

Investigating the Sources and Transport of Benzotriazole UV Stabilizers during Rainfall and Snowmelt across an Urbanization Gradient

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Supporting Information

ABSTRACT: Benzotriazole UV stabilizers (BT-UVs) have attracted increasing attention due to their bioaccumulative nature and ubiquitous presence in surface waters. We apply high-frequency sampling in paired watersheds to describe, for the first time, the behavior of BT-UVs in stream channels during snowmelt and rainfall. Relative to a largely agricultural watershed, concentrations of BT-UVs in an urban watershed were 4–90 times greater during rainfall and 3–21 times greater during snowmelt. During rainfall, a decrease in BT-UV concentrations on particles with increasing suspended sediments and streamflow occurred at all urban sites due to input of relatively clean sediments, while both decreases and increases were observed at rural sites. Where increases occurred in the rural watershed, road sediments were consistently suggested as the source. Contrasts between the urban and rural sites were also observed during snowmelt. While BT-UV concentrations on particles peaked with peak suspended sediment levels at urban stream sites, the opposite was true at rural stream sites. This appeared to be driven partially by different snowpack melt rates in the two watersheds, with earlier melt and presumably higher streamflow facilitating suspension or erosion of more contaminated sediment in the urban stream. In general, it appears that relatively high, consistent emissions in the form of informal (plastic) debris disposal by consumers or industrial releases have likely led to more homogeneous BT-UV profiles and temporal behavior in the urban watershed. In the rural watershed, low emissions instead entail that emissions variability is more likely to translate to variability in chemical profiles and temporal behavior.



INTRODUCTION

Benzotriazole ultraviolet stabilizers (BT-UVs) are a subgroup of benzotriazoles with 2-hydroxyphenol attachments and various alkyl substituents on the phenol ring. Their structures impart broad spectrum UV resistance, and thus they are used to prevent UV-induced discoloration and deterioration of a range of materials including plastics, paints, coatings, and adhesives.¹ As a result of their broad usage profile, some BT-UVs are high production volume chemicals.² The disposal of products containing BT-UVs via formal (e.g., wastewater treatment plants, landfills) and informal (e.g., consumer and industrial littering of plastics) pathways has resulted in the detection of these chemicals in rivers and sediments in many countries including Canada,³ China,⁴ Germany,⁵ and Japan.⁶

The logarithmic octanol–water partitioning coefficients ($\log K_{OWs}$) of the BT-UVs are higher than 4.3.⁷ Consistent with such high hydrophobicity, strong evidence of bioaccumulation has been observed in both marine⁸ and freshwater systems.^{3,5} For example, UV-327 had a bioaccumulation factor of 33 300 in finless porpoises (*Neophocaena phocaenoides*) of the Ariake Sea, Japan,⁹ and a bioconcentration factor of 6500–7600 in carp (*Cyprinus carpio*) in laboratory studies.¹⁰ BT-UVs also have demonstrated persistence in the environment. Field half-lives of UV-P, UV-326, UV-327, and UV-328 ranged from 75 to 328 days in biosolid amended soils,¹¹ while no significant

degradation of UV-326, UV-327, UV-328, UV-329, and UV-234 was observed after 100 days in water–sediment batch systems in a laboratory.⁵ Though toxicological studies are scarce, there are indications that BT-UVs can exert both acute and chronic toxic effects. For example, decreased heart rates and disruption of thyroid function were observed in zebrafish (*Danio rerio*) embryos within 96 h following doses of 1–100 $\mu\text{g}\cdot\text{L}^{-1}$.¹² In addition, a 90 day subchronic study showed adverse effects on the blood, liver, and kidneys of both male and female rats when their feed was spiked with at least 200 $\mu\text{g}\cdot\text{g}^{-1}$ of UV-328.¹³

Their poorly characterized toxicity alongside their demonstrated persistence, bioaccumulation, and widespread detection in surface waters and sediments highlight the need to better characterize the transport of BT-UVs in the environment. As these chemicals can be strongly particle-bound and have anthropogenic sources, they may be of particular concern in urban aquatic systems that see relatively high emissions of both BT-UVs and the particles to which they sorb. High runoff events caused by rainfall and snowmelt can lead to a range of chemical behaviors that in turn depend on emission character-

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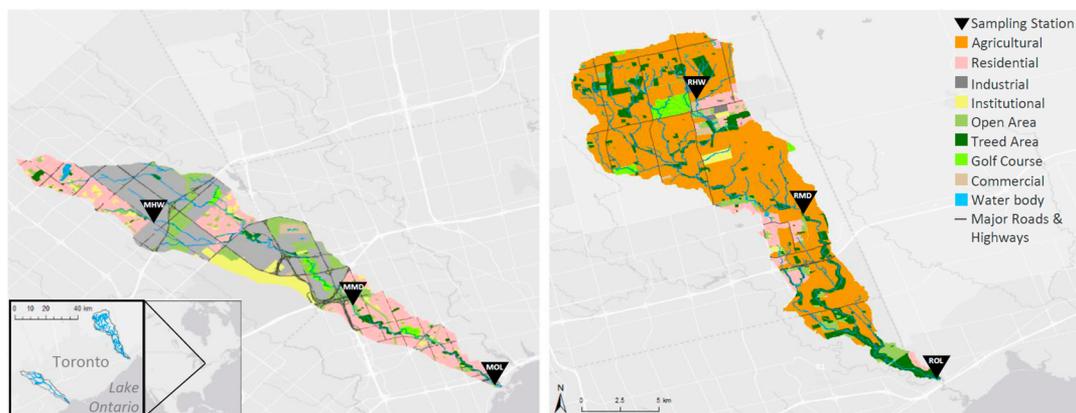


Figure 1. Stream suspended sediment and bulk sediment sampling sites MHW, MMD, and MOL in Mimico Creek (left) and RHW, RMD, and ROL in the Little Rouge Creek (right) watersheds in Toronto, Canada. Data: Toronto & Region Conservation Authority, DMTI Spatial Inc. Basemap: ESRI Inc. (Adapted with permission from the work of Parajulee et al.¹⁴ Copyright 2017 American Chemical Society)

istics and land cover. To our knowledge, insight into the dynamics of BT-UVs during such events is nonexistent. In the current study, we measure BT-UVs in suspended sediments (SS) during two rainfall events and one snowmelt event in paired watersheds in Toronto, Canada. We combine these measurements with particulate organic carbon (POC), stream-flow, and bed, bank, road, and SS concentration data to infer the sources and transport mechanisms of particle-associated BT-UVs during rainfall and snowmelt across a gradient of urbanization.

MATERIALS AND METHODS

The data presented herein is part of a larger data set collected to assess the influence of urbanization on the behavior of organic contaminants during runoff events. To this effect, in 2014 and 2015, measurements of a few different groups of organic contaminants were made in streamwater samples that were collected at high frequency during rainfall and snowmelt events in Toronto, Canada. Our previous works have described the behavior of benzotriazoles¹⁴ and polycyclic aromatic hydrocarbons.¹⁵ Details describing most aspects of the methodology are presented in these previous works. As a result, we present a condensed description of the methods herein but still attempt to provide sufficient methodological context for this particular data set.

Site Description. Mimico and Little Rouge Creeks are in the Greater Toronto Area, Canada, and drain into Lake Ontario (Figure 1). The Mimico Creek watershed (“Mimico”, 68 km²) is one of the most highly urbanized watersheds in Canada, with mostly industrial and residential land cover. The watershed contains several major roads, a few major highways, and part of Pearson International Airport, the busiest airport in Canada. In contrast, 70% of the Little Rouge Creek watershed (“Rouge”, 111 km²) is agricultural, with more suburban land cover in the southern reaches of the watershed. The close proximity between the two watersheds entails comparable climate and subsurface geology, details of which can be found in the work of Parajulee et al.¹⁴ Neither creek receives direct inputs of wastewater treatment plant or chemical manufacturing plant effluent. Several sections of both creeks, from headwater to outlet in Mimico (many of the light green areas along the creek in Figure 1) and in the southern reaches of Rouge, are lined by trails used for recreational activities. In Mimico, this includes three golf courses (bright green in Figure 1).

Sample Collection. Samples were taken at three sites in each watershed during two rainfall events in November 2014 (precipitation, P, falling over 6 h: 19.4 mm at Pearson Airport near Mimico; 18.8 mm at Markham Buttonville Airport closer to Rouge) and October 2015 (P falling over 15 h: 37 mm at Pearson Airport and 42 mm at Buttonville Airport) and one snowmelt event in March 2015 (snow water equivalent: 18.9 mm in Mimico and 37.8 mm in Rouge over the two week sampling period). The nested watershed approach included sampling sites in both watersheds located in headwater areas (MHW and RHW), approximately halfway to the stream outlets (MMD and RMD) and near the stream outlets (MOL and ROL). Each site was collocated with a streamflow monitoring station. Discharge data indicate good sampling coverage across the event hydrographs (SI Figure S1).

Seven to 11 samples of streamwater of up to 2 L, including at least 1 pre-event and 1 postevent sample (see SI Figure S1), were taken in glass bottles via autosampler and/or sampling rod, i.e. a polyethylene bottle attached to a plastic rod. The autosamplers were time-triggered, with time intervals estimated by using historical streamflow and rainfall data at government monitoring stations in the two watersheds. Samples were taken at the same time at all sites (autosampler) or with a difference of a maximum of 5 h (sampling rod). Given the shallowness of the streams at baseflow, autosampler lines were mounted close to the riverbed to ensure complete submergence during baseflow. Considering the minimal contact time with plastic sampler components, it was assumed an insignificant quantity of BT-UVs was lost through sorption. In addition, the streams are turbulent and well-mixed during event flow, significantly reducing concerns related to the point samples (versus composite samples). Samples of bed, bank, and road sediments were also collected at each site in November 2015. At RHW, road sediments were collected from two types of nearby roads: a road in an agricultural area, and a road in a residential area. Stream water and sediment sampling,¹⁵ in addition to flow monitoring methodology, have been described previously.¹⁴

Sample Extraction and Analysis. Sample extraction details can be found in the work of Parajulee et al.¹⁵ In brief, water samples were filtered using a glass filtration apparatus and 0.7 μm glass fiber filters (Whatman, Brentford, UK), thus operationally defining “suspended sediments” as particles greater than 0.7 μm in diameter. The filters were extracted using Accelerated Solvent Extraction (Dionex Corp. California,

USA) with the following settings: 75 °C, 1500 psi, 5 min static time, 3 static cycles, 100% flush volume, and 240 s purge time.¹⁶ Bed and bank sediments and road dust samples were extracted in a Soxhlet apparatus using dichloromethane for 24 h.^{17,18} Sample cleanup was performed with columns containing 6% deactivated neutral alumina and sodium sulfate, using hexane as the elution solvent.¹⁹ A 0.35–1 L portion of each water sample was used to estimate suspended sediment concentrations. If at least 0.1 mg of sediment could be removed from the filters after drying and weighing, particulate organic carbon (POC) analysis was performed using a Flash 2000 Organic Elemental Analyzer (Thermo Scientific, USA). Statistical comparisons of POC between Rouge and Mimico could only be performed for the October 2015 event due to an insufficient number of samples meeting the weight requirement for analysis in Mimico.

Six BT-UVs (“UV-P” 2-(2*H*-benzotriazol-2-yl)-*p*-cresol, “UV-326” 2-*tert*-butyl-6-(5-chlorobenzotriazol-2-yl)-4-methylphenol, “UV-329” 2-(benzotriazol-2-yl)-4-(2,4,4-trimethylpentan-2-yl)phenol, “UV-327” 2,4-ditert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol, “UV-328” 2-(benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol, and “UV-234” 2-(benzotriazol-2-yl)-4,6-bis(2-phenylpropan-2-yl)phenol) were quantified using gas chromatography tandem mass spectrometry. Further instrumental details and detection limits are in [SI Text S1 and Table S1](#). Quality assurance and quality control (QA/QC) measures included extraction of lab and field blanks and some duplicates. Deuterium-labeled PAHs were used as recovery surrogates for the target analytes and were added to all samples prior to extraction as they have been used previously for this purpose.^{4,8,20} Mass-labeled surrogates of the target analytes were not available at the time this study was conducted. To confirm similar recoveries of the labeled PAHs and BT-UVs, spike and recovery experiments including the BT-UVs and deuterium labeled PAHs (phenanthrene-*d*₁₀, chrysene-*d*₁₂, benzo[*a*]pyrene-*d*₁₂, benzo[*ghi*]perylene-*d*₁₂) were conducted. These QA/QC measures are described further in [SI Text S2 and Tables S2–S4](#). Average recoveries from suspended sediments during the events ranged from 92–101% for phenanthrene-*d*₁₀ (surrogate for UV-P), 85–105% for chrysene-*d*₁₂ (surrogate for UV-326), 88–113% for benzo[*a*]pyrene-*d*₁₂ (surrogate for UV-329), and 84–110% for benzo[*ghi*]perylene-*d*₁₂ (surrogate for UV-327, -328, and -234).

Data Analysis. Average BT-UV concentrations for each site during an event were calculated on a time-weighted basis to account for uneven time intervals between samples. Since differing numbers of base flow samples were collected, these averages were calculated using the last pre-event base flow sample, up to and including the first postevent base flow sample. For the Nov 2014 event, to account for quicker increases in SS relative to streamflow, the first sample in the calculation was instead the second to last pre-event base flow sample for all sites except for RHW. Loadings of BT-UVs during the two rainfall events were determined as follows:

$$\text{load [kg]} = \sum_i^n C_i q_i \Delta t_i$$

where samples *i* to *n* were the first and last samples used to calculate the time-weighted BT-UV concentrations and *C_i*, *q_i*, and Δt_i were the concentration in the *i*th sample, streamflow at the time of the *i*th sample, and half of the time period between the collection of sample *i* – 1 and *i* + 1, respectively.

All statistical analyses were conducted with SPSS (v 20, IBM, New York, USA) software. This included regressions between concentrations of each BT-UV and suspended sediment at MMD in Nov 2014 ([SI Figure S2](#)) to estimate individual BT-UV concentrations for sample 5, which was not taken due to autosampler error. In addition, a hierarchical cluster analysis was performed to assess potential BT-UV sources (bed, bank, and road sediments) at each sampling site. BT-UV proportions in bed, bank, and road sediment samples were compared to SS samples for each site–event combination to assess the temporal variation in the contribution of these sources to BT-UVs sorbed to suspended sediments. For each site–event combination, squared Euclidean distances were calculated between each SS sample and potential source sediment samples. Clusters were then created such that the similarity between the average BT-UV profiles in clusters was minimal. The difference between concentrations of UV-234 in duplicate samples of MHW bank sediments was very large (34 and 0.4 ng·g^{–1}; see [Table S5](#) for concentrations in all samples) and also led to very different BT-UV composition profiles. Thus, rather than taking an average of the profiles to use during the cluster analysis, these samples were kept separate. One major limitation of this analysis is the limited spatial (three small areas in each watershed; three potential sources taken into account) and temporal (one day of the year) extent of source sediment sampling. Nevertheless, the analysis should provide some indication of relative differences in within-event sources between the two watersheds.

RESULTS AND DISCUSSION

Widespread and Elevated Presence of UV-P. UV-P is discussed separately from the other BT-UVs because of its lower hydrophobicity and because the observed concentrations were unusually high compared to previous measurements in river sediments elsewhere ([SI Figures S3–4](#), exact concentrations are in [SI Table S6](#)). In Rouge, time-weighted average concentrations of UV-P (TWC_{UV-P}) in suspended sediment samples in Nov 2014, Mar 2015, and Oct 2015 ranged from below detection limits to 0.19 ng·g^{–1}, 44 to 360 ng·g^{–1}, and 3.9 to 8.9 ng·g^{–1}, respectively. TWC_{UV-P} were even higher in Mimico, ranging from 7.0 to 39 ng·g^{–1}, 500 to 800 ng·g^{–1}, and 30 to 77 ng·g^{–1} during the three events. This is well beyond the range that has been observed in riverbed sediments elsewhere: UV-P was detected at an average concentration of 29 ng·g^{–1} in 2 out of 10 samples of river and marine sediments in an unspecified location, presumably Spain.²¹ Concentrations of UV-P in bed sediments in Saitama, Japan, ranged from 1.3 ng·g^{–1} (detection frequency, *df* 1/5) at “background” sites including those influenced by recreational activities and minimal agricultural wastewater input, to 15 ng·g^{–1} (*df* 1/2) at sites receiving direct inputs of domestic wastewater.⁶ Aside from location-specific influences, the dynamic nature of suspended sediments versus riverbed sediments may account for some of this difference.

When considered alongside the relatively low log *K*_{OW} of UV-P (4.5, compared to 5.6–7.7 for the remaining BT-UVs⁷), the observed concentrations of UV-P, particularly during snowmelt, are especially unusual. However, the observed levels of UV-P may appear elevated due simply to the limited number of measurements available for comparison. Measurements of UV-P in stream sediments are extremely limited and clearly vary widely both across sites in similar environmental settings and across cities. Furthermore, to our knowledge, no measurements of UV-P have been taken during the snowmelt

period. Concentrations in lab and field blanks (SI Text S2) exclude the possibility of such high contamination during sample transport, extraction, and brief exposure of water samples to the ambient air. Contamination from sampling equipment also cannot explain the elevated UV-P concentrations as concentrations were much higher in Mimico relative to Rouge despite random placement of autosamplers and use of the same sampling rod to take samples beyond the eighth sample at all sites during all events.

As BT-UVs are associated with products used by humans, a comparison to house dust concentrations could be helpful in understanding the observed UV-P concentrations. UV-P was not detected in 37 samples of house dust from two residential areas in the Philippines, one of which is close to a municipal dumping area.²² In contrast, UV-P was present in house dust samples from private residences in Spain at concentrations close to those observed in the present study: 75–657 ng·g⁻¹ in five samples.²³ These works suggest that UV-P levels are highly location or country-specific, i.e. linked to the use of UV-P as a UV-stabilizing additive in products used in a particular region. No import or usage data exist for BT-UVs in Canada, though our data seem to suggest that UV-P is used as an additive in Canadian consumer products. The differences in UV-P quantities between Mimico and Rouge also indicate that in a given region with UV-P-rich consumer products, the UV-P levels will be higher in areas with more anthropogenic activity. To confirm these hypotheses, further studies could quantify the amount of anthropogenic debris found in the two watersheds (i.e., determine the number of debris per unit area), the UV-P content of different types of consumer debris found in the two watersheds, and leaching from consumer products. Potential washout of UV-P-contaminated airborne dust could also be assessed by e.g. measuring the UV-P content of rainfall.

Comparing Urban and Rural BT-UV Contamination.

Despite similar levels of SS in both watersheds during a particular event (Figure 2), both particle contamination by the BT-UVs (Figure 2) and subwatershed loadings of BT-UVs (SI Figure S5) were higher in Mimico relative to Rouge. Concentration differences were more pronounced during the Nov 2014 (4–90 times) storm compared to the Oct 2015 storm (7–11 times) and Mar 2015 snowmelt (3–21 times).

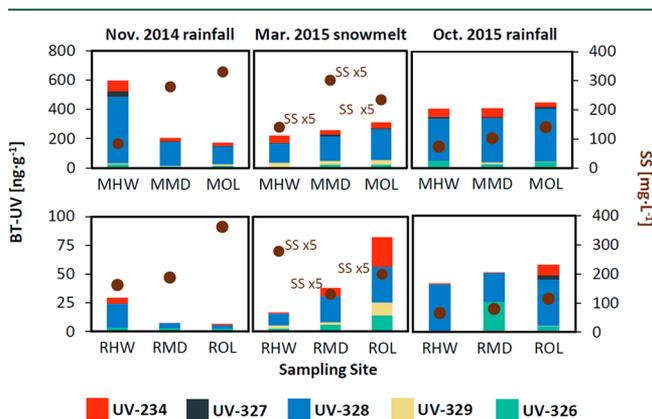


Figure 2. Time-weighted average concentrations [ng·g⁻¹ suspended sediment, SS] of UV-326, UV-329, UV-328, UV-327, and UV-234 during the rainfall and snowmelt events. Brown circles represent time-weighted suspended sediment concentrations. “SS × 5”: concentrations have been multiplied by 5 for the Mar 2015 snowmelt event in order to be visible on the SS scale.

This was more a result of variable concentrations and loads in Rouge rather than changes in BT-UV levels in Mimico (Figure 2). The differences in subwatershed drainage area-normalized loadings of the sum of UV-326, UV-329, UV-328, UV-327, and UV-234 (Σ_5 BT-UV) were 13–39 times in Nov 2014, and 8–34 times in Oct 2015. These differences cannot be explained solely by differences in particulate organic carbon, which were insignificant in Oct 2015 (Mann–Whitney U 107, $p = 0.46$).¹⁵ Instead, the disparity in BT contamination between the two watersheds may be due to differences in the intensity of informal disposal of BT-UV containing products.

Previous work suggests that plastic debris may be an important source of BT-UVs to aquatic systems. Detection frequencies of UV-326, UV-327, and UV-328 ranged from 66 to 100% in a variety of plastic litter types collected from the coast of South Korea.²⁴ Concentrations of UV-326, UV-327, and UV-328 displayed a wide range, from below detection limits up to 82, 20, and 1.6 $\mu\text{g}\cdot\text{g}^{-1}$ respectively. These broad ranges and differences in concentrations were attributed to variation in BT-UV quantities initially added to plastic products, weathering, and transformation following disposal. The wide variability in concentrations and high detection frequencies of BT-UVs in plastic debris, combined with the ubiquitous presence of plastic litter in urban waterways are a strong indication that such waste is an important source of BT-UVs to human-impacted aquatic systems. Field observations confirm the more widespread presence of plastic and plastic-containing debris (e.g., golf balls, bike frame, food and drink packaging) in and near the creek system in Mimico as compared to Rouge. In addition to informal plastic disposal by consumers, the number of plastic manufacturers and distributors in Mimico and findings of industry-associated microplastic morphologies in Greater Toronto Area streams suggest industrial sources of (micro)plastics could also be important.²⁵ The areas for further study suggested above for UV-P would also help to assess the link between consumer products and BT-UVs and, specifically, evaluate the role of plastic debris. Quantifying BT-UVs in industrial discharges in Mimico could also clarify the roles of consumer disposal versus industrial disposal.

Comparisons of BT-UV concentrations and profiles in Mimico and Rouge to those found in sediments elsewhere can offer insight into BT-UV sources. To our knowledge, only one other study has measured BT-UV levels in suspended sediments.⁵ The average of the time-weighted concentrations of the sum of UV-326, UV-329, UV-328, UV-327, and UV-234 across all events ($\text{TWC}_{\Sigma\text{BT-UV}}$) in Mimico was 3.0–18 times higher than the average measured in grab samples of SS taken from major German rivers influenced to varying degrees by industrial/municipal effluent and population pressure (Table 1). These large differences were due to the relatively high concentrations of UV-328 and UV-234 in Mimico. In contrast, in Rouge, $\text{TWC}_{\Sigma\text{BT-UV}}$ were 0.3–2.0 times the averages observed in the German rivers. As with Mimico, differences in favor of Rouge were due to higher concentrations of UV-328 and UV-234.

$\text{TWC}_{\Sigma\text{BT-UV}}$ in Mimico were 1.3–3.3 times greater than the mean measured in bed sediments at “background”, “moderately polluted”, and “heavily polluted” sites in Saitama, Japan, due primarily to the higher concentrations of UV-328 (Table 1).⁶ In Rouge, the $\text{TWC}_{\Sigma\text{BT-UV}}$ were one-third or less the Saitama means. Interestingly, the UV-234 levels in SS from Mimico were much closer to those in the Japanese sediments at the

Table 1. Average Concentrations of BT-UVs (ng·g⁻¹ of Sediment) Across All Three Events in Mimico and Rouge Suspended Sediments^a

[ng·g ⁻¹]	UV-326	UV-329	UV-328	UV-327	UV-234	∑ ₅ BT-UV
This Study: Canada						
Rouge	6.7	1.8	22	0.4	5.6	37
Mimico	26	13	240	13	42	330
Wick et al.: Germany						
Rhine	28	47	12	16	10	113
Elbe 1	7	14	6	2	8	37
Elbe 2	3	4	2	2	7	18
Saar	21	9	10	8	12	60
Moselle	8	5	6	3	7	29
Kameda et al.: Japan						
background	12	0	58	0.7	39	99
moderately polluted	1.8	0.6	59	0.9	47	109
heavily polluted	4.7	26	117	2.4	99	250

^aCompared to average measured concentrations in suspended sediment (Wick et al.⁵ estimated from bar graphs) and river bed sediments (Kameda et al.⁶) at sites affected by varying levels of pollution.

background sites, in addition to those designated as “moderately polluted” by sewage treatment plant effluent, domestic wastewaters, and agricultural runoff and “heavily polluted” by industrial and domestic wastewaters. The similarity in mean measured concentrations of all BT-UVs at these three site types that vary widely in the amount of general waste input suggests that “general” waste input is not a good indicator of BT-UV contamination. Rather, it may be specific types of waste, such as plastic debris, that results in relatively high concentrations of BT-UVs.

Differences in time-weighted congener profiles point toward different sources of BT-UVs in the two watersheds. UV-328 (blue in Figure 2) was the dominant BT-UV across Mimico during all events and for most site–event combinations in Rouge. Strong dominance of UV-328 has been less commonly observed in sediment samples, as in bed sediments of the Saginaw and Detroit Rivers, USA,⁴ and marine sediments near the Gran Canaria Islands (SI Figure S6).²⁶ More often, UV-328 is not so dominant, as in SS samples taken from German rivers,⁵ marine bed sediments of the Omuta River in Japan,⁸ and in bed sediments at three site types in Saitama, Japan, that differ in types and levels of wastewater input (SI Figure S6).⁶ Differences in composition profiles and concentrations may be an artifact of spatial and temporal limits of sampling. Alternatively, considering the high degree of variability in BT-UV profiles and concentrations in plastic debris documented by Rani et al.,²⁴ these differences may also be a result of spatial variability in global usage and emissions. In general, contamination of SS in Rouge with BT-UVs appears to be less consistent between sites and events: changing concentrations and inconsistent BT-UV profiles suggest more variable emissions intensities and sources. Because emissions are lower in Rouge, any variation in debris disposal leads to more noticeable changes in SS compositional profiles. In contrast, in Mimico, where emissions are much higher, compositional profiles are more consistent across rainfall and snowmelt.

BT-UV Patterns and Sources within Events. The temporal patterns in BT-UV concentrations between the two watersheds were similar when considering volumetric (i.e., ng·L⁻¹) concentrations (SI Figure S7). With increasing SS concentrations, the volumetric concentrations of BT-UVs also increased. As a result, pre-event and postevent baseflow samples with the lowest SS levels had the lowest concentrations

of BT-UVs, while maxima were observed at or close to maximum SS and streamflow. This reflects the relatively hydrophobic nature of the BT-UVs.

In contrast, concentrations normalized to suspended sediments reveal divergent BT-UV behavior in the two watersheds. In Mimico, during both rainfall events, the sum of the concentrations of UV-326, UV-329, UV-328, UV-327, and UV-234 ([∑₅BT-UV]) decreased with increasing SS (Figure 3), indicating dilution of in-stream SS by cleaner particles. This was less obvious in Oct 2015 at MMD, when isolated peak concentrations (samples 3 and 9) near pre-event and postevent base flows may have been anomalously high. Due to the high degree of similarity between and across source sediment samples and suspended sediment samples in Mimico (SI Figure S8), cluster analysis provided limited insight into temporal source dynamics of BT-UVs during rainfall. At MHW during both events, bed and bank samples clustered with most samples except those at the lowest SS levels, i.e. the start and end of the event. This suggests that the sources of cleaner particles during rainfall were some combination of suspended bed sediments and eroded bank sediments.

The “dilution” pattern also occurred in Rouge at RHW and RMD in Oct 2015 (Figure 3), wherein BT-UV concentrations were greater in baseflow samples near the start and end of the event. Cluster analysis indicates that at RMD, more contaminated bed sediments early during the event were eventually diluted with bank sediments (SI Figure S9). By the end of the event, with no further contribution from bank sediments, the contaminated bed sediments were again the primary source of BT-UVs in suspended solids. In RHW, agricultural road sediments clustered with most of the suspended solids during the dilution. The remaining site–rainfall events in Rouge instead showed increasing BT-UV contamination with increasing SS and streamflow, indicating mobilization and input of particles more contaminated with BT-UV at higher SS concentrations. In all cases, cluster analysis implicated road sediments (suburban road sediments at RHW) as the source of this elevated contamination.

BT-UV behavior in the two watersheds during snowmelt was also divergent. Source identification by cluster analysis was fairly limited, perhaps due to missing potential source samples such as snowpack solids and surface soils,^{27,28} the latter of which may be especially important in agricultural areas such as

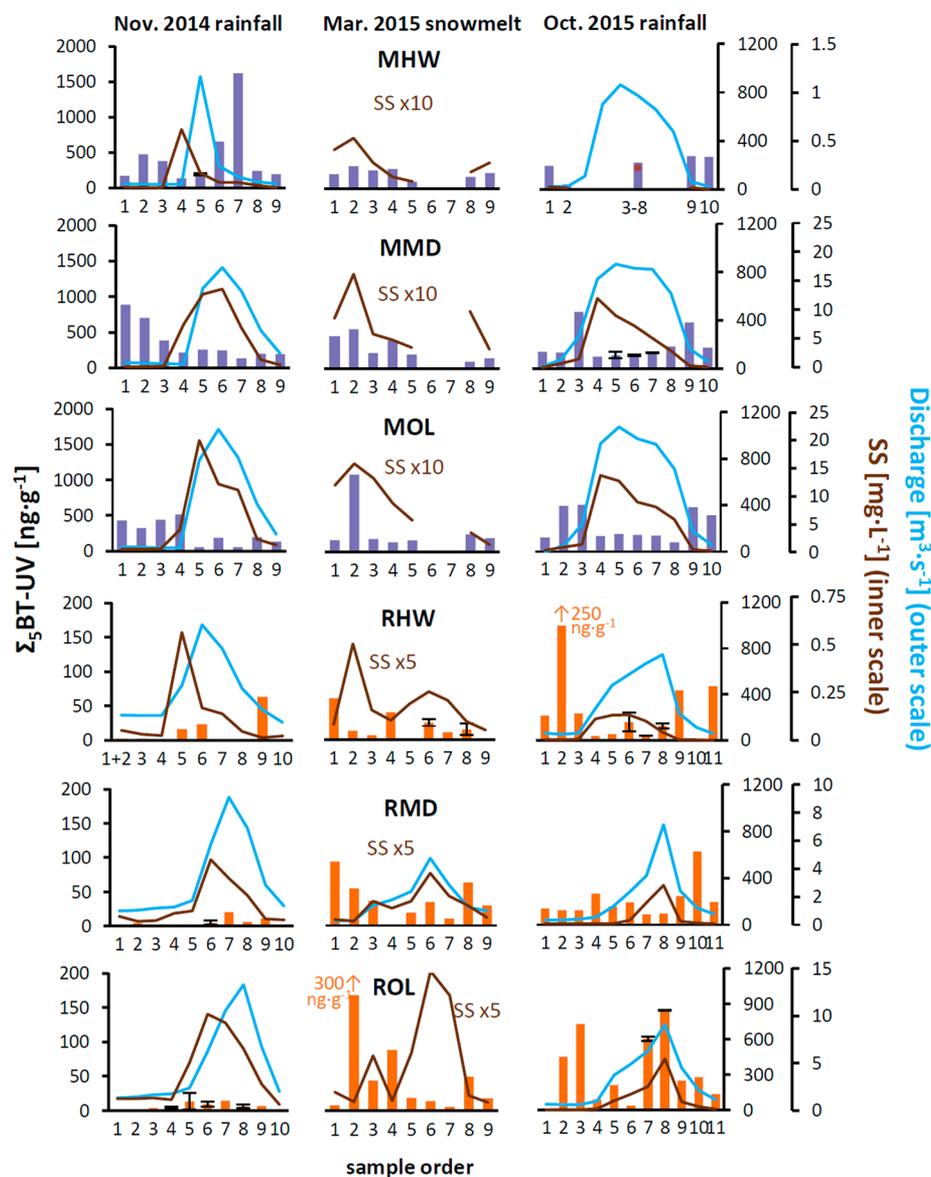


Figure 3. Concentrations of the sum of UV-326, UV-329, UV-328, UV-327, and UV-234 (Σ_5 BT-UV) at all sites during each sampling campaign. Error bars represent the range of duplicate sample measurements. Discharge data are in blue and suspended sediment (SS) concentration is in brown. “SS \times 5” and “SS \times 10” for the Mar 2015 snowmelt event: Mimico and Rouge SS concentrations have been multiplied by 10 and 5, respectively, so as to be visible on the SS scale. “1 + 2” for RHW during the Nov 2014 event is a composite of samples 1 and 2.

Rouge. In Mimico, $[\Sigma_5\text{BT-UV}]$ maxima occurred early during the event (i.e., sample 2) and coincided with peak SS concentrations (Figure 3). Cluster analysis for MHW suggests the peak was due to bed and bank inputs (SI Figure S7), perhaps spurred by increased flow resulting from earlier snowpack melt in Mimico (SI Figures S1, S10). In contrast, in Rouge, lower $[\Sigma_5\text{BT-UV}]$ were instead concurrent with higher SS concentrations. The higher SS concentrations occurred later during the melt period (i.e., samples 6–8) at RMD and ROL, due to slower melting of the snowpack in Rouge (SI Figure S10). Some of the lower BT-UV concentrations clustered with agricultural road sediments at RHW, bed sediments at RMD, and road sediments at ROL (SI Figure S9).

Overall, temporal patterns within events were more consistent across Mimico. Within events, not only did $[\Sigma_5\text{BT-UV}]$ change in a similar manner, the chemical composition of samples was much more similar between and

across source sediments and SS samples. In Rouge, there was more variation in the patterns of $[\Sigma_5\text{BT-UV}]$ across time, both across sites and across events. BT-UV composition also differed across sites during a particular event, and at individual sites across events. These patterns suggest low and variable emissions in Rouge, and high and consistent emissions in Mimico as important drivers of BT-UV behavior in the two watersheds.

Implications. Most previous investigations into the transport and fate of BT-UVs have focused on industrial and domestic wastewaters as key sources of BT-UVs. We demonstrate that BT-UV contamination can be comparable, if not greater in streams that are not directly affected by such wastewater streams. When combined with the wide range of BT-UV levels measured previously in plastic products,²⁴ it appears that informal disposal of consumer products or unintentional industrial releases containing BT-UVs play prominent roles in BT-UV cycling in highly urban, suburban-

ing, and near-urban agricultural rivers. For these types of rivers, elevated BT-UV contamination is likely caused by a combination of the intensity of BT-UV use as additives in consumer products in a particular region, and intensity of urbanization, which likely correlates with informal waste disposal or release. As such, average event-scale concentrations and loads of BT-UVs are greater in highly urban rivers compared to rural rivers despite similar levels of suspended sediments. Our data indicate that UV-328, followed by UV-234, UV-326, and potentially UV-P, are all used very widely as UV stabilizers in Canadian consumer products and/or their parent materials. UV-P in particular warrants further investigation due to the relatively high concentrations observed in the present study.

We also provide a first glimpse into event-scale transport of BT-UVs in stream channels. Our study watersheds indicate that urban streams display similar trends in BT-UV concentrations across runoff events, while this is not necessarily the case in rural streams. During rainfall, with increasing streamflow and SS levels, relatively contaminated SS are diluted by cleaner particles in the urban watershed. In rural watersheds experiencing low emissions intensities resulting from low levels of urbanization, in-stream BT-UV concentrations on the SS may either increase or decrease with higher SS concentrations and streamflow. During snowmelt, urban and rural streams see different timing of BT-UV inputs. Due to accelerated melt leading to suspension of bed sediments or erosion of bank sediments, urban rivers receive more concentrated pulses of BT-UVs earlier during the melt period. In rural rivers, slower melt leads to later peaks in SS that coincide with lower BT-UV levels from different sediment caches that vary according to location within the watershed. Due to spatial variation in the form of “urban” and “rural” watersheds, in addition to country-specific differences in BT-UV content in consumer products, additional work should investigate whether these findings apply to watersheds elsewhere.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.8b00552](https://doi.org/10.1021/acs.est.8b00552).

Hydrographs, GC-MS/MS instrument program, quality assurance and quality control, sample concentrations, graphs with UV-P concentrations, graph with area-normalized fluxes, graph comparing literature data, graph with temporal variation in volumetric concentrations, and graphs with cluster analysis results (PDF)

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Notes

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