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Intensive Spatiotemporal Characterization of the Tire Wear Toxin 6PPD Quinone in Urban Waters

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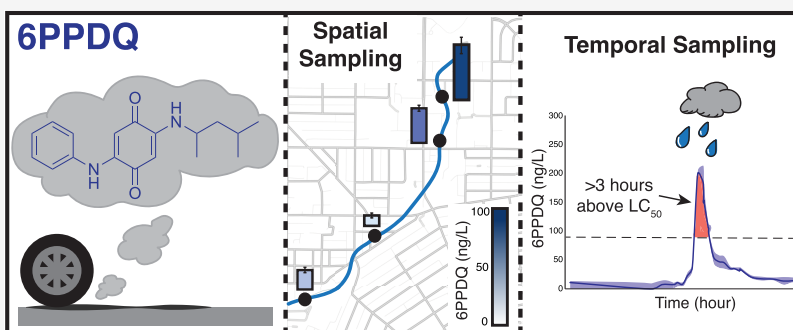Cite This: *ACS EST Water* 2024, 4, 5566−5574

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ABSTRACT: 6PPDQ is a tire-derived contaminant toxic to coho salmon (LC_{50} = 41−95 ng/L) found widely distributed in urban environments. Most monitoring efforts have relied on relatively few discrete samples collected at select locations across rain events. Early work has revealed that 6PPDQ concentrations vary widely over time and space, raising questions about when and where to collect samples. Here, we employ condensed phase membrane introduction mass spectrometry, a high-throughput analysis approach to characterize spatiotemporal variability of 6PPDQ in urban streams. Analytical method detection limits of 0.3−8 ng/L and a duty cycle of 2.5 min/sample enabled high-throughput adaptive sampling. Temporal sampling revealed dynamic 6PPDQ concentrations, with significant changes occurring over minutes during peak rainfall. Spatial variability was characterized at multiple sites along three watercourses during the first significant precipitation of autumn 2023 on central Vancouver Island, B.C., Canada. Site-specific concentrations suggest attenuation of 6PPDQ after point source inputs by some combination of physical (dilution, sorption) or chemical (degradation) processes. This is the first report of an intensive sampling campaign describing the spatiotemporal distribution of 6PPDQ, highlighting the need for careful consideration of sampling strategies to evaluate the risk and impact of 6PPDQ in urban waterways.

KEYWORDS: *tire derived toxins, para-phenylenediamine quinones, direct mass spectrometry, CP-MIMS, high throughput analysis*

INTRODUCTION

In 2020, Tian et al. identified *N*-(1,3-dimethylbutyl)-*N′*-phenyl-*p*-phenylenediamine quinone (6PPDQ) as the cause of 'urban runoff mortality syndrome" (URMS).[1] It is one of several oxidative transformation byproducts of *para*-phenylenediamine (6PPD) antiozonant added at up to 2% by mass to extend the life of tires.[2,3] 6PPDQ is acutely toxic to coho salmon (*Oncorhynchus kisutch*) with a LC_{50} range of 41−95 ng/L for juveniles, with mortality observed within 2 h of exposure.[1] It has recently demonstrated toxicity toward several other freshwater species, such as Chinook salmon (*O. tshawytscha*) and rainbow trout (*O. mykiss*).[1,4−6] Since its discovery, 6PPDQ and analogous *p*-phenylenediamine quinones (PPDQs) have been widely detected in water, soil, atmospheric particulate matter, and humans.[7−9]

6PPDQ is leached from the surface of tire wear particles and transported to receiving waters in roadway runoff.[1,4] Consequently, stream concentrations are observed to vary over time and space throughout a rain-event as particles and

associated leachates are mobilized.[10,11] Monitoring campaigns have largely relied on collecting discrete samples from receiving waters. Concentrations range from 7 to 230 ng/L in the US Pacific Northwest, <1−90 ng/L in an Australian creek, and up to 200−2000 ng/L in urban Hong Kong road runoff.[4,7,10] However, few studies have evaluated the temporal variability of 6PPDQ across individual rain events.[10,12] Early efforts from Johannessen et al. revealed some variability over time, with 3-h pooled stream samples showing distinct before, during, and after rain concentration regimes.[12] Rauert et al. collected 6−9 hly grab samples from rain events in a tributary

of the Brisbane River, storing the samples for subsequent analysis.[10] Collecting and analyzing these time-resolved samples can be logistically challenging, requiring intensive fieldwork and remotely triggered or timed portable sample collectors built for composite water quality assessment. The latter has shown utility by Helm et al. in assessing 6PPDQ in receiving waters entering Lake Ontario.[13] This equipment offers distinct advantages over intensive manual sampling and is easily scaled. However, materials used to construct these samplers (silicone tubing,[14] plastic sample bottles[15]) may adsorb 6PPDQ, complicating interpretation. Further, these systems typically leave samples uncapped and exposed to the atmosphere until they are retrieved by field crews. We and others have observed loss of 6PPDQ from open containers over relatively short periods ($t_{1/2}$ = 51 h at 25 °C).[16,17] While appropriate quality assurance measures such as comparative grab samples[13] can mitigate the risks associated with intermittent samplers, there remains some uncertainty about use protocols and sample integrity. Finally, trace organic contaminants such as 6PPDQ are generally measured using a series of cleanup/pre-enrichment steps (solid phase extraction and liquid−liquid extraction) coupled to liquid-chromatography mass spectrometry (SPE/LLE-LCMS). This approach offers excellent sensitivity and selectivity; however, it can be time- and cost-intensive, therefore limiting the overall sample capacity and adaptability of monitoring campaigns.

To address these challenges and uncover the spatiotemporal variability of 6PPDQ in urban streams, an intensive manual sampling regime was analyzed by a high-throughput direct mass spectrometry method. For this work, more than 270 samples were collected in three urban waterways. The spatial study sampling campaigns utilized individual grab samples before, during, and after rain events at numerous sites separated on spatial scales of 10^2-10^3 m. Time-intensive sampling occurred at 1−6 h frequency across the entirety of two rain events ranging from 2 to 6 days in duration. Analysis was carried out using condensed phase membrane introduction mass spectrometry (CP-MIMS) paired with a custom-built autosampler.[16] This technique uses a semipermeable polydimethylsiloxane (PDMS) membrane immersion probe for online sample cleanup/enrichment, allowing permeation of neutral hydrophobic contaminants while rejecting bulk matrix components (e.g., ions, particulates). This affords sensitive (0.3−8 ng/L detection limits), high-throughput (2.5 min/sample; ≥100 samples/day) analysis of 6PPDQ and structurally related analogs.

■ MATERIALS AND METHODS

Standards and Samples. Analytical standards of 6PPDQ and $^{13}C_6$-6PPDQ (≥95%; 100 μg/mL in acetonitrile) were purchased from ACP Chemicals (Montreal, QC). Standards of IPPDQ, CPPDQ, DPPDQ (10 mg each), and 6PPDQ-d_5 (100 μg/mL in acetonitrile) were purchased from HPC Chemicals (Atlanta, GA) at ≥98% purity. HPLC grade methanol was used in making 20−250 μg/kg stock solutions (Fisher Scientific, Ottawa, ON). Full analyte names and structures are listed in Figure S1. Calibration solutions were made by spiking methanolic 6PPDQ stocks into deionized (DI) water for concentrations between 10 and 300 ng/L (Facility scale reverse Osmosis/Ion Exchange Water Purification System, Applied Membranes, Inc., Vista, CA).

Water samples were collected and analyzed without preservation or filtration in Nanaimo, British Columbia,

Canada (Figure S2) by completely filling 250 mL amber glass bottles (≤5% headspace) before sealing them with PTFE-lined caps. Samples were stored in a cooler or fridge at 4 °C before delivery to the lab within 24 h. Between uses, bottles were cleaned with ≥5× tap water rinses, 3× DI water rinses, and a final rinse with HPLC-grade methanol. Field blanks returned PPDQ concentrations below the method detection limits in all cases. Waterways included an urbanized river (Millstone River), a tributary (Cat Stream) of the larger Chase River, and a creek (Northfield Creek). Site photos for each waterway are available in Figure S3. Only the largest system (Millstone River) is equipped with a hydrometric station.[18] However, flow data was collected using the area-velocity method on the same, dry day to illustrate the relative size of the waterways considered here (Table S1).[19] The region's Mediterranean climate results in a 4−6 month dry period (average < 20 mm per month Apr.−Sept.), followed by a wet period (average > 20 mm per month Oct.−Mar.; Figure S4).[20] Sampling for a rain event required at least 2 dry days before the rain was forecast to begin. The first flush spatial sampling was conducted at 4−6 sample sites per waterway over September 23−27th 2023, when the first significant (>5 mm) rain occurred. Two additional spatially intensive sampling campaigns were conducted between September and December. The initial high temporal (hourly) sampling was performed on Northfield Creek over November 20−23rd 2023. Follow-up time-intensive sampling of three watercourses took place over the week of November 29th to December 6th, 2023.

Samples were transferred gravimetrically to clean 40 mL glass TOC vials (same cleaning as above) and measured as is or with 2−5× dilution when screening revealed concentrations above the working calibration range (10−300 ng/L). 6PPDQ-d_5 internal standard was spiked into the aqueous samples (after any dilution steps) at ca. 200 ng/L before analysis. A first pass analysis of all samples was done within 48 h of sampling. While sample integrity over time for 6PPDQ remains unclear, several studies have demonstrated stability for sealed samples collected/stored under similar conditions over 2−3 weeks.[14,16,21]

CP-MIMS. Detailed descriptions of the CP-MIMS probe are available elsewhere,[22,23] including the use of a modified 3D printer as an autosampler.[16] A schematic diagram and photos of the experimental setup are provided in Figure S5. Briefly, a 7.6 cm segment of PDMS hollow fiber membrane (190 μm inner diameter [ID], 300 μm outer diameter [OD], Permselect, Medarray Inc., Ann Arbor, MI) is mounted on 31-gauge stainless steel capillaries (Microgroup, Medway, MA). Red PEEK tubing (0.005″ ID; 1/16″ OD) was used to connect the probe to a syringe pump (feed side) and the mass spectrometer. A 15/85/0.03 ($v/v/v$) mixture of heptane/MeOH/formic acid (Optima 99.0%+, Fisher Scientific) was used as the acceptor phase at a flow rate of 10 μL/min. $^{13}C_6$-6PPD-Q was included in the acceptor phase to monitor the instrument drift and any ionization suppression. Detection was carried out using positive mode electrospray ionization (ESI) with a triple quadrupole MS instrument (TSQ Altis or TSQ Fortis, Thermo Scientific, San Jose, California, USA). Instrument parameters included: Ion transfer tube temperature: 300 °C, sheath gas flow: 5 (arbitrary units [au]), auxiliary gas: 2 au, capillary voltage: +4 kV. The m/z 299 → 256 transition was used for 6PPDQ quantitation, while the presence of m/z 299 → 243 and 299 → 187 were used to qualify the presence of 6PPDQ. All samples returning 6PPDQ concentrations greater
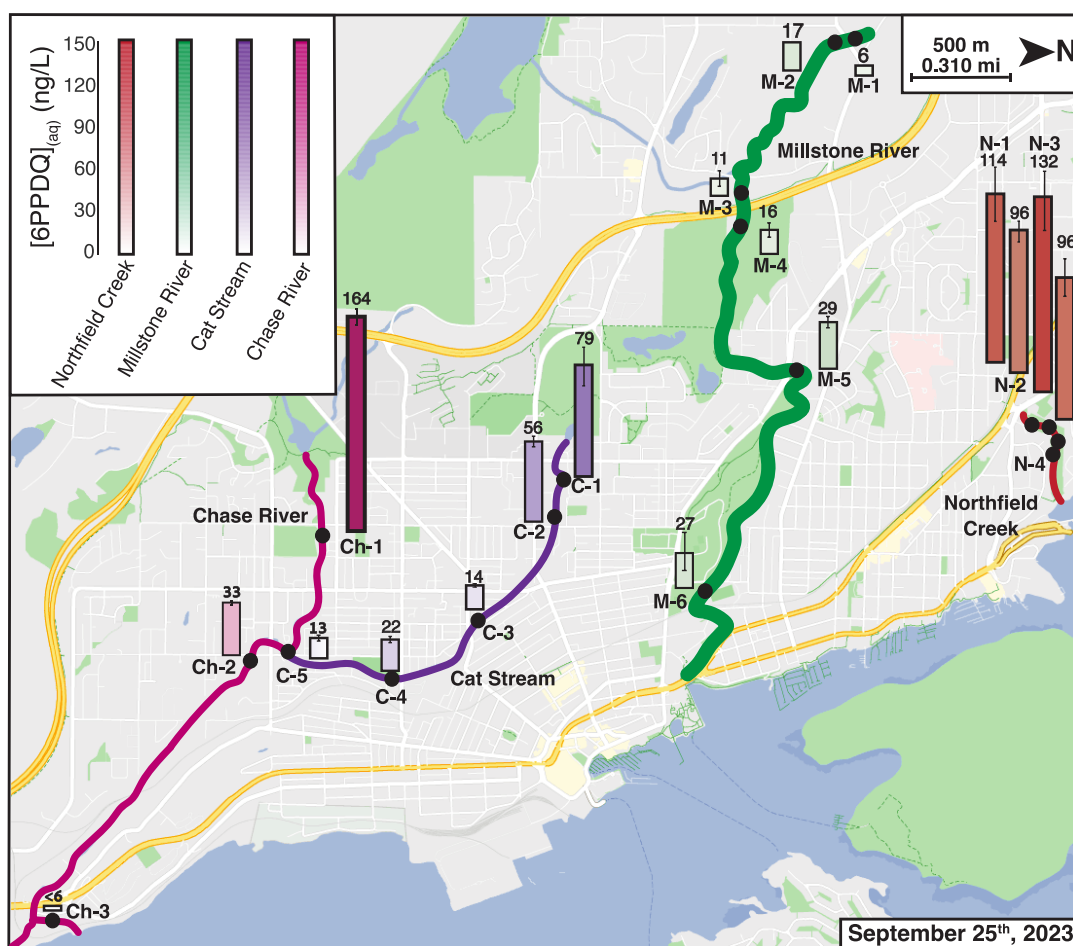
Figure 1. Spatial variability of 6PPDQ across several urban streams in Nanaimo, British Columbia, during the first-flush event on September 25th, 2023. Numbers on the top of the bars represent mean concentrations of 6PPDQ in ng/L. Error bars represent the standard deviation of three replicate measurements. Line thicknesses indicate relative streamflow.

than 10 ng/L were measured in triplicate. Additional MS parameters are listed in Table S2.

Data Processing and QA/QC. Raw MS data were converted from the vendor '.raw' format to '.mzML' using msConvert (Proteowizard, Palo Alto, California), which were subsequently processed in MATLAB using a revised version of the automated data processing toolkit described previously (Monaghan et al.).[16,24] In the revised code, quantitation is based on the signal area for a 2.5 min membrane exposure normalized to the signal area of the 6PPDQ-d_5 internal standard added to each sample/standard. A five-point calibration curve was collected at the beginning and end of each experimental run (examples shown in Figure S6). After every five samples, a calibration check solution (~70 ng/L) and a DI water blank were measured to verify stable instrument performance (Figure S7; 80% of all calibration check solutions fall within the target recovery range of 70−130%). Samples measured in replicates are reported out as the mean concentration ± one standard deviation. Hourly precipitation data was retrieved from Visual Crossing Weather.[25]

■ RESULTS AND DISCUSSION

High-throughput chemical analysis was combined with an intensive manual sampling campaign to measure over 270 samples with near "real-time" feedback to adapt sampling

efforts where needed. For high-throughput quantitation of 6PPDQ, we have automated the data acquisition and processing steps for CP-MIMS.[16] This platform enables quantitative analysis of trace contaminants in ≥100 samples/instrument/day with associated calibration standards and QA/QC checks (≥176 total analyses/day). The 6PPDQ-d_5 added to the sample compensates for both partitioning and ionization effects, improving the quantitative performance for the free aqueous phase concentration. In this work, detection limits were assessed with each batch of 25 samples as previously described[16] and depended on the MS instrument employed. The TSQ Fortis yielded 6PPDQ detection limits comparable to our previous work (2−8 ng/L), while the TSQ Altis provided ~10-fold greater sensitivity (0.3−1 ng/L) with the range reflecting interday variability. We attribute the improved sensitivity of the TSQ Altis to the higher-capacity ion optics (ion funnel and larger ion transfer tube). Quantitative reproducibility with CP-MIMS was on the order of 10−20% for replicate sample analyses (n = 83 samples measured ≥3), in line with previous projects reporting trace 6PPDQ[16,23] and other organic contaminants using this direct membrane sampling technique.[26,27] The combined selectivity imparted by selective membrane transport and tandem mass spectrometry of multiple MS/MS transitions provides confidence in the quantitative results in real-world samples. This is reinforced by a recent cross-validation experiment between CP-MIMS and a
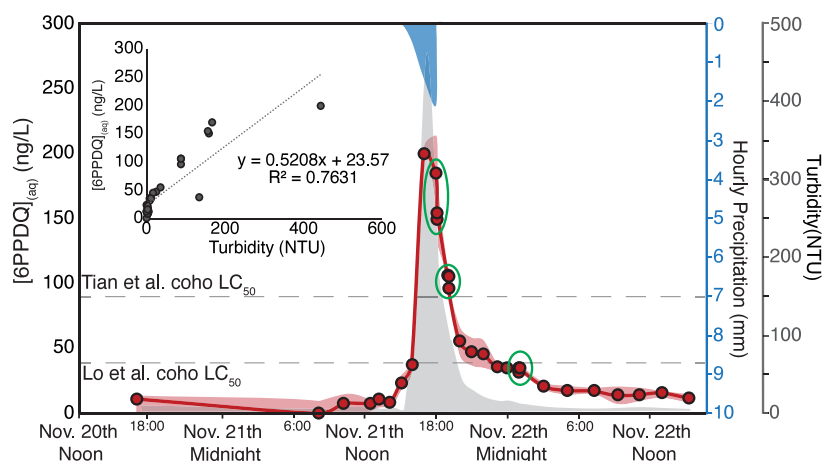
Figure 2. Temporal variability of 6PPDQ at a concentration in ng/L (left axis) at Northfield Creek across a discrete rain event (Nov 21–22nd, 2023). Samples were collected intensively over 28 h. All data points represent the mean of $n \geq 3$ replicate measurements of separate aliquots of the bulk sample collected at that time point. The shaded red area represents the uncertainty using the upper and lower bounds of one standard deviation across those measurements. Precipitation in mm is shown in blue from the top (right axis), and in-stream turbidity is shown in gray (right axis). Field replicates collected within several minutes of each other are indicated with green circles.

commercial LC-MS/MS method, which showed excellent agreement for surface waters (slope: 1.01, R^2 = 0.994, n = 10).[16] Nevertheless, we recommend results be verified with "high-selectivity methods" (e.g., LC-MS/MS) where "absolute quantitation" is important (e.g., results with legal/toxicological consequences) until ongoing interlaboratory comparisons have been completed.

In this work, three urban waterways spanning a range of sizes and inputs were studied (Figure S2 and Table S1). (1) Northfield Creek is a small nonfish bearing system with heavy stormwater influence, consequently exhibiting the highest 6PPDQ levels (max concentration of 132 ng/L across sites on September 25th, 2023). There is ongoing interest in the restoration of this habitat.[28] (2) Cat Stream is also a small urban system running through largely residential areas. It is more naturalized than Northfield Creek with a less obvious direct stormwater influence. It supports small salmonid populations (e.g., coho salmon and cutthroat trout) as a tributary to the Chase River system. Cat Stream and Chase River cross several busy roads and exhibited a maximum of 79 and 164 ng/L 6PPDQ (respectively) during the September 25th, 2023 rain event.[29] (3) The largest system in this study, Millstone River, hosts several salmon species.[30] It intersects a number of potential inputs, including a major highway and busy roads; however, Millstone exhibits the lowest concentrations (max concentration of 29 ng/L across sites on September 25th, 2023), possibly due to greater dilution of incoming roadway runoff and/or larger riparian setbacks.

Spatial Variability of 6PPDQ. We began by evaluating the spatial variability of 6PPDQ across the three urban systems. Before, during, and after rain, samples were collected at up to six locations on each waterway during the first major rain event in the autumn of 2023 (September), as shown in Figure 1, with two more rain events captured at all sites between October and December. Samples were collected within a 3 h window shortly after the onset of rain. During this rainfall, 6PPDQ concentrations were generally high, with 80–120 ng/L for Northfield, 10–70 ng/L for Cat Stream (30–160 ng/L for Chase River), and 10–30 ng/L for Millstone. Before- and after-rainfall samples were also collected for each site, all of

which exhibited significantly lower concentrations (<6–27 ng/L) than samples collected during rainfall (Figure S8).

At Northfield Creek, sampling sites were closely spaced (ca. 400 m total distance between four sites), and we observed relatively little variation in the 6PPDQ concentrations. This is consistent with the fact that all four sampling sites are located downstream of known stormwater inputs (e.g., a long underground section draining light industrial, commercial, and residential areas as well as two artificial turf fields with crumb rubber infill), and there appear to be few additional inputs into this system between sampling locations (N-1 to N-4, Figure 1).[23,31] The Cat Stream and Chase River exhibit more complex variations over space. This system is above-ground through several kilometers of residential area with multiple road crossings and potential stormwater inputs (e.g., culverts and drainage systems). They showed significant variation in 6PPDQ concentrations over the sampling locations (spanning an overall distance of ca. 6 km). The highest concentration was observed near the stream headwaters for Cat Stream, just after the first point source (road intersection and large paved parking area adjacent to a public school and community center), where streamflow is lowest. Concentrations generally decreased further downstream with a minor increase between sites C-3 and C-4 capturing inputs from a busy roadway and several smaller residential streets. A similar pattern was observed for the Chase River with higher 6PPDQ concentrations associated with upstream sample locations where stream flows are lowest. Based on this data, mitigation strategies to reduce tire wear toxin inputs on Cat Stream and Chase River are best suited in and around sampling sites C-1 and C-2 as well as at Ch-1. The concentrations of 6PPDQ increase in the Millstone River as it crosses roadways between M-1 and M-2 and again between M-3 and M-4. Concentrations continue to increase in the lower reaches on the Millstone as it flows through the higher traffic density areas at sites M-5 and M-6, which are ca. 6 km downstream from the first site. The observed spatial distribution of 6PPDQ in the Cat and Millstone is likely due to a combination of factors, including but not limited to (1) dilution with inputs of water with low/no tire wear influence, (2) additional 6PPDQ containing stormwater inputs from road runoff and/or

underground drainage pipes/culverts, (3) sorption/desorption processes, and (4) chemical degradation removing 6PPDQ from the aqueous phase. The observed spatial patterns in the concentration of 6PPDQ in these three waterways were broadly conserved over the two additional rain events in fall 2023, as depicted in Figures S9 and S10. The spatial variability observed here is consistent with previous observations of PAHs in urban water bodies, where PAH contamination was associated with local inputs (% impervious landscape within 300 m) rather than position along the stormwater gradient.[32]

The localized first-flush 6PPDQ concentrations across these three streams are of immediate relevance to local "stream-keeper" groups to protect salmon from URMS and urban planners to site mitigation efforts. This fine-scale data can inform where to invest limited resources for green infrastructure (e.g., near C-1 and C-2 sites on Cat Stream). We believe that the spatial variability of 6PPDQ observed here is of wider relevance as it highlights the need for careful site selection to accurately assess risks in urban waterways. As exemplified here, all waterways are unique, and absolute 6PPDQ concentrations depend heavily on local inputs (surface and underground), hydrology, riparian setbacks, and green infrastructure. Here, the Millstone River appears to be less impacted by 6PPDQ (i.e., lower concentrations than those exhibited in Cat Stream). This may be due to larger dilution ratios and a more naturalized green space as it passes through an urban park.
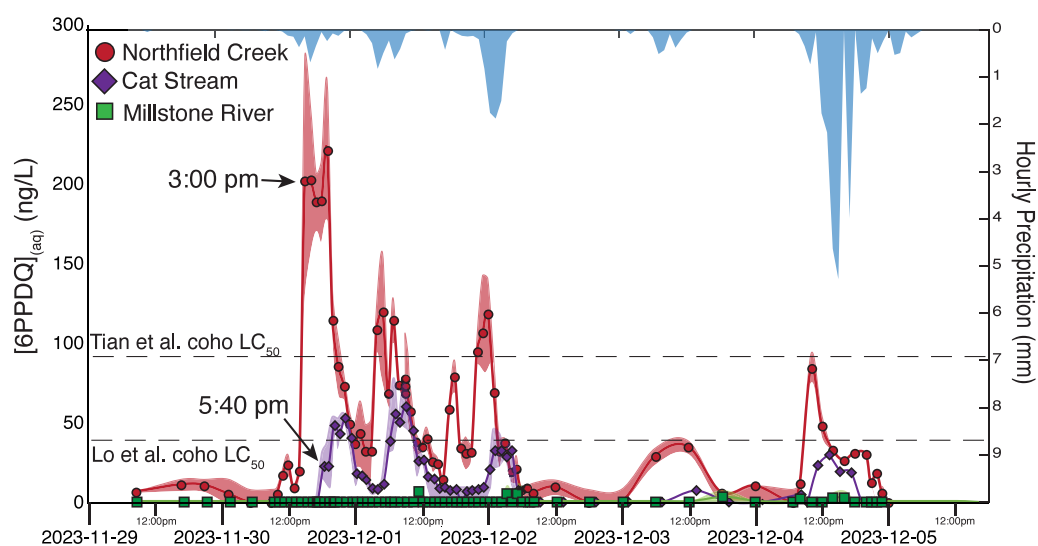
Temporal Variability of 6PPDQ. Stormwater contaminants are expected to exhibit dynamic concentrations throughout a rain event which may depend on a number of factors, including contaminant properties, local hydrology, and the shape of the hydrograph itself.[33] These complex dynamics raise important questions about obtaining a "representative" sample and assessing overall contaminant loads and exposure to aquatic organisms. For 6PPDQ, some researchers have employed flow- or time-weighted composite samples using automated sampling systems.[2,13] In the future, passive sampling strategies may be employed to yield similar time-weighted averages. In other cases, discrete grab samples collected sometime during rain events have been employed (depending on logistical factors such as field crew availability).[4,11] Given the relatively short exposure windows needed for 6PPDQ to induce mortality, at this stage, it is unclear which (if any) of these sampling strategies is most relevant to assessing aquatic toxicity risks in urban streams. To inform this discussion, we set out to intensively monitor 6PPDQ concentrations throughout a rain event to better understand variability on an hourly time scale.

To this end, Northfield Creek (site N-1; Figure 1) was intensively sampled across an entire rain event during November of 2023. This campaign occurred after a 10-day dry period, with initial samples collected ca. 5 h before the onset of rain. Samples were transported back to the lab in small batches (<10) and measured within 12 h of collection, and in some cases, results of the most recent sampling round were reported back to field crews within a few hours. These "decision" samples facilitated an adaptive sampling/analysis campaign, where hourly sampling was initiated before the rain started with 6PPDQ concentrations in the 10 ng/L range and continued through the peak rainfall with 6PPDQ concentration reaching ~200 ng/L. Sampling was continued at longer intervals until 6PPDQ levels returned to near prerain baseline levels (Figure 2). Several features are immediately apparent.

First, the concentration profile is incredibly dynamic, changing rapidly over the course of minutes−hours. As the rain initiates, 6PPDQ concentrations rise immediately and remain greater than the coho LC_{50} of 95 ng/L for 3−4 h. The peak 6PPDQ concentrations coincide with the peak rainfall and turbidity measurements at about 18:00 h (Figure 2). This agrees with field crews' observations that discharge quickly rose with the onset of rain. As the rain stopped, concentrations dropped sharply, exhibiting a rapid initial decrease to ca. 50 ng/L followed by a slower decay over the course of 12 h down to <10 ng/L. This is consistent with first flush dynamics, where the first rain washes contaminants from roads after an extended dry period. This behavior suggests that stream concentrations of 6PPDQ are not limited by water solubility (38 ± 10 μg/L) and that it is quickly mobilized in the stormwater influent.[14] The rapid increase in 6PPDQ concentration with the onset of precipitation is somewhat counterintuitive given its hydrophobicity (log K_{ow} 4.2).[14] This may be influenced by the presence of various surfactants also expected to be present in roadway runoff. Structurally related p-phenylenediamine quinones (IPPDQ, CPPDQ, and DPPDQ) derived from the corresponding p-phenylenediamine antioxidants were also measured alongside 6PPDQ. The concentration profiles of these compounds are similarly dynamic with IPPDQ showing the fastest rise and highest concentrations in these samples (Figure S11). IPPDQ's quick flushing with rain aligns with its more hydrophilic character (EPI Suite predicts a log K_{ow} of 2.6).[7] On the other hand, DPPDQ and CPPDQ with predicted log K_{ow} values of 3.5 and 3.9, respectively,[7] exhibited lower concentrations and a longer time lag before clearing the system. While the structural analogs were quantified using isotopically labeled 6PPDQ, we consider these results semiquantitative until these observations can be verified with labeled analogs and cross-validation experiments with LCMS. On three occasions within this rain event, triplicate sample sets were collected (within several minutes of each other), including at peak rainfall (18:00−19:00) as well as after the rain had stopped (01:00 the following morning), as indicated by green circles in Figure 2 (Table S3). While samples collected after the rain had stopped and concentrations had returned to near baseline levels were in excellent agreement (RSD: 5%), we note that replicates collected just after peak rainfall show an apparent drop in concentration, as illustrated in Figure 2. Concomitant water quality data collected revealed a correlation between turbidity and 6PPDQ concentrations (Figure 2, inset), showing rank-order agreement across the rain event (Spearman coefficient: 0.89; $p \ll 0.05$, $n = 30$), which we will expand on later.

Informed by the initial intensive hourly sampling of a discrete rain event at Northfield, we captured the next series of rain events (starting 8 days later) at the same Northfield Creek site as well as Cat Stream (site C-2) and Millstone River (site M-5). This week-long campaign spanned 4 small rain events (<2.5 mm) followed by a larger rainfall (>25 mm). Samples were collected hourly for 48 h during the initial light rains (Nov 30−Dec second). The sampling interval was relaxed gradually from hourly to as much as 6 h when rain stopped, and the analysis of most recent samples showed substantially decreased 6PPDQ concentrations. Sampling frequency increased again during heavy rains on Dec 4−5th depending on field crew availability.

This expanded campaign reinforces the high degree of 6PPDQ temporal variability in urban waterways (Figure 3) and

Figure 3. Temporal variability of 6PPDQ concentration in ng/L (left axis) at three streams across several rain events (Nov 29–Dec 5, 2023). Precipitation in mm (right axis) appears on the top in blue. Samples were initially collected hourly (first 48 h) followed by 1–6 h frequency depending on field crew availability over the one-week sampling period. Data points represent single measurements or the mean of $n \geq 3$ replicate measurements (when 6PPD-Q > 10 ng/L). Shaded red, purple, and green areas represent the uncertainty using the upper and lower bounds of one standard deviation across measurements.

reveals additional information. Northfield Creek concentrations appeared quickly with the onset of rain accompanied by a sharp rise in discharge and suspended solids (as noted by field crews), with the peak concentrations up to 220 ng/L (ca. 2 fold greater than the upper coho LC_{50} of 95 ng/L).[5] Cat Stream also exhibited a dynamic concentration profile, peaking at 60 ng/L. Both systems exhibited first flush dynamics, where the initial (smaller) rain events yielded the highest levels of 6PPD-Q, with diminishing returns for each subsequent rainfall, even the much larger precipitation event (~25 mm) that occurred ~5 days after the initial rain. Studies of "first flush effects" by Peter et al. observed a similar decrease in subsequent rainfalls, but over a larger time scale (months) as compared to just a few days here.[34] In contrast with Northfield Creek, Cat Stream showed a 4–5-h lag-time between peak rainfall and peak 6PPDQ. This slower response may be due to a combination of factors, including proximity to local inputs, and increased green space between roadways and Cat Stream. Additionally, while both watercourses show similar overall discharge rates under dry conditions (Table S1), the linear flow velocity in Cat Stream is considerably slower (0.10 ± 0.02 m/s) than Northfield Creek (0.55 ± 0.13 m/s). The latter is more consistent with a rapid appearance of contaminant and faster flushing dynamics, although more detailed hydrological data is required to characterize this phenomenon. The largest system, Millstone River, remained consistently low, at or below detection limits (<6 ng/L).

The concentration and time profiles observed here differ from earlier reports by Johannessen et al.[2] that examined pooled 3-h samples collected from a much larger, more urbanized system (Don River, Toronto, Canada; mean annual discharge: 4.1 m³/s).[18] This system exhibited an order of magnitude higher 6PPDQ concentrations (up to 3000 ng/L) than we observe here, as well as a longer lag-time from after precipitation (remaining at peak levels from ~14–30 h after the onset of rain). While both of these observations might be expected from the significantly larger urban catchment area and higher traffic density, we caution against direct quantitative

comparison given the lack of analytical 6PPDQ standards at the time these measurements were carried out. Subsequent analysis of the flow-weighted composite samples (a single pooled sample with contributions weighted by relative streamflow throughout the sampling period) in the Don River shows concentrations of ca. 50 ng/L.[13] While not directly comparable, this latter 6PPDQ level is similar to that of the largest system studied here (Millstone River, mean annual discharge 2.66 m³/s). Work by Rauert et al. in Cubberla Creek (Brisbane, Queensland, Australia) also completed before analytical standards were available revealed levels of 6PPDQ in the low (<90) ng/L range. This creek, which is a tributary to the Brisbane River, flows between 0.009 and 7.94 m³/s, which is in a similar flow regime to the majority of samples described here. However, the authors noted that Australian tire wear emission rates are much lower than in the United States.[10]

The results reported here highlight the need to carefully consider and qualify quantitative results reported from grab samples collected "during" a rain. While this is sometimes the only feasible option (e.g., community-driven citizen science campaigns), Figure 2 illustrates how samples collected during the same rain event varied from ~50 to 220 ng/L over a 3-h window. However, these results also showcase how additional water quality data may supplement these single "point-in-time" grab samples, or even inform when to collect them if/when a correlation has been characterized at the site. The rank-order correlation between 6PPDQ and turbidity noted earlier for Northfield (Figure 2) holds when all samples collected from Northfield are considered (i.e., across multiple rain events, Spearman coefficient: 0.79, $p \ll 0.05$, $n = 107$) and can be extended to both Cat Stream (Spearman coefficient: 0.66, $p \ll 0.05$, $n = 84$) as well as the global data set (Spearman coefficient: 0.68, $p \ll 0.05$, $n = 271$, Figure S12). While the absolute relationship between the turbidity and 6PPDQ is expected to vary between streams and across rain events, the rank-order agreement demonstrated here is encouraging. This observation is consistent with previous work investigating the phase distribution of PAHs in particulate-laden stormwaters.[35]

As expected, the larger (i.e., more hydrophobic) PAHs tended to distribute more on the particulate phase than smaller PAHs, and the total load of PAHs was highest in stormwaters with high suspended solids. While the particulate phase of road runoff includes tire wear particles, which contribute to both turbidity and 6PPDQ concentrations, the nature of the association between these parameters remains largely underexplored. It is worth noting that the 6PPDQ concentrations reported here represent the dissolved aqueous phase fraction rather than the total (dissolved + suspended). Although further verification across more events and streams is needed, turbidity may provide a good proxy for stormwater influence—with suspended particles providing both a source (e.g., tire particles) and transport vector (e.g., high organic content (f_{OC}) suspended sediments) for hydrophobic contaminants. Consequently, turbidity may provide a simple strategy for field crews or automated sampling systems to collect at "expected peak" 6PPDQ concentrations. Ideally, multiple samples over the course of a rainfall should be used to characterize the contaminant mass loading and exposure risks.

■ CONCLUSIONS

This is the first report of an intensive sampling campaign enabled by high-throughput chemical analysis revealing a high degree of both temporal and spatial variability of 6PPDQ in urban waterways. It highlights the need for careful consideration of when and where to collect samples, especially in the context of efficient placement of mitigation strategies aimed at reducing the impacts of stormwater-related contaminants on vulnerable salmonids. The three waterways analyzed here represent a variety of urban systems with different sizes and input potentials. Common among the spatial analyses was no apparent downstream accumulation in 6PPDQ concentrations in the water column. Rather, elevated 6PPDQ levels were proximal downstream from local inputs and were attenuated or diluted further downstream (until the next input). Hourly sampling of waterways through several rain events revealed highly dynamic concentration profiles in response to rain, which differed across streams. During peak rainfall, these concentrations can change rapidly (within min—hours), with samples taken an hour apart giving significantly different concentrations. While further verification is needed, turbidity appears to track with relative 6PPDQ levels in urban systems, suggesting a readily measured proxy for stormwater influence that can be used to trigger manual or automated sampling at peak 6PPDQ levels.

■ ASSOCIATED CONTENT

⑤ⓘ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.4c00614.

> Additional data files containing detailed sample information, water quality, and precipitation (XLSX)

> Temporal sampling (XLSX)

> Additional details on sampling locations, regional precipitation, CP-MIMS quantitation, quality control, and mass spectrometer parameters; 6PPDQ spatial analysis of rain events from September to November; high temporal analysis of analogous tire antiozonant products (PDF)

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CRediT: **Angelina Jaeger** data curation, formal analysis, investigation, methodology, validation, visualization, writing - original draft, writing - review & editing; **Joseph Monaghan** data curation, formal analysis, investigation, methodology, software, validation, visualization, writing - review & editing; **Haley Tomlin** funding acquisition, project administration, resources, writing - review & editing; **Jamieson Atkinson** funding acquisition, project administration, resources, writing - review & editing; **Chris G. Gill** funding acquisition, methodology, project administration, supervision, writing - review & editing; **Erik T. Krogh** conceptualization, funding acquisition, methodology, project administration, supervision, visualization, writing - review & editing.

Notes

The authors declare the following competing financial interest(s): Chris G. Gill and Erik T. Krogh hold patent US 9583325 issued to none.

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