromethane (DCM), methanol, acetone, tert-butyl methyl ether (MTBE)) were OMNISOLV® grade solvents purchased from VWR International Inc. (Mississauga, ON, Canada).

Extraction and cleanup

Detailed analytical methods for TBBPA and tri-BBPA (Chu et al. 2005) and TCS (Chu & Metcalfe 2007) are described elsewhere and briefly described herein.

Solid fractions obtained after centrifugation (PS, AS) and captured on filtration (IN, PE and FE) were ground with 50 g anhydrous sodium sulfate in a glass mortar. The mixture was transferred to a glass extraction thimble and spiked with HO-CB72 as an internal standard. The mixture was Soxhlet extracted with hexane/acetone (50/50, v/v) for 12 hours. Dissolved 1 L samples (IN, FE and PE) were extracted with 3 × 50 mL DCM. Extracts were collected and concentrated to approximately 2 mL under a gentle nitrogen stream. Each extract was transferred to a 60 mL separatory funnel, extracted by 3 × 6 mL 1 M KOH.
water/ethanol solution (50/50, v/v), and the aqueous phase transferred into a 50 mL screw-top centrifuge tube. The combined aqueous solution was washed with 6 mL hexane.

The dissolved fractions after solids centrifugation (PS, AS) were acidified with H2SO4 to pH = 2 and extracted by 6 mL MTBE/hexane (50/50, v/v) three times. The MTBE/hexane solution was dried via a Na2SO4 dry column, concentrated to approximately 1 mL, and transferred into a 15 mL centrifuge tube rinsing with 2 mL hexane. The volume was concentrated to approximately 0.5 mL and was ready for derivatization.

Target compounds and internal standard in the samples were derivatized to their MeO-analogs through a methylamination reaction using diazomethane prepared in hexane with N-nitroso-N-methylurea in a biphasic mixture of sodium hydroxide and hexane. After derivatization, the sample solution was concentrated to approximately 1 mL, cleaned via a sulfuric acid silica column (6 g, concentrated sulfuric acid/silica = 39%), and the derivatized target compounds and internal standard were eluted with 140 mL DCM. Eluent was concentrated, solvent exchanged to isooctane and reduced to 100 μL for gas chromatograph (GC)/mass spectrometer detector (MSD) determination.

**GS/MSD determination**

An Agilent GC 6890 equipped with a 5,973 quadrupole MSD was used for determination of tri-BBPA, TBBPA and TCS. The GC column was a 30 m × 0.25 mm ID HP-5MS capillary column with a film thickness of 0.25 μm. Helium was the carrier gas at a flow of 1 mL min⁻¹. One microliter of sample was injected in splitless mode with an injector temperature of 280 °C and a purge time of 1 min after injection. Oven temperature program was: 80 °C, hold for 2 min, then at 10 °C min⁻¹ to 290 °C and hold for 15 min. MS ionization was performed in electron capture negative ionization (ECNI) mode using methane as reagent gas. The transfer line, source and quadrupole temperatures were 280, 250 and 150 °C, respectively. The optimized operational parameters and transition ions monitored are available in Chu & Metcalfe (2007; Table 2) for TCS and Chu et al. (2005; Table 1) for TBBPA and tri-BBPA. The identification of analyte was based on retention times and the ratios of monitored ions. Quantitative determination was carried out using the internal standard method. The internal standard for the BPA chemicals was 13C₁₂-labeled TBBPA prepared in methanol. The internal standard for TRC was 13C₁₂-labeled TRC prepared in methanol. The limit of detection (LOD) is defined as the minimum amount of analyte, which produces a peak with a signal-to-noise ratio equal to 3.

**RESULTS AND DISCUSSION**

Plant operating data for the three sampling occasions are found in Tables S1 and S2 of the Supporting Information from Song et al. (2006); additionally, total suspended solids and volatile suspended solids measurements are given in Tables S3 and S4 of Song et al. (2006). The average PS flow rate of 138,000 L d⁻¹ was used in the current calculations and is not included in Song et al. (2006).

**Influent concentrations**

Average influent TCS concentrations were 4.53 μg L⁻¹ with a range of 4.46–4.57 μg L⁻¹ (Table 3). These concentrations were similar to the majority of US and Europe MWTPs; however, they were higher than reported in Canada, China and Japan MWTPs (Tables 1 and 2). Extreme values were determined at one site in the USA (26.8 μg L⁻¹) although median concentrations were similar to the current study (5.95 μg L⁻¹), the extreme values being attributed to seasonal variability (Waltman et al. 2006). In a recent US study Kumar et al. (2010) found influent TCS concentrations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample</th>
<th>Mean ± SDa</th>
<th>Range</th>
<th>LODc</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCS</td>
<td>Influent (μg L⁻¹)</td>
<td>4.53 ± 0.62</td>
<td>4.46–4.57</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Final effluent (μg L⁻¹)</td>
<td>0.33 ± 0.15</td>
<td>0.24–0.50</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Sludges (μg g⁻¹; dwb)</td>
<td>5.29 ± 1.96</td>
<td>3.05–6.73</td>
<td>0.01</td>
</tr>
<tr>
<td>TBBPA</td>
<td>Influent (ng L⁻¹)</td>
<td>5.27 ± 2.13</td>
<td>2.81–6.51</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Final effluent (ng L⁻¹)</td>
<td>0.70 ± 0.30</td>
<td>0.50–1.05</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Sludges (ng g⁻¹; dwb)</td>
<td>56.3 ± 17.8</td>
<td>19.9–57.8</td>
<td>0.02</td>
</tr>
<tr>
<td>tri-BBPA</td>
<td>Influent (ng L⁻¹)</td>
<td>1.81 ± 0.48</td>
<td>1.26–2.16</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Final effluent (ng L⁻¹)</td>
<td>2.10 ± 1.45</td>
<td>0.54–3.42</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>Sludges (ng g⁻¹; dwb)</td>
<td>16.8 ± 8.61</td>
<td>7.23–24.0</td>
<td>0.01</td>
</tr>
</tbody>
</table>

aSD: standard deviation.
b dw: dry weight.
c LOD: limit of detection.
over 86 μg L⁻¹; however, reasons for these elevated concentrations were not discussed. One site with a high concentration in Europe (21.9 μg L⁻¹) was attributed to per capita water use being very low (Sabaliunas et al. 2003). Lee et al. (2005) found a median concentration of 0.83 μg L⁻¹ for nine MWTP locations in southern Ontario; however, further study of eight of these locations found an increase in the median concentration to 1.35 μg L⁻¹ (Lee et al. 2005). Lishman et al. (2006) found a median concentration of 1.93 μg L⁻¹ for 12 MWTP locations in southern Ontario. Given the similar geographic areas and assumed similar socioeconomic data in Europe (Table 2). Unfortunately, the ent concentration of human-use chemicals such as TCS and TBBPA can be dependent on many factors including location, socioeconomic status, pharmaceutical cost and other demographic data (Thomas & Foster 2005). Also, influent concentrations are dependant on population served with per capita use values being of greater interest since they negate the effects of variable water usage rates and MWTP population served. Using the population served by LRPCP (80,000 persons) the resultant mass loadings to LRPCP are 0.57 g cap⁻¹ y⁻¹ for TCS and 0.91 mg cap⁻¹ y⁻¹ for TBBPA. Since comparative data are not available for TBBPA, comparisons between studies may only be considered for TCS. The TCS loading is within the range of loadings of other studies in Europe (0.29–1.40 g cap⁻¹ y⁻¹) (Sabaliunas et al. 2003; Bester 2005). For the USA, loading was approximately 2–3 times higher than the present data at 1.03–1.83 g cap⁻¹ y⁻¹ (McAvo et al. 2002; Halden & Paull 2005). Since the per capita usage rates negate the water usage data, the populations served by the MWTPs in the US studies appear to be using products containing TCS at higher rates than the current MWTP. Unfortunately, loading data for both Canadian studies could not be determined due to lack of data (Lee et al. 2003, 2005).

Effluent

TCS concentrations in FEs averaged 0.33 μg L⁻¹ with a range of 0.24–0.50 μg L⁻¹ (Table 3). The average concentration fell within the wide ranges of all locations; however, they were generally higher than most US, China, Japan and Australia MWTPs. These MWTPs had an order of magnitude lower concentrations in FEs which were for the most part in the lower concentrations of each reported range (Tables 1 and 2). As would be expected, the highest influent concentrations reported by Kumar et al. (2010) resulted in the highest effluent concentrations (5.37 μg L⁻¹) which were an order of magnitude higher than the current study (0.33 μg L⁻¹). An extremely high concentration (22.1 μg L⁻¹) was reported in Europe by Aguera et al. (2003) and was attributed to insufficient treatment application in the MWTP. Given the similar influent loading rates of the US MWTPs and the current study, the reduction efficiency of the US MWTP processes appear to be markedly higher than that of the LRPCP. Thomas & Foster (2005) noted that variations could be attributed to both efficiency of the MWTPs, which is dependent on uncontrolled variables (e.g. temperature), as well as differences in both sampling and extraction technique.

The resulting TCS loading to surface waters via effluents (Table 3) was determined to be 3.5 kg y⁻¹ or 40.8 mg cap⁻¹ y⁻¹. This loading was marginally higher
than the range of reported loadings in Europe (14.5–70 mg cap\(^{-1}\) y\(^{-1}\)) (Sabaliunas et al. 2003; Bester 2005) and in the USA (10.3–66.5 mg cap\(^{-1}\) y\(^{-1}\)) (McAvoy et al. 2002; Halden & Paull 2005). Despite the similar effluent concentrations with the European studies, the variations in per capita loadings can be attributed to variable water usage. Per capita measures for other Canadian studies could not be determined due to lack of data availability (Lee et al. 2003, 2005). Interestingly, LRPCP only accounts for 10% of the total population of MWTP discharges to the Detroit River, thus, total loading of TCS to this river system is expected to exceed 33 kg y\(^{-1}\).

To our knowledge, no other study has previously reported on effluent TBBPA concentrations. The TBBPA concentrations in FEs averaged 0.70 ng L\(^{-1}\) with a range of 0.50–0.97 ng L\(^{-1}\) (Table 3). The resulting loading to the ecosystem was determined to be 6.57 g y\(^{-1}\) or 82.1 μg cap\(^{-1}\) y\(^{-1}\). As for the influents, this per capita value may be used for comparison of ecosystem loading in subsequent studies.

**Sludges**

The average TCS concentration in sludges was 5.29 μg g\(^{-1}\) with a range of 3.05–6.73 μg g\(^{-1}\) (Table 3), which were comparable to studies in Canada, USA and Europe (Tables 1 and 2). McAvoy et al. (2002) found higher concentrations in PS (8.75–14.7 μg g\(^{-1}\)) than in secondary sludges (0.90–4.20 μg g\(^{-1}\)). Extreme values over 20.0 μg g\(^{-1}\) were determined at four of 35 sites throughout Canada with a median value of 12.5 μg g\(^{-1}\) (Lee & Peart 2002).

TBBPA average concentrations of 21–56 ng g\(^{-1}\) fell within the range of comparable studies in Canada and Europe (Tables 1 and 2). Extreme values of 350 ng g\(^{-1}\) for Quebec, Ontario (Saint-Louis & Pelletier 2004) and 600 ng g\(^{-1}\) for the Netherlands (Morris et al. 2004) were found; however, possible explanations for high values were not given.

The fate of TCS and TBBPA in sewage sludges is of increasing concern due to potential adverse effects to the AS process (Federle et al. 2002), use of contaminated biosolids as agricultural fertilizers and potential by-products of sludge incineration where brominated flame retardants may produce carcinogens such as brominated dibenzofurans and dibenzodioxins (Borojovich & Aizenshtat 2002; Saint-Louis & Pelletier 2004).

**Tri-BBPA concentrations**

Influent and effluent tri-BBPA concentration ranges were 1.0–2.2 and 0.6–3.4 ng L\(^{-1}\), respectively (Table 3). No other known previous studies included influent or effluent tri-BBPA concentrations. The resulting loading to surface waters via effluents was determined to be 21.5 g y\(^{-1}\) or 0.27 μg cap\(^{-1}\) y\(^{-1}\). Sludge tri-BBPA concentrations of 7.2–24.0 ng g\(^{-1}\) were of the order of two magnitudes higher than previous concentrations at LRPCP by Chu et al. (2003), while Guerra et al. (2010) reported higher concentrations of up to 640 ng g\(^{-1}\) for MWTPs in Europe. Despite these marked differences, comparisons between studies may be difficult due to the lack of influent and FE concentrations in the previous studies that would aid in determining possible variations in loadings.

Commercial sources of tri-BBPA production are unknown; however, commercially produced TBBPA may contain small amounts of tri-BBPA as a by-product (Eriksson et al. 2004). Despite this lack of commercial production, tri-BBPA was found in the current sewage influent with a concentration in the same order of magnitude of TBBPA (Table 2). Environmental sources of pure tri-BBPA are minimal, which suggests that degradation of TBBPA to tri-BBPA can potentially be occurring in the collection system prior to the treatment plant (Ronen & Abieliovich 2000; Eriksson et al. 2004). However, further elucidation of tri-BBPA sources is still needed. During the MWTP process, degradation and partitioning properties of TBBPA has been poorly studied with conflicting results. WHO/ICPS (1995) found that no biodegradation of TBBPA was detected, as measured as biological oxygen demand in a 2-week period. Alternatively, debromination of TBBPA to partially brominated BPA metabolites has been suggested to occur in a stepwise fashion. However, the process would require an anaerobic phase, which is not available in the strictly aerobic MTWP in the current study (Ronen & Abieliovich 2000). Further study of TBBPA will be needed to elucidate potential metabolic pathways that may include biodegradation or other degradation processes to tri-BBPA and other metabolites.

**Mass flows**

Due to the dynamic nature of chemical loadings, the use of ‘grab’ samples and the variations of both solids and hydraulic retention times, the balances of chemical mass ‘flows’ within
MWTPs presented in the current study should be considered as approximate. The LRPCP includes a typical activated-sludge process with removal of PS approximately five times per week and an AS age of approximately 10 d. Since degradation of TBBPA and tri-BBPA is expected to be insignificant based on model predictions (EPISUITE™ BIOWIN; US EPA 2012), input mass calculated based on their concentrations in the two sludges and FE (sum of total outputs) is expected to be more representative of time-weighted average as compared to that calculated based on the ‘grab’ influent sample concentration (Figure 2(b), (c); Song et al. 2006). The same approach cannot be applied for TCS since biodegradation is expected to be a significant loss or ‘output’ process. Influent TCS concentrations in the three samples collected over a period of 6 weeks (Table 2) show limited variability and therefore for the mass balance of TCS the influent mass is calculated based on the measured influent concentration (Figure 2(a)).

Estimated TCS reduction of 93% during the treatment process at LRPCP (Figure 2(a)) is similar to the reported reduction range of 94–98% (Table 4); however, there are differences in the reduction pathways. In the current study, TCS reduction by sorption to sludges is estimated to be 22%, which is lower than the 30–35% reduction reported by Bester (2005) and McAvoy et al. (2002) (Table 4). Additionally, Heidler & Halden (2007) and Stasinakis et al. (2008) have reported higher reductions of 45–50% by sorption to sludges. TCS reduction of 71% was attributed to degradation in the current study, which is somewhat higher than the 61–65% reported by Bester (2003) and McAvoy et al. (2002), with lower TCS reductions by degradation of 46–48% being reported by Heidler & Halden (2007) and Stasinakis et al. (2008). Since degradation is a significant pathway of reduction of TCS, part of the observed variability in reduction pathways may be attributable to differences in hydraulic and solids retention times, populations and type of wastewater being treated (Guerra et al. 2010). Some of the difference could also be due to mass balance errors resulting from sampling. Overall, the results suggest >90% reduction of TCS may be expected in a typical secondary wastewater treatment plant with sorption to sludges and degradation being the dominant reduction pathways which are expected to vary under various plant operating conditions.

Based on the mass balances presented in Figure 2(b) and (c), TBBPA and tri-BBPA reduction in the current study are estimated to be 91 and 92%, respectively, with partitioning to sludge as the only dominant process. These results cannot be compared with literature values since mass balances for the two compounds have not previously been reported. However, these reductions are in good agreement with those reported by other studies (Table 4).

**Table 4** Overall reduction of triclosan during the treatment process for current MWTP and from various other studies which included influent, final effluent (FE) and sludge concentrations

<table>
<thead>
<tr>
<th>Reference</th>
<th>FE (%)</th>
<th>Sludge (%)</th>
<th>Overall reduction (%)</th>
<th>Losses (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>7</td>
<td>22</td>
<td>93</td>
<td>71</td>
</tr>
<tr>
<td>McAvoy et al. (2002)</td>
<td>4</td>
<td>35</td>
<td>96</td>
<td>61</td>
</tr>
<tr>
<td>Bester (2005)</td>
<td>4</td>
<td>30</td>
<td>96</td>
<td>65</td>
</tr>
<tr>
<td>Heidler &amp; Halden (2007)</td>
<td>2</td>
<td>50</td>
<td>98</td>
<td>48</td>
</tr>
<tr>
<td>Stasinakis et al. (2008)</td>
<td>9</td>
<td>45</td>
<td>91</td>
<td>46</td>
</tr>
<tr>
<td>Ref. mean</td>
<td>5</td>
<td>40</td>
<td>95</td>
<td>55</td>
</tr>
</tbody>
</table>

![Figure 2](https://www.ijerph.org/content/14/14/15287.full.pdf)
with the EPISUITETM BIOWIN model predictions of a total reduction of 93% for both TBBPA and tri-BBPA, respectively, which is almost entirely (92%) attributed to sorption to sludge.

**CONCLUSIONS**

Sources of TCS, TBBPA and tri-BBPA are exclusively anthropogenic. The concentration ranges of TCS and TBBPA currently are in reasonable agreement with available literature values. Loadings of TCS, TBBPA and tri-BBPA in MWTP influents are important for treatment considerations; however, FE and sludge concentrations are of the utmost concern for ecosystem health and safety. Given the concentrations of these chemicals in MWTP effluents, it is apparent that they are not completely removed in the MWTP process. The resultant mass loadings of these chemicals to the environment can become substantial over the period of a year, thus concerns arise over environmental fate and potential risks of bioaccumulation potential in aquatic organisms. Further investigation into the fate and transport of these chemicals is required in order to determine the effects of their continuous input into the environment.

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