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Letter

Occurrences of Tire Rubber-Derived Contaminants in Cold-Climate Urban Runoff

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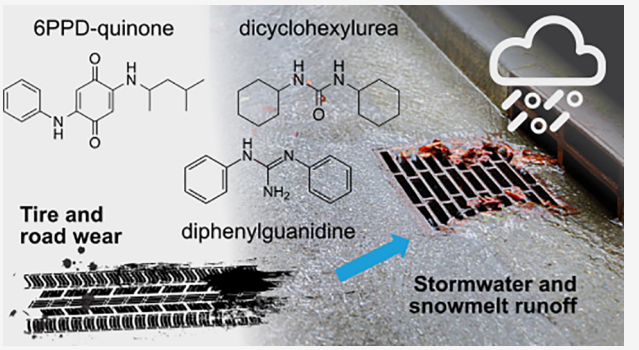
ABSTRACT: Recent findings that 2-anilo-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione (6PPD-quinone), the transformation product of a common tire rubber antioxidant, is acutely toxic in stormwater-impacted streams has highlighted the need for a better understanding of contaminants in urban runoff. This study represents one of the first reports of 6PPD-quinone and other tire rubber-derived compounds in stormwater and snowmelt of a cold-climate Canadian city (Saskatoon, 2019−2020). Semiquantification of the five target compounds, N,N′-diphenylguanidine (DPG), N,N-dicyclohexylmethylamine (DCA), N,N′-dicyclohexylurea (DCU), 1-cyclohexyl-3-phenylurea (CPU), and 6PPD-quinone, revealed DPG was most abundant, with average concentrations of 60 μg L^{-1} in stormwater and 1 μg L^{-1} in snowmelt. Maximum observed concentrations of DPG were greater than 300 μg L^{-1}, equivalent to loadings of 15 kg from a single rain event. These concentrations of DPG represent some of the highest reported in urban runoff globally. 6PPD-Quinone was detected in 57% (12/21) of stormwater samples with a mean concentration of approximately 600 ng L^{-1} (2019) and greater than 80% (28/31) of snowmelt samples with mean concentrations of 80−370 ng L^{-1} (2019 and 2020). Concentrations of 6PPD-quinone exceeded the acute LC_{50} for coho salmon (0.8−1.2 μg L^{-1}) in greater than 20% of stormwater samples. Mass loadings of all target chemicals correlated well with roads and residential land-use area.



INTRODUCTION

Stormwater and snowmelt runoff represent important and complex sources of chemical mixtures entering surface waters. In urbanized environments, runoff events can mobilize nutrients, road salts, and many inorganic and organic contaminants.[1−3] Urbanization has resulted in greater quantities and lesser quality of surface runoff, posing challenges for protection of municipal infrastructure and receiving environments. Additionally, the diffuse and often stochastic nature of urban runoff makes the sampling of these complex mixtures difficult.[1−3] Recently, nontarget analysis using high-resolution mass spectrometry (HRMS) has been employed to characterize urban runoff beyond this typical suite of targeted analytes (e.g., metals, polycyclic aromatic hydrocarbons).[4−13] Common among these studies was ubiquitous detection of compounds related to manufacturing of tire rubber and plastics, including bicyclic amines and melamine derivatives, frequently measured at concentrations of μg L^{-1} in urban runoff[7,13] and even surface waters during precipitation events.[14]

Multiple studies have reported toxic potency of tire rubber leachate to algae,[15] anthropods,[16] molluscs,[15] fish,[17−19] and vertebrate embryos.[20] The rubber vulcanizing agent, N,N′-diphenylguanidine (DPG) has been reported to be a highly abundant feature identified by nontarget analysis in road runoff.[7,13] DPG has measured acute (48 h LC_{50}) and chronic (21 day) toxicities of 17 and 0.6 mg L^{-1} (daphnia).[21] The recent discovery that the tire rubber-derived transformation product 2-anilo-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione (6PPD-quinone) is the primary causal toxicant for urban runoff mortality syndrome affecting Pacific Northwest coho salmon[9] has brought significant attention to this source of contamination. Further confounding this issue are efforts toward recycling and utilization of scrap tire material. For example, in 2009, scrap tire material generated in the U.S. exceeded 4.5 billion kg, with greater than 80% of that being utilized in the scrap tire market.[22] Uses include sporting and playground surfaces, mulch, septic field drainage, and recycled construction materials, including asphalt concrete made with recycled crumb rubber, in some cases, without a comprehensive consideration for, or assessment of potential environmental impacts.[22−26]

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This study reports occurrences of five compounds derived from tire rubber, including the recently discovered transformation product 6PPD-quinone, in stormwater and snowmelt runoff in the semiarid, cold-climate city of Saskatoon, Saskatchewan, Canada.

MATERIALS AND METHODS

Chemical Standards. Chemical standards N,N′-diphenylguanidine (DPG), N,N-dicyclohexylmethylamine (DCA), N,N′-dicyclohexylurea (DCU), and 1-cyclohexyl-3-phenylurea (CPU) were purchased from Sigma-Aldrich (Oakville, ON). The 2-anilo-5-[(4-methylpentan-2-yl)amino]cyclohexa-2,5-diene-1,4-dione (6PPD-quinone) standard was kindly provided by Dr. Kolodziej's research group who identified, synthesized, and purified this compound.[9] Native and isotopically labeled 6PPD-quinone-(d5) was purchased from Toronto Research Chemicals, Toronto, ON. See Supporting Information, Section 1.1, for complete chemical standard and reagent details.

Study Region and Sampling Sites. The City of Saskatoon (City) is the largest municipality in Saskatchewan with a population of approximately 330,000 covering an area of 140 km^2. The Saskatoon climate is classified as warm humid continental (Dfb) according to the Köppen−Geiger classification system with an average annual precipitation of 465 mm and approximately 50% of that falling as rainfall in June, July, and August. The City has more than 100 stormwater outfalls, some of which are connected to a network of treatment ponds, while others are discharged directly into the South Saskatchewan River (SSR). The City also has four snow dump sites for managing winter precipitation. Snowmelt samples were collected between March and May of 2019 and 2020 at four City snow dumps (Supporting Information, Figure S1). Snow from the piles was collected from 8 to 12 random locations on the surfaces and sides of the snow piles and combined in a 25 L container (Supporting Information, Section 1.2.2). Stormwater was collected in June, July, and August, 2019 (Supporting Information, B2) at seven outfalls along the SSR representing a mix of residential, industrial, and retail developments (Supporting Information, Section 1.2.1, Supporting Information, B1).[27] River water samples were also taken from nine SSR sites on one date in each of June, August, and October 2020 (Supporting Information, Figure S2). Only a single SSR site (Downtown) falls inside the City limits. Field and lab blanks containing Milli-Q water were acquired for each sampling event. The target analytes were below limits of detection in all blanks.

Sample Extraction and Processing. Stormwater, snowmelt, river samples, and lab and field blanks were filtered through Whatman GF/F glass microfiber filters (0.7 μm) and extracted using Oasis HLB solid-phase extraction cartridges prior to analysis. Complete details of the extraction protocols are found in Supporting Information, Section 1.2.4.

Instrumental Analysis. Analysis was conducted using a Vanquish UHPLC and Q-Exactive HF Quadrupole-Orbitrap mass spectrometer (Thermo-Fisher, Mississauga, ON). LC separation was achieved with a Kinetex 1.7 μm XB-C18-LC column (100 mm × 2.1 mm) (Phenomenex, Torrance, CA) by gradient elution (Supporting Information, Tables S3 and S4) with water and methanol, both containing 0.1% formic acid at a flow rate of 0.2 mL min^{-1} and column temperature of 40 °C. Method detection limits ranged from 0.3−1.2 ng mL^{-1} (Supporting Information, Table S6). All MS method details including precursor/product ions (Supporting Information, Table S5) and example chromatographs and MS spectra (Supporting Information, Figures S3−S7) can be found in the Supporting Information, Section 1.3. Suspect screening was conducted using Compound Discoverer 2.1 (Supporting Information, Figures S8 and S9), and targeted semiquantification was done with TraceFinder 4.1 (ThermoFisher Scientific).

Semiquantification of Target Compounds. The suspect screening analyses tentatively identified N,N′-diphenylguanidine (DPG), N,N-dicyclohexylmethylamine (DCA), N,N′-dicyclohexylurea (DCU), and 1-cyclohexyl-3-phenylurea (CPU) in the storm runoff and snowmelt samples. These four bicyclic amines are associated with tire rubber manufacturing and have been detected in tire rubber leachate,[28] and road runoff.[7,13] These four compounds also had readily available authentic standards. Additionally, following its recent discovery as a toxic stormwater contaminant,[9] the transformation product 6PPD-quinone was included in the targeted method. These five tire rubber-derived contaminants were retrospectively confirmed by comparison of retention times, accurate masses, and mass fragments to authentic analytical standards. Semiquantification was done using a targeted external calibration method, which based on extraction efficiencies and matrix effects data (Supporting Information, Tables S7−S9) may be underestimated by a factor of 2 or more (Supporting Information, Section 2.2).

RESULTS AND DISCUSSION

Snowmelt. Concentrations of all five target compounds were detected with varying frequencies in snowmelt from 2019 and 2020 (Supporting Information, Table S10 and Figure S10, and Supporting Information, B4). Concentrations of 6PPD-quinone, DCA, and CPU were consistently greater in snowmelt samples from 2019 compared to 2020, by on average 2−8-fold. This yearly trend was less clear for DPG, skewed by a single high concentration in 2020 (8667 ng L^{-1}), and DCU which had a low detection frequency in 2019 (20%). Approximately 35% more snow accumulated in Saskatoon in 2019 versus 2020, potentially influencing concentrations for some of the tire rubber-derived compounds in City snow dumps. Additionally, 2019 samples were snow melted in the lab, while 2020 samples were collected as snowmelt on site. This, and other factors, including age of snow prior to sampling (e.g., compound degradation), frequency of snow clearing, dilution from fresh snow fall, and rate of melting, could be confounding these observations.[27,29,30] Snow samples were taken as composites from 8 to 12 locations representing both new and old snow. Therefore, these samples are not appropriate for a detailed elucidation of fate mechanisms occurring in the snow dump or during melt events. Assuming measured chemical concentrations from Valley Road snow (Supporting Information, Table S10) are representative of the entire snow dump, mass loading estimates are 10 g of 6PPD-quinone, 150 g of DPG, 0.3 g of DCA, 2 g of DCU, and 0.4 g of CPU (Supporting Information, Section 2.4).

Stormwater Concentrations. Sampling of stormwater took place in 2019 across seven sites (Supporting Information, Figure S1) and four sampling events between June and August. Each sampling event typically took place within hours of the onset of a precipitation event with the exception of the July 24−25 event which took place approximately 24 h later (Supporting Information, B2). Concentrations of all target compounds were on average 3−60-fold greater in stormwater

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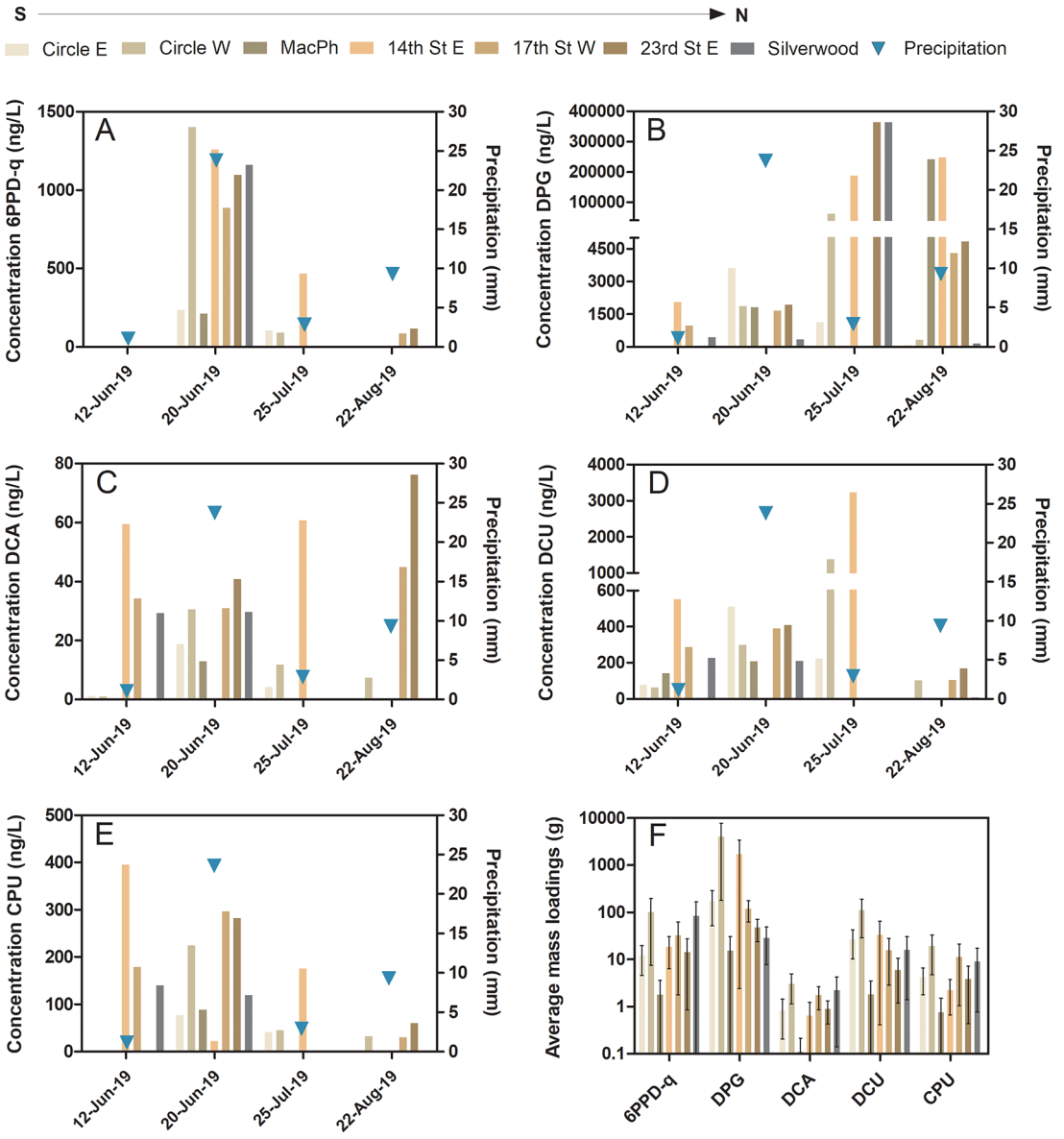

Figure 1. Concentrations (ng L^{-1}) of 6PPD-quinone (A), N,N′-diphenylguanidine (DPG) (B), N,N-dicyclohexylmethylamine (DCA) (C), N,N′-Dicyclohexylurea (DCU) (D), and 1-cyclohexyl-3-phenylurea (CPU) (E) in stormwater samples from 2019 with precipitation events (mm) overlaid. Each bar in A−E represents a single sample. Mass loadings in (F) are the average (±standard error) across all dates at each sampling site (note log scale). Sampling locations correspond to street names in closest proximity to stormwater outfalls (see map in Figure S1).

as compared to snowmelt, a result indicative of the greater maximum concentrations observed during storm runoff events compared to the composite snowmelt samples.

Comparing the June 20, July 25, and August 22 sampling events and resulting compound concentrations (Figure 1, Supporting Information, Table S11 and B3) highlights some of the confounding factors related to studying stormwater runoff. June 20 and August 22 saw single large rain events (24 and 10 mm, respectively, Supporting Information, B2) preceded by multiple days of dry conditions (<0.4 mm), whereas July 25 saw a relatively small amount of rainfall (2.9 mm) on the day of sampling but was preceded by 19.2 mm of rain the day prior (July 24) (Supporting Information, B2). Maximum concentrations of DPG were observed at multiple sites on both July 25 (61−364 μg L^{-1}) and August 22 (242−248 μg L^{-1}), whereas DPG concentrations were less than 4 μg L^{-1} on June 20. The maximum observed DPG concentrations observed on July 25, nearly 18 h after the start of the July 24 event (19.2 mm, Supporting Information, B2), are somewhat surprising given that lag times to peak concentrations in direct runoff are expected to be much less than lag times previously reported in receiving waters (12−18 h).[12,14] These findings suggest that the elevated DPG concentrations either represent the tail end of the chemograph and missed peak concentrations were in fact much higher (i.e., mg L^{-1} range) or this large flush event produced elevated DPG levels over an extended period of time. In contrast, the lower concentrations of DPG observed on June 20 (sampled approximately 9 h into the rain event, Supporting Information, B2) may indicate the contaminant peak was missed. However, a major influence here may relate to street cleaning, which is typically done in May, and could have led to reduced concentrations in June.

All four bicyclic amines (excluding the exceptionally high DPG concentrations at two sites on July 25 and on August 22)

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share similar concentration profiles across sampling dates and sites (Figure 1B−E). In contrast, 6PPD-quinone showed maximum observed concentrations across most sites on June 20 and only select detections on July 25 and August 22 (Figure 1A). Reasons for the observed differences are not clear; however, the sources, fate, and transport dynamics of these compounds are likely playing roles. The transformation product 6PPD-quinone is generated via ozonation of the common tire rubber antioxidant 6PPD,[9] whereas DPG, for example, is expected to leach directly from car tires (i.e., no transformation) and has multiple other industrial applications including use in rubber gloves, footwear, hosing, and cables.[21] To what extent these other sources are contributing to DPG levels is not known at this time; however, we still expect car tires to be by far the major source of DPG in this study.

Recent reports of these compounds in storm runoff and receiving systems come from the heavily urbanized and densely populated Seattle, WA, USA[8] and Toronto, ON, Canada.[31] While population in these regions differ significantly (≈270,000 Saskatoon versus ≈4,000,000 Seattle and ≈6,300,000 Toronto), estimated densities are more comparable (Saskatoon ≈1900 versus Seattle ≈3100 and Toronto ≈4300 persons/km^2). Average concentrations of 10, 300, and 350 ng L^{-1} DCA, DCU, and CPU in Seattle stormwater runoff[13] are comparable to means observed during the present study of 30, 450, and 130 ng L^{-1} DCA, DCU, and CPU, respectively (Supporting Information, Table S11 and B3). However, the mean concentration of 1.8 μg L^{-1} DPG reported in road runoff in the same study[13] was approximately 30-fold less than that observed here (≈60 μg L^{-1}). Concentrations of DPG measured in a small Toronto creek and river ranged from 0.16−0.76 μg L^{-1} during two summer rain events.[31] These concentrations are approximately 80- to 400-fold less than our reported stormwater runoff concentrations, a result attributed to in-stream dilution.

Sampling at 10 South Saskatchewan River sites revealed that of the five target compounds only DPG was measured at detectable levels (Supporting Information, Table S12), allowing for a comparison of surface water concentrations with the Toronto study. DPG was detected in 100% (n = 26) of river samples at 24 ± 76 ng L^{-1} (range = 0.7−401 ng L^{-1}), which agrees well with reported surface water concentrations elsewhere[12,13] but is greater than 20-fold less than those reported in Toronto surface waters.[31] This is consistent with average discharges of 1−4 m^3 s^{-1} in the Don River and Highland Creek,[31] which are 50−100-fold less than average flows in the South Saskatchewan River (≈200 m^3 s^{-1}). Accounting for in-stream dilution in this way would suggest that concentrations of DPG in direct stormwater runoff in Toronto would be similar to the elevated levels found in Saskatoon. Regardless, with maximum observed concentrations greater than 300 μg L^{-1}, to our knowledge these represent some of the highest concentrations of DPG observed in stormwater runoff globally.

Reasons for these exceptionally high concentrations are not known; however, it may relate to the climate, characterized by occasional but intense rainstorms often preceded and/or followed by extended dry periods. Months-long winters are characterized by dramatic temperature fluctuations (seasonal and daily) and low absolute humidity, potentially aggravating mechanical degradation processes of tires and roads.[32,33] These conditions can lead to significant accumulation and subsequent flushing of tire rubber material from roads during rainfall events. Other factors unique to cold-climate regions that may be contributing to these elevated levels include poor road conditions (i.e., potholes), the widespread use of softer-rubber winter tires,[34−36] and application of sand and salt to roads. One report measuring tire wear particles found that concentrations of PM_{10} generated from winter tires and studded winter tires were approximately 10- and 100-fold greater compared to summer tires, respectively.[35] The widespread use of winter tires in Saskatoon and the fact that there are no restrictions on studded tires in the province may be contributing to these high DPG concentrations.

Concentrations of 6PPD-quinone in stormwater runoff ranged from 86−1400 ng L^{-1} with a detection frequency of 57% (12/21) across all sites and sampling events (Figure 1, Supporting Information, Table S11 and B3). Tian et al. observed an average 6PPD-quinone concentration of 7000 ± 4500 ng L^{-1} in roadway runoff from two sites (n = 16),[9] which is approximately 10-fold greater than the average concentration observed here (593 ± 525 ng L^{-1}). Johannessen et al. reported concentrations of 210−720 ng L^{-1} 6PPD-quinone in the same Toronto surface waters discussed above,[31] with likely concentrations in direct runoff (no in-stream dilution) to be much greater. The reported LC_{50} of 6PPD-quinone to coho salmon is 800−1200 ng L^{-1}, meaning that 5 of 12 sampling events where 6PPD-quinone was detected would exceed this LC_{50}. While coho salmon are not found in the South Saskatchewan River, risks of 6PPD-quinone exposure to other species of fishes (e.g., northern pike, lake trout) and other aquatic organisms are currently unknown.

Stormwater Loadings. Stormwater runoff volumes were estimated based on precipitation depth corresponding to each sampling event, catchment area, and land-use data obtained from the City of Saskatoon.[37] Specifically, a stormwater volume was calculated for each land-use (LU) area (Supporting Information, B1) comprising a single sampling catchment ($CR_{LU} \times A_{LU} \times P$) and then summed to obtain the total stormwater runoff volume for that catchment for each precipitation event (Supporting Information, B2). These data were used to estimate chemical loadings (eq 1).

$$L = \left(\sum CR_{LU} \times A_{LU}\right) \times P \times C \quad (1)$$

where L (kg) is the chemical load, $CR_{LU} \times A_{LU}$ (km^2) the dimensionless land-use specific runoff coefficient and land-use specific area, respectively, summed together for a total land-use specific stormwater catchment area, P the event precipitation depth (mm), and C the chemical concentration measured at a specific stormwater outfall on a given sampling day. Measured concentrations were assumed to be constant over the duration of each rainfall event, potentially leading to over- or underestimations of loadings. As such, the reported mass loadings should be considered qualitative estimates.

Average loadings of 6PPD-quinone, DCA, DCU, and CPU across all sites and dates ranged from 1−50 g per rainfall event, whereas average DPG loadings exceeded 1 kg and reached approximately 15 kg maximally, from a single rain event (July 25, Circle W sampling site) (Figure 1F, Supporting Information, Figure S12 and B3). A recent study in urban streams around Toronto, Ontario, Canada reported 6PPD-quinone loadings of 34 and 416 g during a heavy August rainfall (25 mm),[31] consistent with mass loadings of 1.7−384 g observed here. The same study reported DPG loadings of 26 and 454 g during this same storm event, significantly less than

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our calculated DPG loadings (Figure 1F and Supporting Information, B3). The mass loads of DPG reported here are more comparable with HMMM (0.09−13 kg/event)[14] and total HMMM (HMMM + transformation products) (2.8−25 kg/event)[31] measured in the Don River and Highland Creek, Toronto, Ontario, Canada. It should be noted that loading calculations discussed above from Johannessen et al.[14,31] are based on in-stream samples over the course of a storm event, providing greater temporal resolution and accuracy than accomplished here and, thus, are not directly comparable to our stormwater outfall samples.

Land-Use Correlations. Spatial and temporal trends of the target compounds (Figure 1) as a function of precipitation events and antecedent dry periods were not observed, possibly due to the small sample size (2−4 sampling events per site) and other confounding sampling factors (e.g., lag times[12,14]). However, linear regression analysis of mass loadings as a function of land-use area (land-use definitions and breakdowns in Supporting Information, B1) at each of the seven sampling sites indicate strong positive correlations with roads (average r^2 = 0.800) and residential areas (average r^2 = 0.883) and no correlations with industrial areas and green spaces (Table S13). Hou et al. also observed greater surface water concentrations of vehicle-related chemicals (e.g., HMMM, DPG) in areas of higher traffic density. In the current study, DPG demonstrated poorer correlations with roads (r^2 = 0.576) and residential (r^2 = 0.734) areas compared to the other four compounds (r^2 > 0.753 roads and r^2 > 0.844 residential). This may suggest multiple important sources of DPG contributing to the observed levels; however, this requires further research to confirm.

The findings of this study highlight important differences in the occurrences of tire rubber-derived compounds, in particular DPG, when compared across studies conducted in different geographies. While the reasons for these differences are not completely clear at this time, we suspect it is a combination of factors related to land-use, infrastructure, population, climate, study sampling design, and chemical transport dynamics. Future studies should be designed with the purpose of delineating the impact of these variables on the occurrence and fate of stormwater-related compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.1c00682.

Maps and sampling details, instrumental and data analysis details, chromatographic peaks and mass spectra, detection limits, stormwater and snowmelt concentrations (PDF)

B1: Land-use data and runoff coefficients used for loading calculations. B2: Precipitation events and sampling time. B3: Stormwater concentrations and loadings. B4: Snowmelt concentrations (XLSX)

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Notes

The authors declare no competing financial interest.

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