Phase partitioning, transport and sources of Benzotriazole Ultraviolet Stabilizers during a runoff event

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ABSTRACT

Benzotriazole Ultraviolet Stabilizers (BT-UVs) are ubiquitous in the environment, given their wide use as additives in consumer products. Their bio-accumulative and toxic properties are increasingly being scrutinised, evidenced by the recent proposition to add UV328 to the Stockholm Convention on Persistent Organic Pollutants. Here, we measured concentrations of six BT-UVs in the dissolved and particulate phases of stream water collected from an urban and rural stream during a runoff event. Under baseflow conditions, the less hydrophobic BT-UVs were present at low concentrations in the dissolved phase, while much higher loads of particulate BT-UVs occurred during stormflow, especially in the urban creek. Time-weighted average BT-UV concentrations were up to 4 times higher in the urban than in the rural creek. BT-UVs were found to be prevalent in water obtained from laundering textiles, which plausibly constitutes a major portion of domestic wastewater, and can serve as a BT-UV source to aquatic waterways. However, the observed dilution of a sewage tracer during the run-off event suggests that unregulated wastewater seepage is not responsible for the high BT-UV loads in storm water. High levels of UV328 and UV234 were detected in a select few plastic debris items collected from the urban watershed and in artificial turf grass, respectively. Whereas this may allow for the leaching of those BT-UVs into the creek, most plastic debris is more likely a sink than a source of BT-UVs. The observed input of particle-bound BT-UVs at the onset of the rain event indicates that most of the BT-UVs reach the creek with contaminated particles that had built up on surfaces during the antecedent dry period. UV328 was the dominant BT-UV in those particles. If such particle build-up occurs on road surfaces, it may suggest that the use of UV328 in automotive applications contributes to their presence in urban storm water.

1. Introduction

Due to their ability to absorb the full spectrum of ultraviolet (UV) light, Benzotriazole Ultraviolet Stabilizers (BT-UVs), which have a phenolic group attached to the benzotriazole ring, are used in a variety of products, particularly those constantly exposed to sunlight. This is done to prevent yellowing and degradation that could result from prolonged exposure to UV radiation (Andrady and Rajapakse, 2016). Such widespread use leads to detectable concentrations of BT-UVs in environmental matrices, which have been reported for surface water (Lu et al., 2016), sea water (Montesdeoca-Esponda et al., 2020), sediment (Cantwell et al., 2015), biota (Lu et al., 2019), wastewater (Song et al., 2014) and plastic debris (Rani et al., 2017). The toxic and bio-accumulative properties of BT-UVs are well documented (Kim et al., 2011; Liang et al., 2019); and as a result, some BT-UVs have been classified under the European Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation as substances of very high concern (European Chemicals Agency (ECHA), 2014).

In Canada, from as early as 1986, 63% of imported UV328, a member of this group, has been used in the plastics sector and the rest in automotive paints and coatings (Environment and Climate Change Canada, 2016). Analysis of suspended sediment collected from Mimico Creek, located in an urbanized watershed in Toronto, Canada, showed relatively high concentrations of BT-UVs (13-240 ng/g), especially UVP, UV328 and UV234 (Parajulee et al., 2018). Whereas wastewater has been shown to be a vector of BT-UVs into aquatic environments (Lu et al., 2017), Mimico Creek receives no direct wastewater effluent, suggesting the presence of an alternate source of BT-UVs. One objective of this study was to elucidate the sources of BT-UVs to Mimico Creek and thereby also to urban surface waters elsewhere. The three possible sources of BT-UVs being considered include plastics, unregulated wastewater input and atmospheric washout.

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Plastics in the environment are broadly divided into macro plastics (>5 mm) and microplastics (<5 mm) (Hahladakis et al., 2018). Microplastics can further be classified as primary and secondary. The former are specifically manufactured in the <5 mm range and include pre-production pellets and microbeads used in personal care products (Horton et al., 2017; Napper et al., 2015); whereas the latter are formed from the fragmentation of larger plastic pieces upon entering the environment (Barnes et al., 2009; Thompson, 2004). Manufactured plastic materials often contain a wide range of additives, i.e. chemical compounds added to improve the performance, functionality and ageing properties of the polymer (Hahladakis et al., 2018). These include UV stabilizers, which are typically added to consumer products at concentrations of 0.05–3% by weight of the polymer, and in most cases, are not chemically bound to the plastic polymer, increasing their potential to leach out of the plastic (Hahladakis et al., 2018). The presence of additive-containing plastics could over time result in weathering-induced migration of these chemicals into the surrounding environment, as has been observed previously for BT-UVs (Gao et al., 2011; Hahladakis et al., 2018). Plastic particles in aquatic systems could further act as vectors for the transport of pollutants (Muto et al., 2001).

Considering the widespread occurrence of plastic debris, and the presence of plastic manufacturing and distribution industries in the Mimico Creek watershed, we hypothesized that the informal disposal of consumer plastics and industrial pre-production pellets could play a role in the BT-UV contamination of the creek.

The use of BT-UVs in textiles and fabrics provides a route for BT-UVs from consumer homes to wastewater via laundering of clothes (Avagyan et al., 2015; Luongo et al., 2016). BT-UVs observed in sediment and water samples collected from rivers in Japan (3.4–117 ng/g) (Kameda et al., 2011) and China (0.08–4 ng/L, estimated from graphs) (Zhao et al., 2017) implicated wastewater discharged into the rivers as a BT-UV source. Also, Peng et al. (2017) suggested that relatively high concentrations (14–22 ng/g) of the UV absorber 2-Ethylhexyl 4-methoxycinnamate observed at sites not proximate to sewer outfalls in a Chinese river could be a result of illegal discharges of untreated wastewater along the river. Here, we use caffeine, a common indicator for wastewater contamination in aquatic systems (Henderson et al., 2020; Sauvé et al., 2012) to assess the possibility of wastewater seeping or overflowing into the creek during extreme wet weather events.

Wet and dry atmospheric deposition to the watershed has also been suggested as a source of BT-UVs to rivers and lakes where BT-UVs were detected but which received no domestic or industrial wastewater input (Kameda et al., 2011). BT-UVs have been detected in particulate matter from outdoor air in industrialized areas (Macêira et al., 2019), similar to Mimico Creek watershed which has a high number of plastics manufacturing and distribution sites. Scavenging and washout from the atmosphere during precipitation has been found for other organic compounds with similar properties to BT-UVs including polycyclic aromatic hydrocarbons and polychlorinated biphenyls (Lei and Wania, 2004; Offenberg and Baker, 2002), and is also plausible for BT-UVs in Mimico Creek watershed.

A secondary objective of this study was to better understand dissolved phase-particle phase partitioning, transport dynamics and the influence of land use on BT-UV concentrations during runoff events. Stormwater is a well-documented transport pathway for contaminants into aquatic systems (Codling et al., 2020; Masson et al., 2019), but studies addressing the transport dynamics of BT-UVs during runoff events are scarce (Parajulee et al., 2018; Peter et al., 2020). Furthermore, because BT-UVs are hydrophobic compounds and are predisposed to sorbing to particles, most studies on BT-UVs in surface water tend to involve the analysis of the particle phase alone (Parajulee et al., 2018), or unfiltered water samples (Lu et al., 2016; Zhao et al., 2017; Kameda et al., 2011) and Zhang et al. (2015) analyzed for BT-UVs in the dissolved fraction of surface water and in stream sediments, but not suspended sediments. Here, we analyze for BT-UVs in both the dissolved and suspended particle phases of baseflow and stormflow samples collected from Mimico Creek and Little Rouge Creek - another watershed in Toronto which drains a rural landscape. This study presents a holistic view of BT-UV transport in the dissolved and particle phases of surface water during a rainfall event, and the likely sources which lead to BT-UV enrichment in urban streams.

2. Methods

2.1. Sampling

Mimico Creek Watershed (“Mimico”, 68 km²), located in the Greater Toronto Area (GTA) in Canada, on the western edge of the City of Toronto, is highly urbanized and contains roads, highways, golf courses, industrial and residential areas and part of a major airport. Little Rouge Creek Watershed (“Rouge”, 111 km), on the eastern edge of Toronto, has a less developed landscape which is covered mostly by agricultural land (70%) and some suburban development in the south (Fig. 1). Both creeks drain into Lake Ontario and receive no direct input of effluent from wastewater treatment plants or manufacturing industries. Samples of baseflow and stormflow were taken during a summer storm event in August 2018 at a headwater (HW) drainage point, near the middle (MD), and near the outlet (OL) of both watersheds (Fig. 1) using automated samplers (Teledyne ISCO, Lincoln, Nebraska). These were programmed to collect 1-2 L of discrete water samples from the sites at 3-hour intervals. When the sampler capacity was reached, 1 L grab samples were collected daily until stream flow returned to base conditions. Macro-plastic debris was collected in August 2017 from different locations in Mimico, spanning the length of the watershed. Pre-production plastics were obtained from nearby plastic manufacturers in Toronto and consisted of nylon and polyester as fibers, polystyrene (PS), polypropylene (PPY), low-density polyethylene (LDPE) and polyethylene terephthalate (PET) as resin pellets. Grab samples of wastewater effluent were collected in September 2018 from a nearby wastewater treatment plant in Toronto, while laundry water, used as a proxy for wastewater influent, was generated by machine-washing clothing items. Detailed descriptions of stormwater, rainwater, plastic, wastewater and laundry water sampling can be found in Text S1.

2.2. Sample extraction and analysis

After filtration (glass fiber filters (GFFs), Whatman, Brentford, UK; 0.7 µm), dissolved phase samples were extracted by solid phase extraction (SPE), while particle phase samples were subjected to accelerated solvent extraction (ASE). Extraction of plastic debris was based on the method described in Rani et al. (2017). Details of all sample extraction processes, including extraction conditions and solvents, volume reduction and reconstitution steps can be found in Text S2.

2-(Hydroxy-5-methylphenyl) benzotriazazole (UVP), 2-tert-Butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (UV326), 2,4-Di-tert-butyl-6-(5-chloro-2H-benzotriazol-2-yl) phenol (UV327), 2-(2H-Benzotriazol-2-yl)-4,6-di-tert-pentyphenol (UV328), 2-(2H-Benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (UV329), 2-(2H-Benzotriazol-2-yl)-4-bis(1-methyl-1-phenylethyl) phenol (UV234), caffeine and labelled standards – UVP-d₃, UV328-d₄, UV329-d₄, UV234-d₄ and caffeine-d₄ were quantified using gas chromatography tandem mass spectrometry. Analyte concentrations in water samples were determined from the full Instrument of the ratio of the analyte to injection standard response as a function of analyte concentration in the calibration standards. The full instrumental procedure is provided in Text S3.

2.3. Quality assurance and quality control

To reduce background contamination during sample extraction, all glassware was baked at 450°C for at least 8 hours before use. SPE and ASE equipment (SPE manifold, SPE tubes, ASE cells) were cleaned with hexane, acetone and methanol prior to use. Lab blanks, which comprised...
of surrogate spiked de-ionized water (SPE), and surrogate spiked pre-baked GFFs (ASE) were included for every batch of 6–8 samples. Field blanks, which were generated by exposing de-ionized water and clean GFFs for one minute at the sampling sites, were also analyzed. Duplicate samples collected at the Rouge sites were analyzed as well. Average recoveries of surrogate BT-UVs for dissolved and particle phase extractions were 61–83% and 97–113%, respectively, and recoveries from ultrasonic extractions of plastic samples ranged from 78–100%. Compound specific concentrations and percent recoveries are detailed in the supporting information (Tables S1–S4). All reported concentrations are blank and recovery corrected.

### 2.4. Calculations

Statistical analyses were performed using OriginPro 2021, version 9.8.0.200 (Learning Edition). These include regressions and a hierarchical cluster analysis. The cluster analysis was performed using group average linkages and squared Euclidean distances. A significance level of \( \alpha = 0.05 \) was used to determine statistical significance. Values below the detection limit were substituted with half of the detection limit for each compound for the calculation of averages and loads (Hites, 2019).

Average concentrations in units of ng/L were primarily calculated on a time-weighted basis due to differing intervals between stream water samples. This was done using:

\[
\text{[BTUV]}_{\text{TWA}} = \frac{\sum_i (C_i \Delta t_i)}{\sum_i (\Delta t_i)} \tag{1}
\]

For comparison, flow-weighted average concentrations were also calculated using:

\[
\text{[BTUV]}_{\text{FWA}} = \frac{\sum_i (C_i Q_i \Delta t_i)}{\sum_i (Q_i \Delta t_i)} \tag{2}
\]

Total storm loads at each site in g were calculated using:

\[
\text{Load} = \sum_i (C_i Q_i \Delta t_i) \tag{3}
\]

In these equations, \( i \) and \( n \) represent the first to last samples, \( C_i \) is the concentration of the \( i \)th sample, \( Q_i \) is the stream discharge at the time of the \( i \)th sample, and \( \Delta t_i \) is the time interval over which \( C_i \) and \( Q_i \) are considered to apply.

Mass loads from precipitation in g were calculated using:

\[
\text{Load (rain)} = [\text{BTUV}]_{\text{rainfall}} \ast \text{subwatershed area} \ast \text{rainfall amount} \tag{4}
\]

### 3. Results and discussion

#### 3.1. Dissolved-particle partitioning of BT-UVs

Average frequencies of detection at all six sites ranged from 11–80% and 36–83% in the dissolved and particle phase, respectively. Average frequencies were generally greater in samples collected from Mimico – the more urbanized site (21–94% vs 0–84% at Rouge). UV327 and UV329 were least frequently detected in the dissolved and particle phases, respectively, while UV328 was most frequently detected in both phases. In terms of concentration, UVP and UV326 dominated the dissolved phase, while the particle phase was mostly composed of UV328 (Figs. 4, S5).

Using time-weighted averages of organic carbon fraction (\( \text{f}_{\text{OC}} \)), combined with time-weighted average concentrations in water and on suspended solids (SS), we calculated the field-derived logarithm of the organic carbon-water partitioning ratio, \( \log K'_{\text{OC}} \) at sites where a particular BT-UV could be detected in both phases. Time-weighted averages were employed in this case due to the fact that not many paired water and SS samples had detectable BT-UV concentrations. \( \log K'_{\text{OC}} \) values calculated from the average of individually paired water and SS samples are shown in Table S5. A comparison of our measured values with \( \log K_{\text{OC}} \) and \( \log K_{\text{OW}} \) predicted using poly-parameter linear free energy relationships (Goss, 2005; Nguyen et al., 2005) (which were fed with predicted solute descriptors (Ulrich et al., 2017)) is shown in Fig. 2. Strong but non-significant correlations were observed at MOL (\( R^2 = 0.86 \) and 0.89, \( p < 0.05 \)). \( \log K_{\text{OC}} \) values calculated from the concentrations measured in the Rouge were considerably lower than those in Mimico and correlated poorly with the predicted values (Fig. 2).

Measured \( \log K_{\text{OC}} \) for BT-UVs have rarely been reported, because BT-UVs often could not be detected in one of the two compartments (Díaz-Cruz et al., 2019; Lu et al., 2016). Whereas our measured values for UV234 (5.2–5.6) (Table S5) were higher than the values calculated in another Southern Ontario watershed (Lu et al., 2016), both studies observed a higher \( \log K_{\text{OC}} \) at the urban sites than at rural sites. Generally, field-derived \( \log K'_{\text{OC}} \) for the BT-UVs are lower than might be expected based on predicted \( \log K_{\text{OC}} \) and \( \log K_{\text{OW}} \) values for these compounds, i.e., the concentrations in the dissolved phase were often higher than one might expect. One potential explanation would be the sorption of BT-UVs to dissolved organic matter that can pass the particle filter (0.7 μm) used in this study. Furthermore, the target BT-UVs have pK\(_A\) values ranging from 8.2 to 9.5 (Table S5) (Carpinteiro et al., 2010; Zhang et al., 2021), making them weak acids. The average pH of the water samples was 8.1 at Mimico and 8.2 at Rouge (see Table S2 for all pH data). These values indicate that the BT-UVs can exist in dissociated form, especially for UVP, whose pK\(_A\) is closest and sometimes lower than the pH values. Such dissociations could result in lower concentrations of the neutral form of the compound in either phase, leading to
3.2. Spatial differences within and between watersheds

No obvious spatial trends were observed in time-weighted average concentrations of BT-UVs in the dissolved and particle phases of samples collected from Mimico (Fig. 3a). While the dissolved phase had higher concentrations at MHW, and the particle phase had higher concentrations at MMD, both phases had nearly equal concentrations at MOL. In Rouge samples, dissolved phase concentrations were consistently higher than particle phase concentrations (Fig. 3a). The same trend is observed at both sites when calculated on a flow-weighted basis (Fig. S4). Flow-weighted average concentrations were similar to time-weighted averages at most sites in both phases, with the exception of MOL. Overall, total concentrations in Mimico were 2–6 times higher than in Rouge. Time-weighted average SS concentrations ranged from 17–85 mg/L at MHW and MOL and 32–100 mg/L in Rouge, reflecting similar SS loadings at both watersheds, with the exception of MMD, where copious amounts of visually-observed sand, likely from the creek bed, resulted in high [SS] of ~2000 mg/L (Fig. 3a). When normalized by sub-watershed area, which comprises the entire area upstream of a sampling point, BT-UV fluxes in both phases were highest at the Mimico outlet (MOL) and were 7 times the highest flux at Rouge (RMD) (Fig. 3b).

Higher urban vs. rural stream concentrations for BT-UVs have been reported in China (Peng et al., 2017), and in the same watersheds studied here (Parajulee et al., 2018) – attributable to higher anthropogenic activity and less permeability in urban areas. In comparison with the previous study on particle bound BT-UVs in these same watersheds, we observed particle bound BT-UVs concentrations that are 3–6 and 2–75 times lower in Mimico and Rouge, respectively. One reason for this could be the differences in seasonal and event characteristics. The two weeks preceding our sample collection in August 2018 had significantly more rainfall (average, 41 mm) than in the previous study (3 and 19 mm). The drier antecedent period in 2014 and 2015 was interpreted as more BT-UV contaminated particles being built up on surfaces and subsequently washed off, resulting in higher BT-UV concentrations in Mimico and Rouge (Parajulee et al., 2018). Sample collection and extraction methodologies were similar between this study and (Parajulee et al., 2018). Differences, apart from the rain events, include the analysis of dissolved phase samples in this study, and the use of labelled BT-UVs (which were unavailable during the previous study) as surrogates.

3.3. Temporal patterns during the runoff event

In order to provide insight into transport dynamics, Fig. 4 shows the distribution between the dissolved and particle phases across the rainfall event for UVP and UV328. Plots for UV326 and UV234, which showed some values below and some above the detection limit are displayed in Fig. S5. Concentrations of UV327 and UV329 were generally observed below the limit of detection, or not at all and are not included in this discussion. All data, including duplicate values (which are averaged in Figs. 4 and S5) are included in the SI (Tables S2 and S3). In Mimico (Figs. 4a and S5a), the dominance of the dissolved phase (blue bars) for the less hydrophobic UVP and UV326 and of particles (yellow bars) for
the more hydrophobic UV328 and UV234 is immediately apparent. Especially at MMD and MOL, increased particle phase concentrations of UVP and UV326 (log $K_{OW} = 3.6$ and 6.1, respectively) (Ulrich et al., 2017) at peak stream discharge and SS concentrations indicate that at high flow, there is an influx of particle bound compounds to the creek. This is similarly the case for UV328 and UV234, for which high particle phase concentrations dwarf dissolved phase concentrations. They have a higher affinity for the particle phase because of high hydrophobicity (log $K_{OW} = 8.2$ and 8.6, respectively) (Ulrich et al., 2017). Total BT-UV concentrations in Mimico were in the order of UV328 > UVP > UV326 > UV234. In the Rouge watershed, total BT-UV concentrations were lower, especially for UV328 (Figs. 4b and S5b). This is entirely due to lower particle phase concentrations. In fact, time-weighted average dissolved phase concentrations of UV328 at all Mimico and Rouge sites only range between 0.1 and 0.8 ng/L. The presence and enrichment of UV328 in this system is thus predominantly a result of contaminated particle transport. UVP (2.4–3.8 ng/L) and UV234 (0.04–0.2 ng/L) also show similar time-weighted average dissolved phase concentrations across all sites (with the exception of UVP at ROL ~ 0.25 ng/L). Pronounced differences in dissolved phase concentrations were observed only for UV326. While time-weighted average dissolved concentrations for UV326 in Mimico range from 3.7 to 10.2 ng/L, they only go up to 1.7 ng/L in Rouge. Notwithstanding the lower concentrations in Rouge compared to Mimico, the same trend of higher particle phase concentrations at peak flow is also observed here, especially for UV328 and UV234. Among the BT-UVs, UVP had the highest total concentrations in Rouge, followed by UV328.

The temporal patterns of BT-UVs in Mimico and Rouge are similar, regardless of the concentration gradient. Freely dissolved BT-UVs, especially UVP and UV326, dominated base flow samples, and were either slightly enriched (MOL, RMD), diluted (MMD, RHW) or showed no decipherable changes (MHW, ROL) at high flow. This divergent behaviour of dissolved phase BT-UVs coupled with the relatively constant concentrations at both watersheds suggests that there is no significant input of freely dissolved BT-UVs during the rainfall event. The exception to this is UV326, whose time-weighted dissolved concentrations in Mimico were about 6 times higher than in Rouge, suggesting a prominent source of this compound in the Mimico watershed. This is similar to the observation of relatively high concentrations of UV326 in urban creek water in Southern Ontario (Lu et al., 2016). Analysis of baseflow and stormflow water samples from an urban creek in Washington State, USA also showed more enrichment of UV326 at high flow (Peter et al., 2020). Whereas both studies above analyzed unfiltered water samples, the absence of similarly high UV326 concentrations in sediment (Lu et al., 2016), and the dilution observed for

Fig. 4. Total concentrations of UVP and UV328 at (a) Mimico and (b) Rouge sites. Dissolved phase concentrations are shown in blue and particle phase concentrations are in yellow. The greyed-out bottom of the plots show concentration values below the LOD for that analyte in ng/L. Stream discharge and SS concentration are also shown in orange and dark red, respectively. During the event, samples (1 – 8) were taken at 3-hour intervals, whereas the last few samples (9 and above) were taken at 24-hour intervals. Similar plots for UV326 and UV234 can be seen in Fig. S5.
UV234 (analyzed along with UV326) (Peter et al., 2020) suggest that UV326 is transported predominantly in the dissolved phase. Because BT-UV levels are dependent on location-specific use and can vary spatially (Kameda et al., 2011; Zhang et al., 2011), perhaps the best comparison is with a study conducted within the same watersheds: Parajulee et al. found UV326 to contribute slightly more to the BT-UVs in SS in Rouge (7%) than in Mimico (5%) (Parajulee et al., 2018). Similar contributions are observed in SS in this study – 10% in Rouge and 6% in Mimico. However, when dissolved phase concentrations are included, UV326 contributes 36% of the total BT-UVs in Mimico and only 12% in Rouge. It follows that the dissolved phase can sometimes be the dominant partitioning phase for BT-UVs, notwithstanding their high $K_{OW}$ values, and should be included in studies to avoid underestimating BT-UV levels in environmental samples.

Particle transport is the major entry route of BT-UVs to surface water during rainfall events. In both Mimico and Rouge watersheds, higher particle phase concentrations are observed at high flows, which mostly coincide with high SS loads. Correlations between [BT-UV] and [SS] have been observed elsewhere (Langford et al., 2015; Parajulee et al., 2018), reflecting particle transport of BT-UVs. UV328 and UV234 were detected predominantly in the particle phase, corresponding to them having the highest log $K_{OW}$ values of the target compounds. Similar observations have been made in landfill leachate (Langford et al., 2015) and surface water (Kameda et al., 2011). Particle concentrations of UV328 and UV234 were strongly and significantly correlated with each other ($R^2 = 0.84, p < 0.0001$). UV328 was also significantly correlated with UV326 ($R^2 = 0.87$) and UV327 ($R^2 = 0.73$), and UV234 with UV326 ($R^2 = 0.83$) and UV327 ($R^2 = 0.79$), $p < 0.0001$ in all cases. Such particle phase correlations are consistent with observations for these compounds in similar studies (Kameda et al., 2011; Lu et al., 2016; Nakata et al., 2009), and are indicative of similar sources and transport mechanisms in the particle phase. The observation of peak particle phase concentrations at peak flow at most sites shows that contaminated particles are rapidly transported into the stream during the event. The particle-bound first flush at MMD and to a lesser extent at MOL, i.e., peak in particle phase BT-UV concentration prior to peak flow, additionally suggests that there is a wash off of contaminated particles that are readily available and that the dynamics of BT-UV transport at these sampling points differ from the others. Likely sources are discussed further below.

### 3.4. Source elucidation of BT-UVs to Mimico creek

Even though the particulate BT-UV concentrations measured in Mimico creek (2–113 ng/g, expressed in ng/g for ease of comparison) are lower than previously reported for Mimico (Parajulee et al., 2018), they are still on par with levels in rivers heavily polluted by domestic and industrial wastewater (2–117 ng/g) (Kameda et al., 2011). In the following paragraphs we explore the various hypotheses formulated in the introduction as to the source of these BT-UVs based on the collected evidence.

#### 3.4.1. Unregulated wastewater seepage

UVP, UV326, UV328 and UV234 were the dominant congeners in laundry water (Fig. S1), in line with the same compounds (except UVP which was not considered in the study) being ubiquitous in wastewater influent collected from Canadian WWTPs (Lu et al., 2017). Laundry water thus appears to be a suitable proxy for untreated wastewater. The large fraction of UV234 in laundry water is consistent with its use as an additive for applications of high surface area, such as films and fibers (Mayzlo Inc. 2020). BT-UV concentrations measured in the wastewater effluent were lower than in laundry water for all analytes except UVP, UV327 and UV329. However, concentrations in both the laundry water and WWTP effluent were greater than average concentrations in the stream.

Even though the same congeners were dominant in Mimico Creek water, WW effluent and laundry water, a hierarchical cluster analysis between average BT-UV concentrations at each site, laundry water and wastewater effluent (using fractions of each congener in each sample) indicated that total BT-UV compositions in stream water samples are very similar to each other but different from WW effluent and laundry water (Fig. 5a). The concentrations of the sewage tracer caffeine in stream water did not change appreciably as the event progressed (Fig. 5b). This is in contrast to BT-UVs in Mimico Creek water, which generally were enriched at high streamflow (Figs. 4a, S5a). Both these observations suggest that unregulated seepage of wastewater, treated or otherwise, is not likely to be responsible for the high BT-UV concentrations observed in Mimico Creek.

Having eliminated unregulated wastewater input as a source to Mimico, it is evident that non-wastewater sources can deliver amounts of BT-UVs to surface water in amounts that are comparable to those found in wastewater impacted systems (Kameda et al., 2011).

#### 3.4.2. Atmospheric watershed deposition

The concentration and composition of BT-UVs in rainwater were very similar in the two watersheds. In both Mimico and Rouge, UVP and UV328 were dominant and the rain falling at the headwater site was about twice as contaminated with BT-UVs than the rain at the outlet sites (Fig. 6a). One difference between watersheds was that BT-UVs were present in approximately equal abundance in dissolved and particle phase in rain falling at Mimico, while rain in the Rouge watershed was more dominated by BT-UVs in the sorbed phase (Fig. 6a). This was because more particles were washed out at the Rouge sites (26–75 mg/L vs 0.4–6.9 mg/L at Mimico), and not because the particles were more contaminated.

The dominance of UVP and UV328 in rainwater provides some insight into stream concentrations at high flow. At both Mimico and Rouge, these compounds were enriched in both phases at high flow, especially at MMD, MOL and RMD; suggesting that atmospheric watershed deposition is a plausible entry route to the streams (Fig. 4). At Rouge, UVP and UV328 also contribute the highest fractions in the stream. A hierarchical cluster analysis for rainwater and stream water further links the stream BT-UV profile to the rainwater profile and implicates atmospheric watershed deposition as a source of BT-UVs to RHW and RMD (Fig. S2).

Comparing BT-UV mass loads in rainwater and stream water suggests that the mass of BT-UVs washed out from the atmosphere would be sufficient to explain the mass of BT-UVs recorded in the stream water collected in the Rouge and in the headwater catchment of Mimico (Fig. 6b). However, the stream mass load of BT-UVs at the Mimico outlet is more than an order of magnitude higher than the mass we estimate to have been deposited to the Mimico watershed with the rain. Furthermore, the dominant congener in Mimico creek water is UV328, and not UVP as in the rainwater. These discrepancies and higher BT-UV concentrations in Mimico stream water compared to Rouge cannot be explained by wet atmospheric deposition alone, suggesting that the area draining at MOL is supplied with BT-UV by sources other than or in addition to wet atmospheric deposition.

#### 3.4.3. Plastic debris and pre-production pellets

UV stabilizers are typically added to plastics in amounts ranging from 0.05 – 3% w/w (Hahladakis et al., 2010). The majority of plastic items analyzed had BT-UV concentrations lower than would be expected if these compounds were incorporated as additives during production. Only in four items – the outer white shell of two golf balls, artificial grass and a traffic cone (ID 21–24, Table S4), were concentrations high enough to suggest that they contain BT-UVs as additives and are potential sources of these compounds to the environment (Fig. 7a). UV328 was most abundant in the golf balls and the traffic cone with concentrations ranging from 136 – 729 μg/g, corresponding to 0.02–0.07% of UV328 by weight of the plastic. UVP and UV234 were detected in the traffic cone and artificial grass at similar concentrations of 21 and 20
μg/g, respectively, considerably lower than UV328, but still high enough to suggest their addition as light stabilizers. UVP, UV328 and UV234 are the BT-UVs that were found to be ubiquitous in SS from Mimico Creek in this and an earlier (Parajulee et al., 2018) study, providing credence to the possibility that items such as these are a source of BT-UVs to the creek, especially the golf balls. The Mimico watershed has three golf courses in the vicinity of the MMD and MOL sampling sites from which both golf balls analyzed here were collected. UV328, which is dominant in the golf balls, also contributes the highest fraction of particle phase BT-UVs to Mimico creek water. It follows that the many golf balls in Mimico creek, may indeed be leaching their BT-UV additives into the creek water. The measured concentration of about 0.02% of UV328 by weight of the golf ball polymer falls short of the typical amount of UV stabilizers added to plastics and could be a result of additives having leached out into the surrounding environment. Although we did not analyze new golf balls to confirm or refute this, the study of plastic debris and new products by Rani et al. (2017) showed that discarded plastic debris can contain over 50% less additives than their new counterparts. The presence of golf balls, however, does not explain the enrichment in UV328 observed at high streamflow in Mimico.

Single use plastic bags and tarps were the most frequently observed type of debris in the Mimico watershed. Plastic bags are widely used by consumers on a daily basis, creating a significant amount of waste, and prompting bans on their use. The Canadian government aims to ban single-use plastic, including plastic bags, and achieve zero plastic waste by 2030 (Environment and Climate Change Canada, 2021). While these items gave no indication of containing BT-UV additives, the composition of BT-UVs observed in them were very similar to those observed in the creek. UVP, UV326 and UV328 were most abundant in these items,
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Fig. 7. BT-UVs in (a) additive containing plastics and (b) plastic bags and tarps. PB: plastic bag, RB: resealable bag, PT: plastic tarp, GB: garbage bag. * indicates samples that were collected from around (not inside) the creek.

BT-UVs were largely absent in the pre-production pellets and fibers (Table S4). The highest observed concentration was for UV in nylon fibers ~ 0.3 μg/g. These low concentrations may suggest that the addition of BT-UVs occurs at a later manufacturing stage (Fries et al., 2012; Khairy et al., 2014). The variable BT-UV amounts on these plastic bags, along with the similar compositions indicate that sorption of BT-UVs from the environment onto these items is likely occurring. Given that we had no way of ascertaining when each item was discarded at the creek, it is possible that items that had been discarded for longer periods are the ones with higher concentrations of adsorbed BT-UVs.

BT-UVs were largely absent in the pre-production pellets and fibers (Table S4). The highest observed concentration was for UV in nylon fibers ~ 0.3 μg/g. These low concentrations may suggest that the addition of BT-UVs occurs at a later manufacturing stage (Fries et al., 2012; Khairy et al., 2014), and do not necessarily rule out pre-production pellets and fragments of up to 43 particles per m² were observed in samples (predominantly wet weather samples) from Mimico creek, indicating that stormwater indeed transports such items from nearby plastic industries (Tsui et al., 2020).

### 3.4.4. Flushing of particles accumulating on surfaces

None of the three hypothesized sources is likely to be fully responsible for the high BT-UVs levels measured in Mimico Creek. However, the measurements provide some new hints about the characteristics of the source of BT-UVs.

The enrichment of BT-UVs in Mimico creek during the event (Fig. 4a, SSa) is predominantly due to an influx of contaminated particles. Particle-bound BT-UV first flushes observed especially in MMD and in MOL for UV328 and UV234 further point to the washing off of surfaces on which BT-UV particles have built up. Both of these effects occur to a lower extent at the Rouge watershed, consistent with the increased natural land cover and infiltration in Rouge. Of the three sampling campaigns that have been undertaken at Mimico for BT-UVs (Parajulee et al., 2018 and this study), the highest concentrations were observed in November 2014, a period when the topsoil was likely frozen due to sub-zero temperatures, and which had the driest antecedent period preceding the rain event; while the lowest concentrations were found in this study, undertaken during a wet, summer period. There is evidently a relationship between BT-UV stream water concentrations and the existence of environmental factors which promote increased overland particle wash off. During the driest antecedent period in 2014, more BT-UV contaminated particles repeatedly accumulated on surrounding imperious surfaces and were readily available for wash off into the creek when the rain event finally occurred.

The use of UV328 in automotive coatings and paints in Canada (Environment and Climate Change Canada, 2016) provides a plausible source of this contaminated particle buildup. As of 2013, 10,000 to 100, 000 kg of UV328 was imported into Canada annually, not including the amount present in finished articles (Environment and Climate Change Canada, 2016); and 37% of UV328 in Canada is used in the automobile industry. Mimico Creek watershed contains major highways and road networks and has a population of over 110,000 people (Toronto and Region Conservation Authority 2020) — corresponding to at least 1600 people/ km². Such a dense urbanized region is likely to have a lot of vehicles (personal and public) and thus, more UV328 containing materials. Paint chippings from cars have previously been shown to contribute to road surface buildup of heavy metal contaminants (Deletic and Orr, 2005), and contaminants on road surfaces are easily transported into surface water during wet weather, as is evidenced by the detection of tire and road wear particles in stormwater samples (Grbić et al., 2020). In addition, road dust samples from Mimico Creek watershed analyzed for BT-UVs contained up to 88% of UV328 (Parajulee et al., 2018). Although the composition of the road dust was not investigated again here, the high fraction of UV328 and the absence of UVP (which is not known to be used in automotive applications in Canada) in these samples suggests that vehicle paint chippings may very well be a major component. Since BT-UV profiles within a given region are similar, a hierarchical cluster analysis was performed using the road dust samples from Parajulee et al. (2018), golf balls, stream water SS samples and rainwater SS samples from this study (Fig. S3). The close clustering of MOL stormflow samples with road dust and rainwater, and baseflow samples with golf balls support the elucidation above. Samples at MHW and MMD, however, displayed no obvious clusters from which inferences could be drawn. In addition to UV328, our results indicate that UVP, UV326 and UV234 are most ubiquitous in Ontario, consistent with other studies in this region (Lu et al., 2016; Parajulee et al., 2018).

### 4. Conclusion

BT-UVs, which are hydrophobic compounds, are shown here to sometimes be transported in the freely dissolved phase in aquatic systems. UV326, which has a predicted log K_{OW} of 6.1 was found to be predominantly transported in the dissolved phase during a rainfall event. Studies of BT-UVs in aquatic environmental systems should consider both partitioning phases to prevent underestimations. Whereas BT-UV compositions are consistent in similar regions, actual concentrations can be influenced by seasonal and event characteristics. In urban and rural areas, BT-UVs have similar transport mechanisms but variable concentrations which correspond to differences in emissions and land use in these areas. The rapid transport of accumulated BT-UV contaminated particles to surface water is a major entry route for BT-UVs. Although wastewater is an important vector for BT-UV transport, we assert that these other possible routes need to be evaluated, as they could be delivering comparable or higher amounts of BT-UVs. We also show that informal disposal of plastic debris can provide both sources and sinks of BT-UVs in aquatic systems.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.wra.2021.100115.

References

Alimi, O.S., Farner Budzar, J., Hernandez, L.M., Tufenjki, N., 2018. Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport. Environ. Sci. Technol. 52, 1704–1724. https://doi.org/10.1021/acs.est.7b05008.

Andrady, A.L., Rajapakse, N., 2016. Additives and chemicals in plastics. The Handbook of Environmental Chemistry. Springer International Publishing, pp. 1–17. https://doi.org/10.1007/978-1-4939-2947-2_1.

Avagyan, R., Luongo, G., Thouin, G., Ostman, C., 2015. Benzothiazole, benzotriazole, and their derivatives in clothing textiles—a potential source of environmental pollutants and human exposure. Environ. Sci. Pollut. Res. 22, 5842–5849. https://doi.org/10.1007/s11356-014-3691-0.

Awonaike, B., Lei, Y.D., Parpulescu, A., Mitchell, C.P.J., Wanisa, F., 2021. Polycyclic aromatic hydrocarbons and quinones in urban and rural stormwater runoff: effects of land use and storm characteristics. ACS E&T Water 1, 1209–1219. https://doi.org/10.1021/2acsawater.0c00287.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. Philos. Trans. R. Soc. B Biol. Sci. 364, 1089–1098. 1995–1998.

Cantarrell, M.G., Sullivan, J.C., Katz, D.R., Burgess, R.M., Bradford Hubeny, J., King, J., 2015. Source determination of benzotriazoles in sediment cores from two urban estuaries on the Atlantic coast of the United States. Mar. Pollut. Bull. 101, 208–218. https://doi.org/10.1016/j.marpolbul.2015.10.075.

Carpinteiro, L., Abreu, B., Rodríguez, L., Cela, R., Ramil, M., 2010. Headspace solid-phase microextraction followed by gas chromatography tandem mass spectrometry for the sensitive determination of benzotriazoles UV stabilizers in water samples. Anal. Bioanal. Chem. 397, 829–839. https://doi.org/10.1007/s00216-010-3548-0.

Coddling, G., Yuan, H., Jones, P.D., Glesy, J.P., Hecker, M., 2020. Metals and PFAS in stormwater and storm sewer runoff in a semi-arid Canadian city subject to large variations in temperature among seasons. Environ. Sci. Pollut. Res. 27, 1822–18241. https://doi.org/10.1007/s11356-020-09870-2.

Deletic, A., Orr, D.W., 2005. Pollution buildup on road surfaces. J. Environ. Eng. 131, 49–59. https://doi.org/10.1061/(ASCE)0733-9372(2005)131:1(49).

Díaz-Cruz, M.S., Molins-Delgado, D., Serra-Roig, M.P., Kalogianni, E., Skoulikidis, N.T., Barceló, D., 2015. Personal care products decomposition in EVROTAS river (Greece): water-sediment partition and bioaccumulation in fish. Sci. Total Environ. 561, 3079–3089. https://doi.org/10.1016/j.scitotenv.2015.10.008.

Environment and Climate Change Canada, 2021. Government of Canada invests in reducing plastic waste and supporting the transition of a circular economy for plastics. URL https://www.ec.gc.ca/bls-234.html (accessed 12.15.20).

Luongo, G., Avagyan, R., Hongyu, R., Ostman, C., 2016. The washout effect during laundry on benzotriazole, benzothiazole, and their derivatives in clothing textiles. Environ. Sci. Pollut. Res. 23, 2537–2548. https://doi.org/10.1007/s11356-015-5717-5.

Maceira, A., Borrull, F., Marc, R.M., 2019. Occurrence of plastic additives in outdoor air particle matters from two industrial parks of Tarragona, Spain: human inhalation intake risk assessment. J. Hazard. Mater. 373, 649–659. https://doi.org/10.1016/j.jhazmat.2019.04.014.

Masoner, J.R., Kolpin, D.W., Cozzarelli, I.M., Barber, L.B., Burden, D.S., Foreman, W.T., Forsby, K.J., Furlong, E.T., Groves, J.F., Hladik, M.L., Hopton, M.E., Jaeschke, J.B., Keefe, S.H., Krabbebohn, D.P., Lowrance, R., Romanak, K.M., Rus, D.L., Selby, W.B., Williams, B.H., Bradley, P.M., 2019. Urban stormwater: an overlooked pathway of extensive mixed contaminants to surface and groundwater in the United States. Environ. Sci. Technol. 53, 10070–10081. https://doi.org/10.1021/acs.est.9b02867.

Moto, Y., Isebe, T., Takada, H., Kanehira, T., Otake, K., Kamimini, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in marine environments. Environ. Sci. Technol. 35, 318–324. https://doi.org/10.1021/es010049h.

Mayo Inc., 2020, n.d. BLS 234 – [Mayo Website] URL. https://www.mayo. bls.gov/234.html (accessed 12.15.20).

Montesdeoca-Espinosa, S., Tomé, M.A., Suárez-Meza, L., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2020. Fate and distribution of benzotriazole UV filters and stabilizers in environmental compartments from Gran Canaria Island (Spain): a comparison study. Sci. Total Environ. 144086. https://doi.org/10.1016/j.scitotenv.2020.144086.

Nakata, H., Murata, S., Filatova, I., 2009. Occurrence and concentration of benzotriazole UV stabilizers in marine organisms and sediments from the Ariake Sea, Japan. Sci. Total Environ. 43, 6920–6926. https://doi.org/10.1016/j.scitotenv.2009.09.039.

Napper, I.E., Bakir, A., Rowland, S.J., Thompson, R.C., 2015. Characterisation, quantity and predictive properties of disc-based extractable pollutants. Environ. Pollut. Bull. 99, 178–185. https://doi.org/10.1016/j.jmarpolbul.2015.07.029.

Nguyen, T.H., Goss, K.U., Ball, W.P., 2005. Polyparameter linear free energy relationships for estimating the equilibrium partition of organic compounds between water and the natural organic matter in soils and sediments. Environ. Sci. Technol. 39, 913–924. https://doi.org/10.1021/es048839a.
Offenberg, J.H., Baker, J.E., 2002. Precipitation scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons along an urban to over-water transect. Environ. Sci. Technol. 36, 3763–3771. https://doi.org/10.1021/es025609b.

Parajulee, A., Lei, Y.D., Kananathalingam, A., Mitchell, C.P.J., Wania, F., 2018. Investigating the sources and transport of Benzotriazole UV stabilizers during rainfall and snowmelt across an urbanization gradient. Environ. Sci. Technol. 52, 2959–2962. https://doi.org/10.1021/acs.est.8b05052.

Peng, X., Xiong, S., Ou, W., Wang, Z., Tan, J., Jin, J., Tang, C., Liu, J., Fan, Y., 2017. Persistence, temporal and spatial profiles of ultraviolet absorbents and phenolic personal care products in riverine and estuarine sediment of the Pearl River catchment. China. J. Hazard. Mater. 323, 139–146. https://doi.org/10.1016/j.jhazmat.2016.05.020.

Peter, K.T., Hou, F., Tian, Z., Wu, C., Goehring, M., Liu, F., Kolodziej, E.P., 2020. More than a first flush: urban creek storm hydrographs demonstrate broad contaminant pollutographs. Environ. Sci. Technol. 54, 6152–6165. https://doi.org/10.1021/acs.est.0c00872.

Rani, M., Shin, W.J., Han, G.M., Jang, M., Song, Y.K., Hong, S.H., 2017. Benzotriazole-type ultraviolet stabilizers and antioxidants in plastic marine debris and their new products. Sci. Total Environ. 579, 745–754. https://doi.org/10.1016/j.scitotenv.2016.11.033.

Sauvè, S., Abouilladl, K., Dorner, S., Payment, P., Deschamps, G., Prévost, M., 2012. Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area. Chemosphere 86, 118–123. https://doi.org/10.1016/j.chemosphere.2011.09.033.

Song, S., Ruan, T., Wang, T., Liu, R., Jiang, G., 2014. Occurrence and removal of Benzotriazole Ultraviolet Stabilizers in a wastewater treatment plant in China. Environ. Sci. Process. Impacts 16. https://doi.org/10.1039/c3em00483j, 1076.

Zhang, Q., You, L., Chen, B., He, M., Hu, B., 2021. Reduced graphene oxide coated nickel foam for stir bar sorptive extraction of benzotriazole ultraviolet absorbents from environmental water. Talanta 231, 122332. https://doi.org/10.1016/j.talanta.2021.122332.

Zhao, X., Zhang, Z.F., Xu, L., Liu, L.Y., Song, W.W., Zhu, F.J., Li, Y.F., Ma, W.L., 2017. Occurrence and fate of benzotriazoles UV filters in a typical residential wastewater treatment plant in Harbin, China. Environ. Pollut. 227, 215–222. https://doi.org/10.1016/j.envpol.2017.04.072.