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Analysis of rubber-derived contaminants in surface water and snow by liquid chromatography coupled with a hybrid linear ion-trap-Orbitrap high-resolution mass spectrometry

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ABSTRACT

Analytical methods were developed to quantify eight rubber-derived organic contaminants, including four *p*-phenylenediamine-derived quinones (PPDQs), 1,3-diphenylguanidine (DPG), 1,3-diphenylurea (DPU), N,N-dibutylbutan-1-amine (TBA), and 1,3-dicyclohexylurea (DCU) in the dissolved phase and suspended particulate matter (SPM) of surface water and melted snow. Dissolved-phase samples were prepared using solid-phase extraction with hydrophilic-lipophilic balance cartridges and a 3/7 (*v/v*) mixture of acetonitrile and dichloromethane as elution solvents. SPM samples underwent ultrasonic-assisted extraction using the same solvent mixture. Reduced glutathione was added before extraction to improve recovery and reduce variability of target compounds. Quantification was performed using ultra-high-performance liquid chromatography coupled with a hybrid linear ion-trap-Orbitrap high-resolution mass spectrometry (UHPLC/ESI-LTQ-Orbitrap) in positive electrospray ionization and full-scan mode (*m/z* 100-500). Method detection limits for surface water ranged from 0.2 to 7.0 ng/L in the dissolved phase and 0.1-2.6 ng/L in SPM. For melted snow, detection limits ranged from 0.2 to 5.0 ng/L in the dissolved phase and from 0.1 to 5.4 ng/L in SPM. Sample storage tests (4°C and -20°C) indicate that the dissolved phase should be extracted on the sample collection day, while SPM samples (filters stored at -20°C) should be extracted within seven days. Three of the eight target compounds, including DPG, DCU, and 2-((4-methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione (6PPDQ), were detected in environmental surface water and snowmelt samples from Quebec, Canada. This is the first reported method using UHPLC/ESI-LTQ-Orbitrap to simultaneously determine these eight contaminants in the dissolved and SPM phases of surface water and melted snow.

1. Introduction

Rubber-derived contaminants have attracted increasing environmental concern due to their large production and consumption volumes, leachability from products into the environment, and toxicity [1–4]. *p*-Phenylenediamines (PPDs) are used in rubber products as antioxidants, antiozonants, and anti-flex cracking agents [5]. They are known to transform in the environment into PPD quinones (PPDQs), which are highly toxic to some fish species [6,7]. For example, Tian et al. [7] reported that 2-((4-methylpentan-2-yl)amino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione (6PPDQ), a transformation product of the parent compound N1-(4-methylpentan-2-yl)-N4-phenylbenzene-1,4-diamine (6PPD), is a potent toxin to coho salmon (*Oncorhynchus kisutch*) even at the ng/L level. In addition, 1,3-diphenylguanidine (DPG) and 1,3-diphenylurea (DPU) are additives used for the vulcanization of rubber products, whereas N,N-dibutylbutan-1-amine (TBA), and 1,3-dicyclohexylurea (DCU) are byproducts or degradation products that emerge during rubber production [3,8,9]. These compounds have the potential to leach into the environment [3]. DPG, when present in water, may exhibit toxicity to aquatic organisms, including fish (96 hours exposure, LC_{50}: 4.2-11 mg/L for fathead minnow (*Pimephales promelas*) and rainbow trout (*Oncorhynchus mykiss*)), *Daphnia* (21 days chronic exposure, Lowest Observed Effect Concentration: 1.9 mg/L), and algae (e.g., the green algae (*Selenastrum capricornutum*)) (96 hours exposure, EC_{50}: 1.7 mg/L) [9]. DCU and DPU are known to be toxic to the microalgae *Scenedesmus obliquus* (96 hours exposure, EC_{50}: 1.04

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mg/L and 1.97 mg/L, respectively) [10]. Therefore, monitoring their concentrations in surface waters is crucial for understanding their transport, fate, and associated ecological risks. In cold regions, snowmelt serves as a key pathway, releasing contaminants that have accumulated over the winter into surrounding water bodies during the spring thaw. This seasonal pulse can lead to elevated concentrations in aquatic environments. Thus, developing robust analytical methods to detect these compounds in both surface water and snowmelt is essential for accurate risk assessment and effective environmental management.

Recent studies (Table 1) have reported the presence of some of these contaminants in various environmental matrices, including urban runoff water, courtyard surface runoff, sewage treatment plant water, and snow [11–13]. Only two of these studies [14,15] reported data on suspended particulate matter (SPM) in surface water, and only one [12] reported data on the dissolved phase of melted snow. They only targeted some of the compounds mentioned above. A summary of the methods used in the literature is shown in Table 1. Most studies used solid phase extraction (SPE) with hydrophilic-lipophilic balanced (HLB) cartridges to prepare water samples for the analysis of PPDQs and other rubber-derived compounds (e.g., DCU, DPU, and DPG) (Table 1). Liquid chromatography coupled with triple quadrupole mass spectrometry (LC-MS/MS) was employed in most studies [11,15,19,20] due to its high sensitivity and selectivity for quantitative target analyses. The limitation of these instruments is their selective acquisition mode, where specific parameters (e.g., collision energy and acquisition time window) must be defined for each compound, and the obtained data cannot be used for retrospective analysis of other contaminants when necessary. As mentioned in several studies [12,16,17], the Orbitrap MS-based method is a suitable alternative to address the limitations of triple quadrupole MS. However, previous studies have focused either on a limited subset of compounds or on a single environmental matrix [12,16,17]. To our knowledge, no method has simultaneously validated Orbitrap-based quantitative analysis of multiple PPDQs, DPG, urea- and amine-based rubber-derived contaminants in both dissolved phase and SPM of surface water and snowmelt. The inclusion of snowmelt matrices is especially important for cold-climate environments, where snowmelt represents a major transport pathway to surface waters [21] but remains analytically underexplored. Moreover, due to the instability of these compounds, evaluating the impacts of storage conditions on analytical method performance is critical for ensuring accurate results and standardizing protocols for inter-study comparisons. Limited data are available on this topic.

The objective of this study was to develop methods for the simultaneous analysis of four PPDQs, DPG, TBA, DPU, and DCU in the dissolved phase and SPM of surface water and snow samples using LC coupled to a hybrid linear ion-trap-Orbitrap MS. Different instrument conditions, dissolved phase and SPM sample preparation methods, and sample storage conditions were compared. The optimized method was applied to analyze these contaminants in the dissolved and SPM phases of river and estuarine surface water and snowmelt samples.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards of 6PPDQ (97.6%) and the isotope-labeled standard of 6PPDQ-d$_5$ (98.5%) were purchased from LGC Standards (Ontario, Canada). Standards of DPG (>98%), TBA (>98%), DPU (>98%), and DCU (>98%) were obtained from Tokyo Chemical Industry America (Portland, USA). The supplier of 2-(isopropylamino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione (IPPDQ, 98.11%), 2,5-bis(phenylamino) cyclohexa-2,5-diene-1,4-dione (DPPDQ, 93.30%), and 2 (cyclohexylamino)-5-(phenylamino)cyclohexa-2,5-diene-1,4-dione (CPPDQ, 99.26%) standards was HPC Standards Inc. (Atlanta, USA). The isotope-labeled standard 1,3-diethyl-1,3-diphenylurea-d$_{10}$ (DEDPU-d$_{10}$;98%) was obtained from Toronto Research Chemical (Toronto, Canada). The structure and properties of target contaminants are presented in Fig. 1 and Table 2, respectively. HLB cartridges (OASIS HLB 6cc, 500 mg) were supplied by Waters (Mississauga, Canada). C18 SPE cartridges were purchased from Sigma-Aldrich (Darmstadt, Germany). HPLC grade acetonitrile, dichloromethane, and methanol were purchased from Avantor (Mississauga, Canada), while HPLC grade water and L-Glutathione reduced (GSH; ≥98%) were purchased from Thermo Fisher Scientific (Waltham, Massachusetts, USA).

2.2. Finalized method for sample preparation

2.2.1. Dissolved phase

In the same day of sample collection, 500 mL of surface water/thawed snow sample (with 1.5 g of GSH added before surface water sampling or after snow melted) was filtered through a 0.7 μm glass fiber filter (GF/F 47mm, previously baked at 400°C for 24 h) (Cytivia, Wilmington, USA) to separate SPM from the dissolved phase. The dissolved phase was spiked with 25 μL of isotope-labeled surrogate standards at 1

Table 1
Summary of the representative MS-based methods for analyzing selected rubber-derived contaminants in environmental matrices. WWTP: Waste Water Treatment Plant influent and effluent; DWTP: Drinking Water Treatment Plant effluent. IQL: instrument quantification limits. NA: information not available.

Rubber-derived compounds relevant to the present study	Matrix	Pretreatment method	Detection method	Recovery range (%)	LOD range	References
6PPDQ, CPPDQ, IPPDQ, DPPDQ	Urban runoff water	HLB SPE	UHPLC- Triple Quadrupole MS - Selected Reaction Monitoring	73-89	IQL 0.019-0.055 ng/mL	[11]
DPG, DCU, DPU, 6PPDQ	Stormwater, river, snow	HLB SPE	UHPLC- Q-Exactive Orbitrap HRMS-heated ESI-Full Scan	66-88	0.4-1.2 ng/mL	[12]
IPPDQ,CPPDQ,6PPDQ, DPPDQ, DPG, DCU, DPU	Sewer and receiving waters and SPM	HLB SPE	LC- QTRAP tandem MS-ESI- Multiple Reaction Monitoring	88-134	0.02-0.2 ng/L	[14]
6PPDQ	Surface and ground water and SPM	HLB SPE	LC-Triple quadrupole MS	NA	0.029 ng/L	[15]
6PPDQ, DPG	Urban surface water (River)	HLB SPE	UHPLC- Q-Exactive Orbitrap HRMS-heated ESI- Parallel reaction monitoring	NA	6.5 ng/L	[16]
DPG, 6PPDQ	Urban surface water (River)	HLB SPE	UHPLC- Q-Exactive Orbitrap HRMS-heated ESI- Parallel reaction monitoring	93-98	9.8 ng/L	[17]
DCU, DPG	Creeks (Agricultural watershed)	HLB SPE	UHPLC-Quadrupole TOF HRMS-ESI-Full Scan	NA	NA	[18]
DPU,DPG, 6PPDQ	Surface runoff, WWTP, surface rivers, DWTP	HLB SPE	UPLC-Triple quadrupole MS- ESI-Multiple Reaction Monitoring	72-148	0.05-0.09 ng/L	[19]
IPPDQ,CPPDQ,6PPDQ, DPPDQ	Surface water	Liquid-liquid extraction with Envi-Carb SPE	LC-Triple quadrupole MS	80-108	0.017-0.045 ng/L	[20]

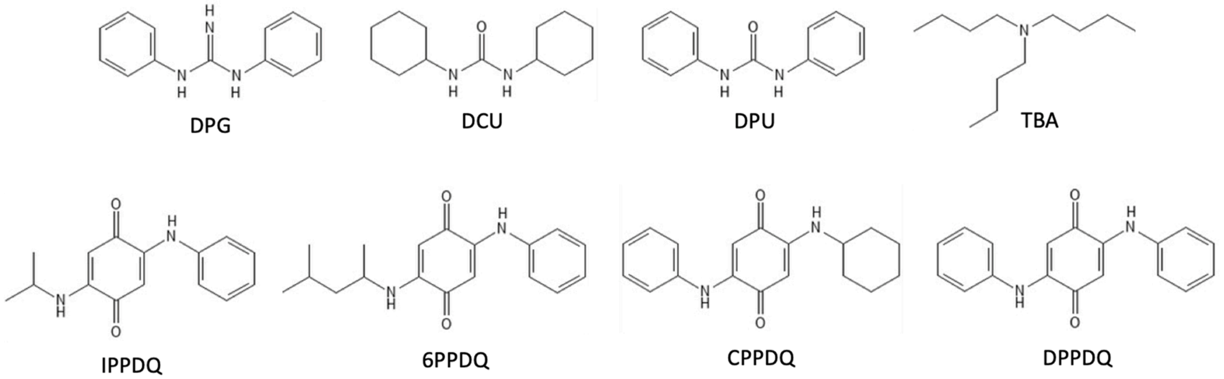


Fig. 1. Molecular structure of target compounds.

Table 2
Detailed information of target contaminants and their LC-LTQ Orbitrap MS analysis data (ordered by retention time). [1] Data were calculated using the U.S. Environmental Protection Agency's Estimation Program Interface (EPI) Suite (version 4.11).

Acronyms	#CAS	Water Solubility[1] (mg/L)	Log K_{ow}^{1}	Elemental composition $[M+H]^{+}$	Retention time (min)	Theoretical *m/z*	Experimental *m/z*	Error Mass (ppm)	MS^2 fragment ion (NEC 35%)
DPG	102-06-7	129	2.89	$C13H14N3^{+}$	2.31	212.1188	212.1183	-2.2157	119.0603
TBA	102-82-9	82.2	4.46	$C12H28N^{+}$	3.19	186.2221	186.2217	-1.9332	130.1589
DCU	2387-23-7	14.8	3.92	$C13H25N2O^{+}$	4.22	225.1967	225.1963	-1.7762	100.1120
DPU	102-07-8	104	2.97	$C13H13N2O^{+}$	4.24	213.1028	213.1022	-2.6745	94.0650
IPPDQ	68054-73-9	1400	2.58	$C15H17N2O2^{+}$	4.27	257.1290	257.1284	-2.3724	215.0814
DPPDQ	3421-08-7	15.4	3.46	$C18H15N2O2^{+}$	4.73	291.1133	291.1129	-1.3740	263.1179
CPPDQ	68054-78-4	56.9	3.94	$C18H21N2O2^{+}$	4.97	297.1603	297.1599	-1.3461	215.0814
6PPDQ	2754428-18-5	51.3	3.98	$C18H23N2O2^{+}$	5.17	299.1759	299.1755	-1.3036	215.0814

μg/mL (6PPDQ-d_5 and DEDPU-d_{10}). HLB SPE cartridges were used to prepare the dissolved phase sample. The HLB cartridge was conditioned with 2 × 6 mL of acetonitrile/dichloromethane (3/7, *v/v*) and 6 mL of HPLC water, followed by loading 500 mL of the sample of dissolved phase. Then, the cartridge was dried under vacuum for 5 minutes and eluted with 2 × 6 mL of acetonitrile/dichloromethane (3/7, *v/v*). The eluent was concentrated under nitrogen flow (temperature $\leq$ 30°C) to a final volume of 1 mL in acetonitrile and kept at -20°C in an amber glass vial until analysis.

2.2.2. SPM

The filter was stored at -20°C in clean glass Petri dishes for approximately one day before extraction and analysis. Each filter was folded and placed at the bottom of a glass tube. The sample was spiked with 25 μL of isotope-labeled surrogate standards at a concentration of 1 μg/mL (6PPDQ-d_5 and DEDPU-d_{10}). One mL of GSH solution (40 mM) was added to the filter before extraction. The three extractions consist of adding 6 mL of solvent directly into the tube, followed by 20 minutes of sonication and 10 minutes of centrifuging. The first extraction was conducted using dichloromethane. After sonication and centrifugation, water (from the GSH solution) was removed with glass Pasteur pipettes. Then, the second and third extractions were performed using acetonitrile/dichloromethane (3/7, *v/v*). All extracts were transferred to a glass centrifuge tube and concentrated by gentle N_2 flow to 1 mL. The sample was kept at -20°C in an amber glass vial until analysis.

2.2.3. Instrumentation

The analyses were performed with a Thermo Fisher Scientific Accela UHPLC coupled with a linear ion-trap-Orbitrap high resolution (HR) MS (LTQ-Orbitrap XL). The chromatographic separation was performed on a C8 analytical column (100 mm × 2.1 mm, Kinetex 2.6 μm; Phenomenex, Torrance, USA) at 25°C. The mobile phases have consisted of 0.1% formic acid in both acetonitrile (A) and water (B). The gradient was initiated at a composition of 90% B, ramped to 10% B over 5 minutes, and held for 2 minutes. Then, the gradient returns to its initial composition at 10 minutes and is held for a 2-minute stabilization before running the next analysis. The injection volume was 10 μL, and the flow rate was set at 0.3 mL/minute. The positive electrospray ionization (ESI) with full scan mode was used for sample analysis. The ESI temperature was 375°C, with a spray voltage of 3.60 kV and a tube lens voltage of 40V. Several scan events were used for the experiments. The first was a full scan with the *m/z* range set at 100-500 and a resolution of 30,000. The full scan was used for quantification. As a simultaneous second scan event altered the analysis results (peak shape and intensity), samples were analyzed for a second time with MS^2 scan events in different time segments (up to 4 scan events, details in Table S1). Each scan event has been set up to fragment a selected target ion with a collision induced dissociation (CID) energy of 35 eV.

2.2.4. Environmental sample collection

Sampling sites are shown in Fig. S1. Surface water from Parc Lepage stream (n=3) (Site 1-Lepage; 48°26′16.472"N; 68°31′16.208"W), Marina of Rimouski (n=3) (Site 2-Marina; 48°28′45.138" N; 68° 30′ 37.519" W) and Rimouski River (n=3) (Site 3-R. River; 48°26′41.665"N; 68°32′26.390"W), as well as snow (n=3) (Site 4-Snow; 48°27′7.819"N; 68°30′34.074"W) were collected between October 2023 and March 2024 in Rimouski, Quebec, Canada. Site 1, located in an urban recreational park, was chosen as a reference site anticipated to exhibit lower concentrations of target contaminants due to minimal traffic-related inputs. In contrast, Sites 2 and 3, situated near high-traffic zones, are likely to be more affected by the deposition of tire wear particles and urban runoff, and are expected to have higher levels of target contaminants. Surface water samples were transported to the laboratory within ~1 hour of collection and processed immediately upon arrival. Snow samples were collected from Site 4, adjacent to a car parking lot, where tire wear particles are likely to accumulate during winter, and potentially have higher concentrations of target contaminants. Site 4 was located on campus next to the laboratory building and was transported to the lab within minutes. Thawing immediately started at room temperature and took a few hours before it completely melted. Although some analyte loss during thawing cannot be ruled out, starting the process immediately after collecting and processing samples without delay minimizes this risk.

Before sampling, 1.5 g of GSH was added to the empty bottles to preserve the target analytes in the samples from collection to extraction. On the field, surface water was transferred from a glass beaker into the prepared sampling bottle (1 L stainless steel and amber glass bottles). The snow was directly collected in a 1 L stainless steel bottle and melted under a fume hood at room temperature (a few hours, until completely melted). Then, 500 mL of melted snow was transferred to a new clean bottle containing 1.5 g of GSH before the extraction process. Field blanks (n=3 for each site) were collected using 1 L stainless steel and amber glass bottles containing 500 mL of HPLC-grade water and 1.5 g of GSH, opened during the sampling time in the field.

2.2.5. *Method evaluation*

To evaluate the linearity range of the standard calibration curve, target compounds were injected into the UHPLC-Orbitrap MS at 12 concentrations (0, 0.10, 0.19, 0.39, 0.78, 1.56, 3.12, 6.25, 12.5, 25, 50, 100 ng/mL). Quantitation was performed using external calibration, with corrections for recovery and matrix effects made using isotope-labeled surrogate standards (6PPDQ-d_5 for PPDQs and DEDPU-d_{10} for other target compounds). However, quantification of DPG, TBA, and IPPDQ in SPM was not corrected by surrogate standards. Water samples from the Rimouski River and the St. Lawrence River (Quebec, Canada) were used for the spike-recovery exploration. The selected method was further tested for recoveries at 50 ng/L and 400 ng/L in both the dissolved phase and the SPM phase using St. Lawrence River water samples. The matrix effects for the target compounds were calculated for the St. Lawrence River water samples and snow samples from site 4, as the ratio of peak area between the matrix sample (25 μL of standards at 1 μg/L were spiked after extraction and cleanup) and the same concentration in acetonitrile. Method detection limits (MDLs) were determined according to the United States Environmental Protection Agency (US EPA) guidelines [22] using eight samples spiked with a 5 μL standard solution (1 μg/mL). The MDL was calculated as 3 times the standard deviation (SD) of the final detected concentrations. Field blanks (n=12 total) were analyzed to evaluate background contamination. For those compounds that were detected in some field blanks (dissolved phase: DPG and 6PPDQ; SPM: DPG and DCU), the MDL was determined using the highest level of the analytes in the blanks [22]. For those compounds that were detected in all blanks (dissolved phase: TBA and DCU; SPM: TBA), the MDL was defined as the 3 × SD of the concentrations detected in the blanks [22]. To evaluate instrument performance and background contamination during analysis, three standards (25 ng/mL) were analyzed at the end of each analysis, and two acetonitrile blanks were analyzed as controls between every three samples by the UHPLC-Orbitrap MS.

2.2.6. *Data analysis*

GraphPad Prism (Version: 10.3.1) and Microsoft Excel were used to analyze the data. Absolute recovery was calculated using the peak area ratio between the spiked (before extraction) sample and the standard in acetonitrile with the same concentrations. Surrogate standard corrected recovery was calculated using the ratio of the response factor between the spiked (before extraction) sample and the standard in acetonitrile at the same concentration. In environmental samples, the concentrations of all quantifiable analytes were corrected for background contamination in blanks. Half MDL replaced the non-detect for estimating descriptive statistics when the target compound was detected in one out of three samples. The data is reported as mean ± SD. Before comparisons, the concentration data of environmental samples were transformed using natural logarithms to approximate normal distributions. Welch's Analysis of Variance, followed by Dunnett's T3 multiple comparisons, was used to compare the contaminant levels among three or more than three groups. Differences in the contaminant concentrations between the two groups were compared using the unpaired t-test with Welch's correction. The statistically significant level was set as $p < 0.05$.

3. Results and discussion

3.1. *Optimization of LC-LTQ Orbitrap MS conditions*

Acetonitrile and methanol, both with 0.1% formic acid, were compared as mobile phases (phase A) combined with water (0.1% formic acid) (phase B) for the separation and detection of target analytes. Acetonitrile showed better peak shapes and higher peak area than methanol for most target compounds, including DPG, DPU, DCU, DPPDQ, CPPDQ, and 6PPDQ (Fig. S2). This may be due to acetonitrile's better protonation efficiency and droplet desolvation than methanol in the ESI positive mode. As a polar aprotic solvent, acetonitrile does not compete with formic acid for protons, resulting in formic acid dissociating more effectively, providing a higher concentration of free protons (H^+) to protonate the basic groups of target compounds [23,24]. In contrast, as a protic solvent, methanol can form hydrogen bonds with formate ions, reducing the availability of H^+ ions for protonation. Additionally, acetonitrile has a lower surface tension and is more volatile than methanol, which promotes solvent evaporation and the formation of small droplets during nebulization in ESI [25]. Enhanced desolvation efficiency could lead to improved ionization efficiency. Therefore, acetonitrile and water, both containing 0.1% formic acid, were chosen as the mobile phases in the present study.

To determine how column temperature affects the separation and detection of target compounds, standards were analyzed at column temperatures of 20°C, 25°C, 30°C, and 40°C. As shown in Fig. S3, no significant differences were found in the peak area of the different column temperatures. This result indicates that the target analytes remain stable over the temperature range of 20°C to 40°C during analysis. Their interactions with the C8 column are unaffected by temperature variations when using a mobile phase of acetonitrile and water containing 0.1% formic acid. We finally chose 25°C for the analysis as it is close to room temperature.

The protonated molecular ion $[M+H]^+$ was selected using the full scan mode to achieve robust detection. The experimental m/z values of the target analytes for $[M+H]^+$ closely matched the theoretical m/z values, yielding a mass error between 1.3 and 2.7 ppm (Table 2), which is well within the high-resolution accuracy of the Orbitrap (<5 ppm), confirming the reliable identification of target contaminants. The MS^2 experiments were performed with the normalized collision energy (NCE) of 15%, 25%, and 35%. Since most compounds were not completely fragmented at 15% and 25% NCE, except for DCU, DPU, and DPPDQ, 35% was selected for further investigation. The results are summarized in Table 2 and Fig. S4. However, the sensitivity of the analysis involving simultaneous full scan MS^1 and MS^2 at NCE 35% was low, with detectable peaks only at concentrations ≥500 ng/mL, making it unsuitable for trace-level quantitative analysis in environmental samples where target analytes typically occur at ng/L levels. Consequently, the full scan mode without MS^2 was selected for quantification to maximize sensitivity. The high-resolution capability of the Orbitrap in full scan mode provided high mass accuracy and low mass error (<2.7 ppm), which offers sufficient selectivity for the reliable quantification of these contaminants in surface water and snowmelts. However, we recognize that HRMS-only quantification lacks the extra confidence provided by diagnostic fragments at low concentrations and/or in complex environmental matrices. The MS^2 results obtained in this study may be useful for future applications in more contaminated matrices (e.g., wastewater, stormwater, or biosolids) where target compounds occur at higher levels.

3.2. Dissolved phase sample preparation

Extraction of dissolved phase samples with 25 ng target contaminants was compared between C18 and HLB cartridges using 10 mL of dissolved phase samples from the Rimouski River with various eluting solvents (12 mL), including acetonitrile, dichloromethane, and methanol. HLB showed better recovery than C18 for DPG, TBA, and DCU (Fig. S5). Therefore, HLB was selected to further optimize the elution solvent. Mixtures of acetonitrile and dichloromethane with different ratios were used to elute the samples. The mixture of acetonitrile/dichloromethane (3/7, *v/v*) yielded better results than using individual solvents for most compounds (Fig. S5). However, the recoveries for DPG were very low (<1%; Fig. S5).

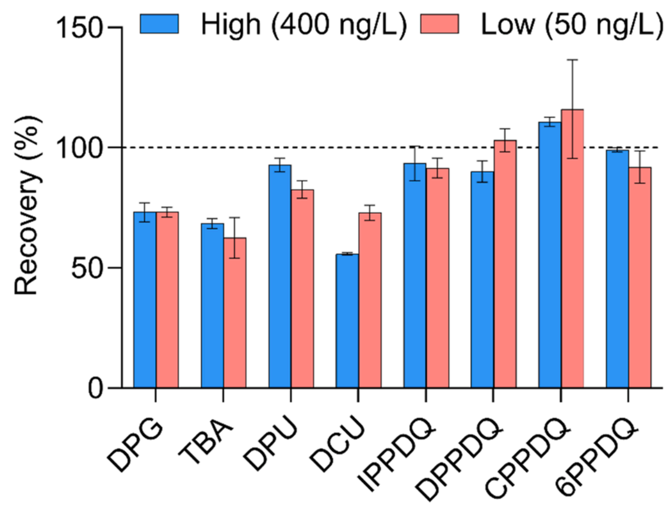
Glutathione (GSH), an antioxidant that can protect compounds from oxidative degradation during extraction, was added to the dissolved phase sample before extraction to enhance the SPE extraction recovery. Various levels of GSH were added for comparison, including 0 mM, 2 mM, 10 mM, and 20 mM concentrations in the dissolved phase samples (10 mL). The results indicated that adding 10-20 mM GSH can significantly improve the recoveries for DPG and TBA (Fig. S6). Given the better repeatability of samples with 10 mM GSH (Fig. S6), this concentration was selected for further testing with 500 mL of dissolved phase sample.

To further test recovery, surface water samples (500 mL each) from the St. Lawrence River (Canada) were spiked at low (50 ng/L) and high (400 ng/L) concentrations and processed using the dissolved-phase preparation protocol. The samples without the addition of target compounds were analyzed in parallel, and the background levels were subtracted from the recovery test results. The absolute recovery of target compounds was in the range of 35 ± 2% - 90 ± 19% and 47 ± 2% - 111 ± 11% for 50 ng/L and 400 ng/L spikes, respectively. After the correction using 6PPDQ-d_5 and DEDPU-d_{10}, the recoveries of target compounds were between 73 ± 2% and 116 ± 20% for 50 ng/L samples and between 56 ± 0.5% and 111 ± 2% for 400 ng/L samples (Fig. 2).

3.3. SPM sample preparation

A solvent mixture of acetonitrile and dichloromethane (3/7, *v/v*) was used to extract the target compounds from the SPM of the Rimouski River water. This solvent mixture was selected based on its effectiveness as the elution solvent of the same compounds in SPE from dissolved phase samples, as shown above. Initial extraction experiments (25 ng/filter) using this method with blank filters yielded average absolute recoveries ranging from 70% (DCU) to an unexpectedly high 196% (CPPDQ, with a SD of 72%) for the target analytes (Fig. S7). To improve extraction performance and reproducibility, the GSH solution was added directly to the filter before extraction. The GSH concentration was optimized at 1 mL of 40 mM to show the best results. In addition, the extraction protocol was modified to mitigate the effects of residual water from the GSH solution in the sample, which is miscible with acetonitrile if not removed, thereby reducing solvent efficiency and analyte recovery. Specifically, the filter was first extracted with 6 mL of dichloromethane. The dichloromethane extract was transferred to a new tube, and the water residue was discarded. Two sequential extractions were then performed with 6 mL of the acetonitrile/dichloromethane mixture (3/7, *v/v*). This optimized method improved analytical results, yielding absolute recoveries ranging from 71 ± 4% (DPU) to 112 ± 0.1% (TBA) with significantly reduced variability (relative standard deviation, RSD, less than 5% for most analytes) (Fig. S7). In particular, the absolute recoveries for DPPDQ and CPPDQ stabilized at consistent levels of 77 ± 2% and 78 ± 0.1%, respectively, compared to the previously erratic and inflated recoveries of 160 ± 24% and 196 ± 72% observed without GSH (Fig. S7). The low variation demonstrated improved method reproducibility, confirming the suitability of this protocol for reliable environmental monitoring of SPM-associated contaminants.

(A) Dissolved phase



(B) SPM

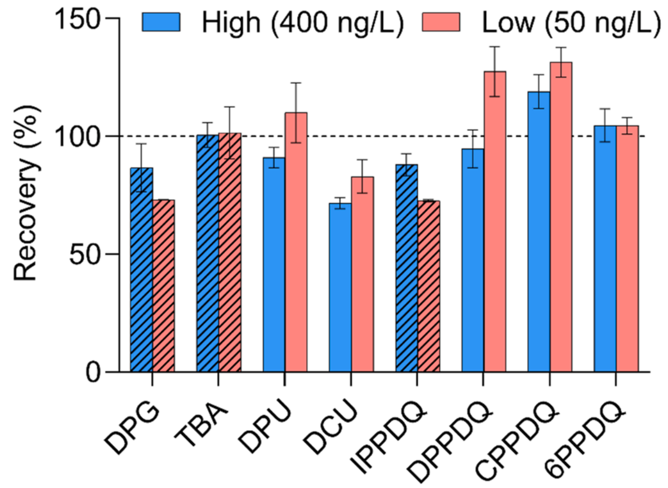


Fig. 2. Surrogate standard corrected recovery (Mean ± SD%, n=3) in 500 mL of surface water at different spike levels. For DPG, TBA, and IPPDQ in SPM, the data represent absolute recovery (striped).

Then, the St Lawrence River water samples were filtered to prepare for the SPM spike-recovery test. At high (400 ng/L or 200 ng/filter) and low (50 ng/L or 25 ng/filter) spike levels, surrogate standard-corrected recoveries ranged from 72 ± 2.3% (DCU) to 119 ± 7.2% (CPPDQ) and 83 ± 7.1% (DCU) to 171 ± 44% (IPPDQ), respectively. At the 50 ng/L spike level, recoveries for TBA (159 ± 33%) and IPPDQ (171 ± 44%) exceeded those of other target compounds (<132%), indicating that surrogate standard corrections for these contaminants may introduce bias in some environmental water samples. Absolute recoveries were 73 ± 0.5% for IPPDQ and 102 ± 11% for TBA (Fig. 2), suggesting these compounds can be quantified without surrogate standards correction in SPM.

3.4. Storage conditions

Storage conditions were tested at 4°C in glass bottles and -20°C in stainless bottles for dissolved phase samples. Bulk water samples are typically stored at 4°C because glass containers may break at -20°C. But these contaminants are not very stable, so -20°C was also tested. Storage of SPM samples was only tested at -20°C because the target analytes are more stable at this temperature than at 4°C. Additionally, there is no concern about a glass container breaking under these conditions for SPM samples, unlike with water samples. So, it is not necessary to further test at 4°C for SPM samples.

Environmental water samples were collected at Site 1 (Parc Lepage stream) to test the stability of target compounds under different storage conditions. GSH (1.5 g) was added to the sampling bottles before collection. On the same collection day, the samples (500 mL) were filtered through 0.7 μm glass fiber filters, and 25 ng of target compounds were spiked into both dissolved phase (*n*=9) and SPM (*n*=6) samples. Then, the spiked dissolved phase (*n*=3) and SPM (*n*=3) samples, along with the unspiked dissolved phase (*n*=3) were extracted immediately on day 0 (sample collection day). The remaining dissolved phase samples (spiked with 25 ng of target compounds) were stored at 4°C (glass bottles) and -20°C (stainless steel bottles) and extracted after 7 days. The SPM samples were stored at -20°C in glass petri dishes and extracted on day 1 and day 8. Recovery results were corrected using the unspiked dissolved phase and SPM samples.

For dissolved phase samples, surrogate standard corrected recoveries for target analytes ranged from 70 ± 3.3% (DCU) to 123 ± 2% (CPPDQ) on day 0 (Fig. 3). DPU and DCU remained stable after 7 days of storage at 4°C or -20°C (Fig. 3). The recoveries for TBA decreased by approximately 40% after 7 days of storage at 4°C and -20°C compared to the results from day 0. In addition, recovery of PPDQs decreased significantly (up to 90% or even undetectable) after 7 days of storage at 4°C or -20°C compared to the results from day 0 (Fig. 3). These results suggest that dissolved phase samples must be extracted immediately on the same day to obtain the most accurate data for the target analytes, which is consistent with the suggestions by Xu et al. [14]. If the target analytes were only DPU and DCU, samples could be stored at 4°C or -20°C for at least 7 days. These results suggest that some previous studies may underestimate target contaminant concentrations in the dissolved phase if not extracted immediately after sampling.

For SPM samples, surrogate standard corrected recoveries for target analytes, except for DPG, TBA, and IPPDQ, ranged between 99±7.6% (DCU) and 131±2.1% (DPPDQ) on day 1 (Fig. 3). The absolute recoveries for DPG, TBA, and IPPDQ on day 1 were 92±17%, 105±20%, and 72±12%, respectively (Fig. 3). After 7 more days of storage at -20°C (extracted on day 8), the recovery of PPDQs decreased by approximately 30-50% compared to day 1, while other target analytes remained stable (Fig. 3).

In our study, DPU, DPG, and DCU remained stable in the dissolved phase during storage, likely because oxidative or hydrolytic pathways for these compounds proceed slowly under dark and cold conditions and in the presence of the antioxidant GSH. In contrast, TBA in the dissolved

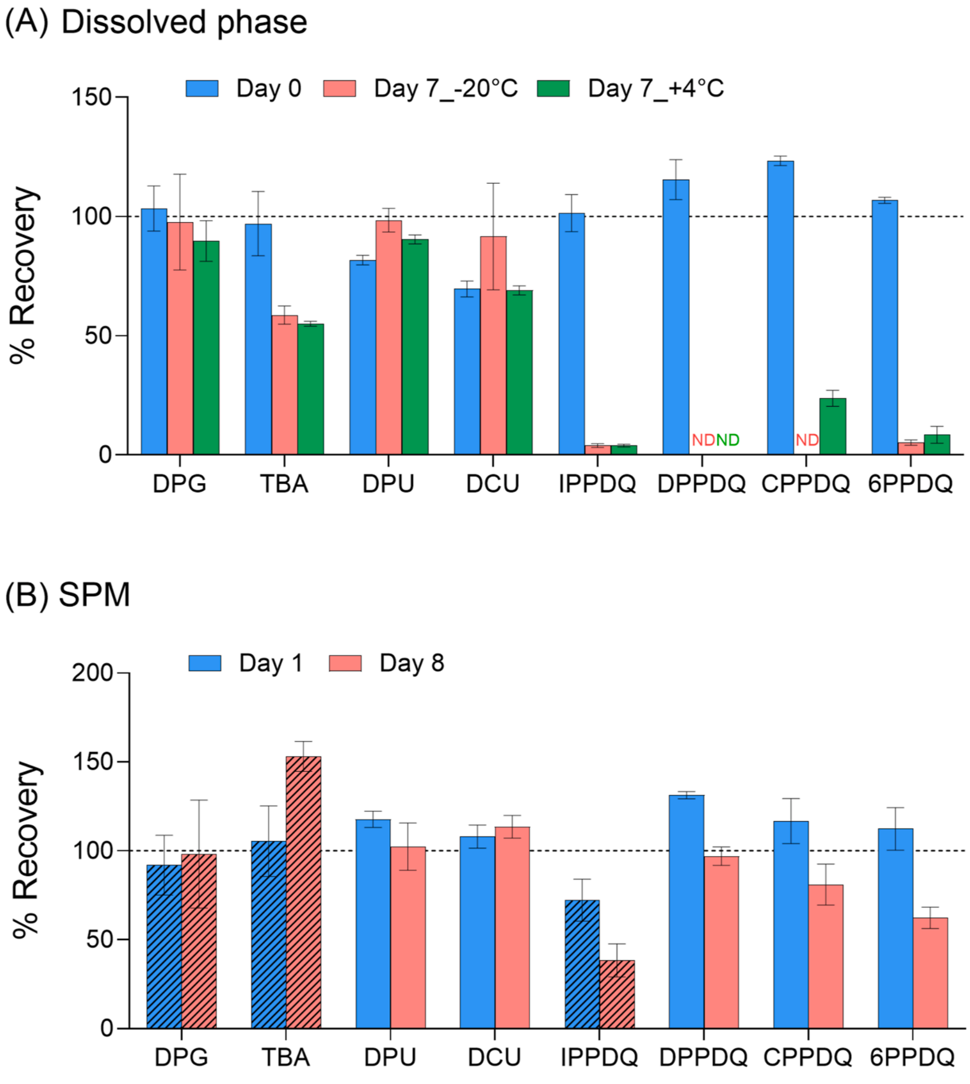


Fig. 3. Surrogate standard corrected recovery (mean ± SD) of (A) dissolved phase and (B) SPM of surface water stored under different conditions. For DPG, TBA, and IPPDQ in SPM, the data represent absolute recovery (striped).

phase showed much lower recovery after 7 days storage. Given our dark storage conditions and the chemical structure of TBA, both photolysis and hydrolysis can be excluded as major transformation pathways. Although direct evidence for TBA is lacking, the biodegradation of structurally similar tertiary amines, such as triethylamine, was previously reported [26], supporting the possibility that microbial processes contributed to the observed instability of TBA in the dissolved phase. PPDQs were also unstable in the dissolved phase. Adsorption to stainless steel surfaces may be a potential factor, while adsorption to glassware is unlikely [27]. Since photodegradation can be ruled out under dark storage, other processes, such as reactions with dissolved oxidants, hydrolysis, and microbial degradation, are plausible causes of instability of PPDQs. Previous studies have reported different findings: Hiki et al. observed a half-life of 33 hours for 6PPDQ in dechlorinated tap water under a 16 hours light/8 hours dark cycle using ambient fluorescent light (where photodegradation contributions were likely minor) without identifying a clear mechanism [28]; Di et al. reported hydrolysis half-lives of 12.8-13.2 days in river water [29]; and Han et al. showed aerobic microbial degradation half-lives of 3 ± 1 days for 6PPDQ and 1.9 ± 0.1 days for IPPDQ [30]. In contrast, Yan et al. concluded that photodegradation was the dominant degradation pathway in water, with negligible contributions from hydrolysis and microbial processes for 6PPDQ [31], while Hu et al. found 6PPDQ to be largely stable in buffer solution with only a 26 ± 10% decrease over 47 days [27]. Overall, these results show that degradation rates greatly depend on experimental conditions, water chemistry, microbial community compositions, and the target contaminant concentration tested. Since evaluating the storage stability of each compound in every environmental aqueous sample is impractical and results may vary widely, it is better to analyze samples immediately after collection to reduce uncertainty. In SPM, all target contaminants were more stable than in the dissolved phase, likely because sorption reduced exposure to dissolved oxidants, reactive species, and microbial-mediated transformation.

3.5. *Method evaluation*

The results of linearity, MDLs, and matrix effects of the optimized method are shown in Table 3. The linearity of the standard calibration curve (0 ng/mL-100 ng/mL) of target rubber-derived contaminants in acetonitrile was in the range of R^2=0.9947 and R^2=0.9990. The MDLs of the analytes in this study ranged from 0.2 to 7.0 ng/L and 0.1 to 2.6 ng/L for dissolved and SPM phases of surface water, respectively. For snow samples, the MDLs of the analytes were 0.2-5.0 ng/L for the dissolved phase and 0.1-5.4 ng/L for the snow SPM (Table 3). Johannessen et al. [16,17] quantified DPG and 6PPDQ in surface water using LC-Orbitrap MS, determining detection limits of 6.5-9.8 ng/L based on the lowest calibration curve concentration (Table 1). LC-MS/MS methods typically achieve lower detection limits for these compounds in the dissolved phase of surface water (Table 1) but rely on signal-to-noise ratios, often overlooking the performance and reproducibility of the entire sample preparation process. Our study used the EPA-recommended method, which includes replicate spiked samples and method blanks through all steps of sample preparation and analysis. Unlike detection limits based only on signal-to-noise ratios, this method considers sample preparation repeatability and routine process variability, thereby providing a more reliable and reproducible estimate of method sensitivity.

In this study, surrogate standard-corrected recoveries of target compounds in the dissolved phase ranged from 63 ± 8.5% (TBA) to 116 ± 20% (CPPDQ) at 50 ng/L and from 69 ± 2.1% (TBA) to 111 ± 1.9% (CPPDQ) at 400 ng/L spike levels (Fig. 2). For SPM, surrogate standard-corrected recoveries, excluding DPG, TBA, and IPPDQ, ranged from 83 ± 7.1% (DCU) to 132 ± 6.4% (CPPDQ) at 50 ng/L and from 72 ± 2.3% (DCU) to 119 ± 7.2% (CPPDQ) at 400 ng/L (Fig. 2). For DPG, TBA, and IPPDQ, using surrogate standards DEDPU-d_{10} and 6PPDQ-d_5 may overestimate their concentrations in SPM. However, their absolute recoveries were robust: 73 ± 0.6% (50 ng/L) and 87 ± 10.2% (400 ng/L) for DPG, 102 ± 11% (50 ng/L) and 101 ± 5.3% (400 ng/L) for TBA, and 73 ± 0.5% (50 ng/L) and 88 ± 4.7% (400 ng/L) for IPPDQ, enabling quantification via external calibration in SPM.

Matrix effects were in the range of 42 ± 6% (TBA) -111 ± 14 % (DPPDQ) for the dissolved phase and 53 ± 4 % (DCU) -96 ± 10% (TBA) for the SPM of the surface water samples (Table 3). TBA, DCU, and DPU exhibited ion suppression in dissolved phase and/or SPM of surface water, but the surrogate standard DEDPU-d_{10} effectively corrected these effects. Matrix effects in the dissolved phase of melted snow ranged from 71 ± 4 % (DPU) to 141 ± 14% (CPPDQ), while in snow SPM, they ranged from 45 ± 23% (DPG) to 125 ± 8% (TBA). The observed matrix effects for DPG in snow SPM were unexpectedly low and highly variable despite its robust absolute recovery in surface water SPM tests. This difference was attributed to relatively high background levels of DPG in the snow samples compared to the spike concentration, influencing the matrix effect outcomes. To improve recovery assessment in future studies, isotope-labeled DPG should be added to snow SPM samples.

Compared to previous HRMS-based methods, which typically targeted only specific rubber-related compounds or a single matrix, this new method broadens the scope both analytically and environmentally. It enables the simultaneous detection of eight rubber-derived contaminants in the dissolved phase and SPM in surface water and snowmelt, with systematic stability tests to establish a more reliable monitoring protocol. Detection limits in the sub-ng/L to low-ng/L range ensure that concentrations relevant to ecotoxicology can be accurately measured. Although the two isotope-labeled surrogates applied here provided robust performance in the dissolved phase, they were less suitable for DPG, TBA, and IPPDQ in SPM. For these compounds, external calibration supported by spike recoveries provided reliable quantification. Future studies should incorporate additional compound-specific isotope-labeled surrogates to further improve accuracy, particularly for SPM matrices. In addition, it is worth exploring other preservation methods in future work; however, such approaches must be carefully evaluated to ensure they do not alter contaminant partitioning or

Table 3

Summary of linearity, MDL, and matrix effects. SD: standard deviation (*n*=3). * Detected in blanks, and MDL was determined using blanks.

Target Compounds	Linearity	MDL (ng/L)				Matrix Effects (%)							
		Surface water		Snow		Surface water (50 ng/L)				Snow (50 ng/L)			
						Dissolved phase		SPM		Dissolved phase		SPM	
		Dissolved phase	SPM	Dissolved phase	SPM	Mean	SD	Mean	SD	Mean	SD	Mean	SD
DPG	0.9990	0.2*	0.1*	0.2*	0.1*	90	4	96	10	73	5	45	23
TBA	0.9977	4.0*	1.5*	4.0*	1.5*	42	6	95	15	103	8	125	8
DCU	0.9959	5.0*	0.6*	5.0*	0.6*	50	6	53	4	73	5	75	7
DPU	0.9993	2.0	1.1	2.0	1.0	59	8	58	4	71	4	70	6
IPPDQ	0.9947	5.0	2.0	1.0	1.0	103	12	83	9	82	6	84	9
6PPDQ	0.9966	4.0*	1.6	4.0*	5.0	102	10	80	6	89	3	106	11
DPPDQ	0.9974	7.0	2.6	3.0	3.0	111	14	88	11	85	8	92	12
CPPDQ	0.9974	5.0	2.2	2.0	2.3	101	17	84	7	141	14	107	12

speciation.

3.6. Application to surface water and snow samples

DPG, DCU, and TBA were detected in the dissolved phase of environmental surface water and snow samples. DPG was detected in all 12 dissolved phase samples with concentrations up to 15.8 ng/L in surface water and up to 236 ng/L in snowmelts (Table S2), indicating its widespread distribution in the environment around the sampling area. Concentrations of DPG in the dissolved phase from different sites followed the order of Snow > Rimouski River > Marina ≈ Lepage (Fig. 4). This is reasonable because the snow samples were collected at a car parking lot, where the accumulation of tire wear particles (a major source of DPG and related rubber-derived contaminants) is expected to be high [3,12], leading to elevated concentrations. DCU was detected in dissolved phase of surface water samples from the Rimouski River and snowmelts, with mean concentrations of 8.2 ± 1.3 ng/L and 34.1 ± 13.5 ng/L, respectively. Other target contaminants, including all PPDQs, were not detected in the dissolved phase of the collected surface water and snowmelt samples.

In SPM, DPG was detected in samples from three sites, with the following order: Snow (Site 4) > Lepage (Site 1) ≈ Rimouski River (Site 3) (Fig. 4) with concentrations of 34.4 ± 0.2 ng/L in snow and 0.4 ± 0.1 ng/L and 0.1 ± 0.2 ng/L in Lepage stream and Rimouski River, respectively. The levels of DPG in the snow SPM were significantly higher than in the surface water samples (Fig. 4). In addition, 6PPDQ was detected only in the SPM of the snow samples, with concentrations ranging from 15.4 to 21.1 ng/L (18.2 ± 2.9 ng/L). These results suggest that melted snow may be a major pathway for transporting DPG, DCU, and 6PPDQ into the surrounding environment.

The concentrations of target contaminants in the surface water and snowmelt samples in this study were generally lower than or comparable to previously reported data worldwide (Table S3). The concentrations of DPG and DCU in the dissolved phase of surface water in this study are comparable to those reported by Tian et al. in an agricultural watershed in the State of Washington, USA, with concentrations of DPG in the range of 0.49-98 ng/L and a concentration of DCU ranging from 1.3 to 31 ng/L [18]. Although 6PPDQ has been reported in some Canadian urban watersheds [16,17,32–34], its occurrence and distribution are highly variable and strongly influenced by watershed size, land use, and sampling conditions. Detections are more common in large urban centers (e.g., Vancouver, Toronto) and at sites affected by stormwater events, whereas concentrations can remain below detection limits in less urbanized watersheds [32–34]. In some studies, raw water was analyzed without filtration [32,33], meaning the reported concentrations may not exclusively represent the dissolved phase; therefore, such comparisons

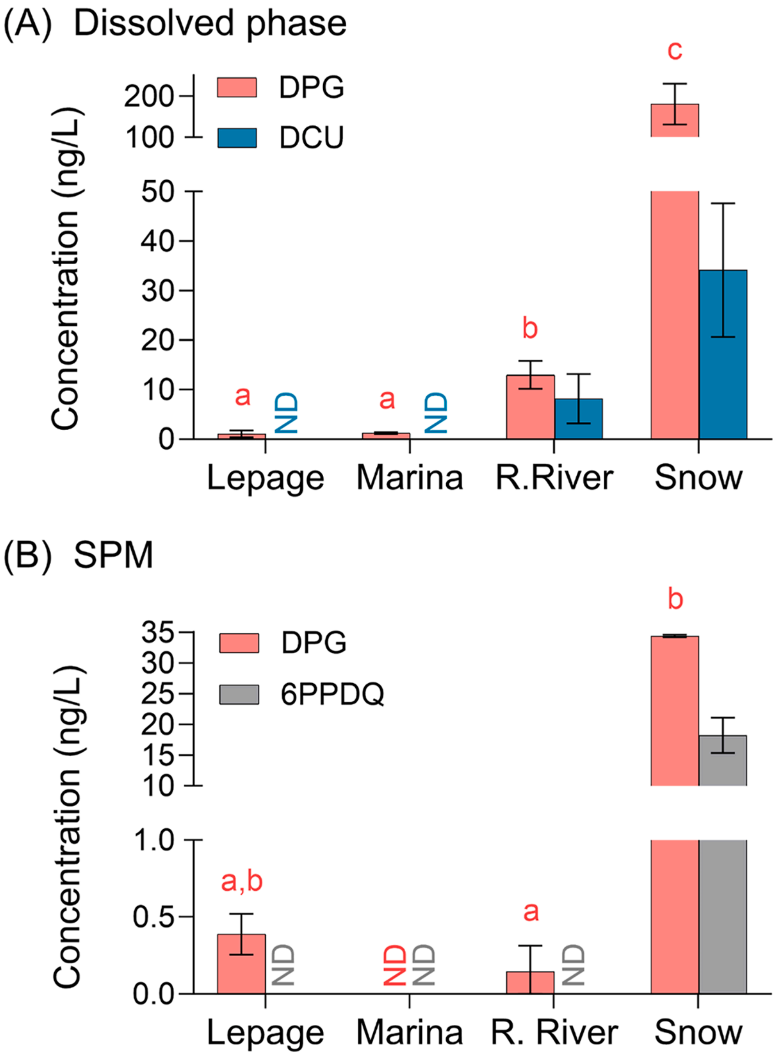


Fig. 4. Concentrations (mean ± SD) of (A) DPG ($W(3.000, 4.286) = 193.1$, $p < 0.0001$) and DCU (comparison between Rimouski (R.) River and snow: $t(2.716) = 2.94$, $p = 0.069$) in dissolved phase and (B) DPG ($W(2.000, 3.516) = 24.59$, $p = 0.0086$) and 6PPDQ in SPM of environmental surface water and snow samples. ND: Not Detected. Different letters indicate significant differences.

should be interpreted with caution. In this study, 6PPDQ was not detected in surface water collected from rivers and creeks within Rimouski, nor in samples taken from the adjacent St. Lawrence Estuary. This may be partially attributed to the relatively lower population density (~50,000) and local anthropogenic pressure in Rimouski compared with larger cities (e.g., 7 million in Greater Toronto Area). In addition, 6PPDQ concentrations in surface water can fluctuate dramatically within short timeframes (minutes to hours), depending on the inputs from stormwater [33]. Our samples were collected under baseflow/winter conditions and were not influenced by stormwater or snowmelt, which may also explain the non-detection of 6PPDQ. Furthermore, the St. Lawrence Estuary is a large water body with strong dilution capacity, which could further contribute to the absence of detectable concentrations. However, these factors alone cannot fully explain the non-detection of 6PPDQ. Other rubber-derived contaminants (e.g., DPG and DCU) were measured at concentrations comparable to those reported in some aquatic environments worldwide, indicating that certain rubber-associated chemicals are still released in significant amounts even in less urbanized regions. The absence of 6PPDQ in our study is therefore more likely explained by a combination of factors, including its high temporal variability, rapid transformation in the aquatic environment, strong particle affinity, and the dilution effect of the estuarine system. These results also highlight the need to expand both the spatial coverage and temporal resolution of sampling in future investigations.

DPG (768 ± 483 – 1110 ± 1810 ng/L), DCU (37 ± 35 – 136 ± 47 ng/L), DPU (9.2 ± 15 – 72 ± 69 ng/L), and 6PPDQ (81 ± 53 – 367 ± 206 ng/L) were previously detected in melted snow from Saskatoon (2019-2020), Canada, at much higher concentrations than in the snow collected in the present study [12]. The spatial variations of rubber-related contaminants in snowmelt, as well as the factors affecting them (e.g., sources, weather, transport, and transformation), merit further investigation.

Although ecotoxicological assessment was not the focus of this study, the detection of 6PPDQ, DPG, and DCU is noteworthy given their reported adverse effects on aquatic organisms [7,9,10]. DPG and DCU show acute toxicity with EC50 and LC50 values in the mg/L range [9,10], which are several orders of magnitude higher than the concentrations detected here (ng/L). However, the lowest predicted Chronic Value (ChV) for DCU is approximately 800 ng/L for *Mysid* (estimated by the Ecological Structure-Activity Relationships (ECOSAR, v2.2) model), only one to two orders of magnitude above the levels measured in the dissolved phase of surface water and snow in the present study. Considering that hazard quotient calculation typically applies additional assessment factors (e.g., 100-1000), the concentrations observed in this study may still be of concern, particularly for the scenario of chronic exposure. For 6PPDQ, species sensitivity varies greatly, with juvenile coho salmon reported to be highly sensitive (acute LC50 of 41 ng/L) [35]. Although 6PPDQ was not detected in the dissolved phase of surface water or snowmelt, its presence in the SPM of snowmelt at ng/L levels raises concerns about its transport to aquatic environments and the potential exposure of sensitive species during snowmelt events. Other target analytes were not detected, which may reflect low environmental occurrence, rapid transformation, or concentrations below our detection limits. Although our dataset is too limited to allow for quantitative risk assessment, the occurrence of these compounds in both surface waters and snowmelt further highlights the need to incorporate them into future monitoring and risk assessment frameworks.

While our results demonstrate the applicability of the method in environmental matrices and indicate the presence of rubber-related contaminants at the studied sites, the limited number of samples and replicates prevents a comprehensive assessment of their environmental prevalence. Broader studies with larger sample sizes and extended spatial and temporal coverage will be required to draw more general conclusions about their occurrence and distribution.

4. Conclusion

This study presents analytical methods developed and evaluated for the simultaneous determination of eight rubber-derived contaminants in the dissolved phase and SPM of surface water and snowmelts. An SPE protocol using HLB cartridges and an acetonitrile/dichloromethane (3/7, *v*/*v*) elution mixture was optimized for samples in the dissolved phase, while ultrasonic-assisted extraction with the same solvent system was effective for the SPM samples. Notably, adding GSH before extraction effectively enhanced the method's performance for certain compounds in both matrices. Storage stability tests revealed that the dissolved phase must be extracted immediately upon sample collection and that SPM extractions must be completed within a week of filtration to ensure accuracy. These methods were applied to real environmental samples, and DPG, DCU, and 6PPDQ were detected in surface water and snow collected in Quebec, Canada. Elevated concentrations were detected in snow from a parking lot, indicating that snowmelt in cities may serve as a vector for transporting these contaminants into surrounding environments. While the current workflow allows for reproducible quantification of multiple rubber-derived contaminants in water and snow samples, future improvements should include additional isotope-labeled surrogates to enhance accuracy for SPM samples. The developed method differs from previous approaches that were restricted in compound coverage or matrix specificity, with the added novelty of evaluating storage stability and recommending appropriate storage conditions. In addition to analytical advances, this research highlights snowmelt as an important pathway for transporting rubber-derived contaminants from urban surfaces into surrounding environments, which are often overlooked in cold-climate regions. This work provides foundations for further investigating the sources, spatial and temporal variability, environmental fate, and ecological risks of these rubber-derived contaminants of emerging concern.

CRediT authorship contribution statement

Julie Anquetin: Writing – review & editing, Writing – original draft, Visualization, Project administration, Methodology, Investigation, Formal analysis, Conceptualization. **Mathieu Babin:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Rachid Amara:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization. **Zhe Lu:** Writing – review & editing, Writing – original draft, Visualization, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2025.466417.

Data availability

Data will be made available on request.

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