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Article

Occurrence of Benzene Polycarboxylic Acids in Ash and Streamwater after the Cameron Peak Fire

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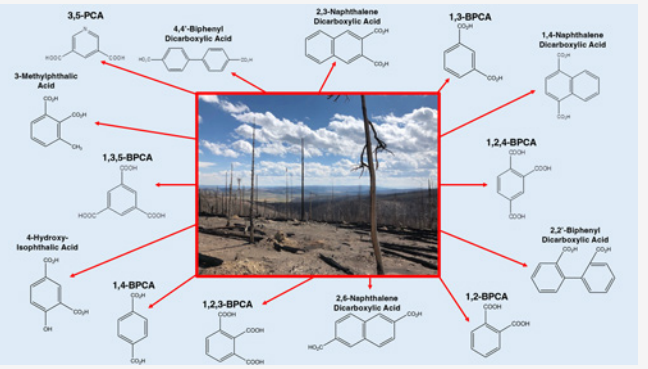
ABSTRACT: To better understand the effects of wildfire on water quality, water and ash samples were collected at multiple stream and river locations following the Cameron Peak Fire. These sites included both burned and unburned parts of the Cache La Poudre watershed in northern Colorado. A series of benzene polycarboxylic acids (BPCAs), including benzene, naphthenic, and biphenyl polycarboxylic acids, were quantitatively measured in streamwater samples for their occurrence in the watersheds; numerous isomers were also detected. High-flow storm events, containing high concentrations of charred organic matter and ash, were sampled during storm runoff (typically high intensity rainfall >5 cm/h). Concentrations of BPCAs ranging from 1 to greater than 100 μg/L were measured following storm events but were absent from unburned sites and occurred at lower levels (ng/L) during nonstorm conditions. The most concentrated and abundant BPCA in burned samples (1,2,4-benzene tricarboxylic acid) was absent in unburned samples and thus may potentially serve as a tracer of wildfire impacts on water quality. Ash collected immediately following the fire contained the same suite of compounds (μg/g concentration range) as streamwater samples. These results demonstrate that these BPCAs constitute an important proportion of the organic matter exports after wildfires.



KEYWORDS: *wildfire, water quality, ash, benzene poly(carboxylic acid)s, dissolved organic carbon, LC/QTOF-MS*

INTRODUCTION

The threat of wildfires to natural resources and water supplies is growing globally. Higher temperatures and prolonged droughts have extended fire seasons worldwide and generated larger, more intense wildfire events.[1−3] During the 2020 fire season, the U.S. states of California and Colorado each reported the largest within-state fires on record. Fueling these wildfires are combustion reactions which create a suite of organic compounds that are frequently detected in air,[2,3] ash,[1,3] soil,[4,5] and water samples.[1,3−6] In part, understanding the source and fate of combustion-related compounds requires an evaluation of chemical constituents that are both dissolved in and mobilized by water during storm events.[7,8]

Combustion of vegetation and surface organic soil layers by extreme wildfires exposes burned landscapes to soil erosion and alters how watersheds regulate water supplied to both aquatic habitats and downstream use.[6] In addition to short term, postfire responses, loss of upland and riparian vegetation, and rearrangement of stream and floodplain geomorphology alter biogeochemical processes that regulate nutrients (N and P), metals, and organic matter retention and losses over longer timeframes.[6,9−12] In the western United States, approximately 11% of all fluvial networks are estimated to be affected by postfire changes.[9−12] However, highly variable wildfire behavior, coupled with spatially complex vegetation, landscape, and hydrologic factors, complicates anticipation of postfire surface water and drinking water quality. Further, convergence of intense rainstorms over recently burned areas, although unpredictable, determines the occurrence of significant hillslope, watershed, and water quality responses, which affect downstream drinking water treatment plants.[7]

Combustion of vegetation also impacts the concentration and reactivity of dissolved organic matter (DOM) exports into surface waters.[7,8] For example, the concentration of DOM in surface streams can increase after a wildfire, with wildfires increasing the overall export of black carbon.[13,14] Furthermore, postfire DOM is more aromatic and has a lower molecular weight than the prefire material.[5] In previous work, Cawley et al.[15] demonstrated that an increase in combustion temperature

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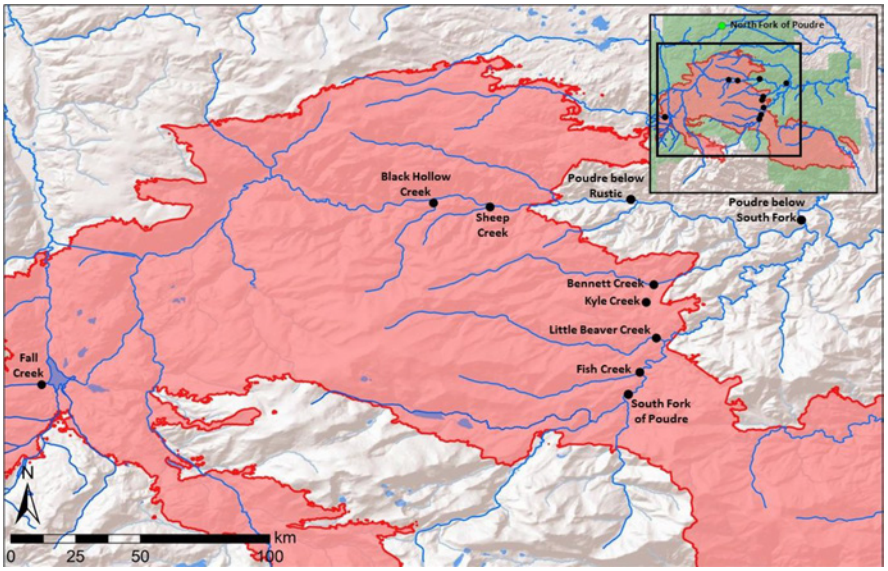

Figure 1. Cameron Peak Fire (red) and sampling sites within the CLP watershed. The inset shows the fire perimeter within the national forest (green).

shifted the composition of the DOM toward a higher proportion of oxygen- and nitrogen-containing moieties. When applying sensitive, structure-elucidating techniques, Thurman et al.[5] reported the occurrence of benzene polycarboxylic acids (BPCAs) as a major component of the DOM in water leachate from burned soils using liquid chromatography/quadrupole time-of-flight mass spectrometry (LC/QTOF-MS) and solid-state ^{13}C NMR spectroscopy. On the same set of samples, Bahureska et al.[16] used Fourier transform high-resolution mass spectrometry (FT-HRMS) to show a clear transition of organic compounds toward the formation of poly(carboxylic acid)s. Furthermore, Ferrer et al.[1] reported the presence of BPCAs, naphthenic carboxylic acids, quinolinic acids, and benzene furanoic acids and quantitated BPCAs for the first time in river water and ash samples from wildfires in California and Colorado. Analysis of additional samples will help determine the prevalence of these compounds following wildfires and further elucidate their contribution to observed DOM shifts within burned watersheds.

The objective of this study was to further our understanding of the concentrations and distributions of BPCAs in surface waters after a wildfire event. Specifically, ash samples were collected immediately following combustion during the Cameron Peak Fire in Colorado; streamwater samples were collected approximately 5−12 months postfire during storm and nonstorm conditions in both fire-impacted and unburned control sites along the mainstem of the Poudre River and several of its tributaries. Both ash and streamwater samples were analyzed for dissolved organic carbon (DOC) and for the concentrations of 14 select BPCAs, for which standards are commercially available, using LC/QTOF-MS. The findings detail the significant contributions this suite of BPCAs provides to the overall composition of mobilized postfire DOM within the watershed.

MATERIALS AND METHODS

Site Description. The August−December 2020 Cameron Peak Fire was the largest fire in Colorado history (844 km^2) and burned through most of the forested portion of the Cache La Poudre (CLP) watershed located on the northern edge of the Colorado Front Range in Northern Colorado, USA. The CLP is the primary drinking water source for the cities of Fort Collins, Greeley, and Thornton (approximate population of 330,000) and the irrigation source for much of the agricultural land of the northern Front Range. The Cameron Peak Fire ignited in subalpine mixed conifer forests near the CLP's headwaters and burned at mixed severity both eastward and to lower elevations in the watershed into lodgepole and ponderosa pine forests. Combined, the Cameron Peak Fire and the 2012 High Park Fire burned more than 60% of the forested portion of the CLP watershed. Postfire water quality responses increase with the proportion of a watershed exposed to high-severity burning,[7] so this study evaluated DOM in tributaries of the CLP across a range of burn severity and extent throughout the Cameron Peak Fire (Figure 1).

Sampling and Water Quality Analysis. Overall, 47 streamwater samples were collected from five locations along the mainstem of the CLP River and seven tributaries (six burned and one unburned control) throughout the summer of 2021 to analyze postfire effects on water quality (Table S1). Fourteen of these samples were collected immediately following four intense rainstorms (precipitation >5 cm/h) during the first postfire year which caused blackwater events when ash and sediment from burned hillslopes were mobilized into streams; these intense rainstorms generated high-flow conditions strong enough to cause streambank scouring and loss of sampling instrumentation. The remainder of the samples were collected during nonstorm, low-flow conditions in which turbidity within the stream channels was measurably lower than that observed during high-flow rainstorm events.

Ash was collected within the Black Hollow Creek watershed in November 2020, immediately following combustion but prior to measurable precipitation, and leached in the laboratory within 48 h of collection. Ash samples were leached at a ratio of 1 g of ash to 5 mL of ultrapure water and acidified with formic acid to achieve a pH of 2.5. A 10 mL aliquot of ash aqueous leachate was further processed through a 500 mg HLB (Waters Corporation, Milford, MA, USA) solid phase extraction (SPE) cartridge and eluted with 5 mL of MeOH.

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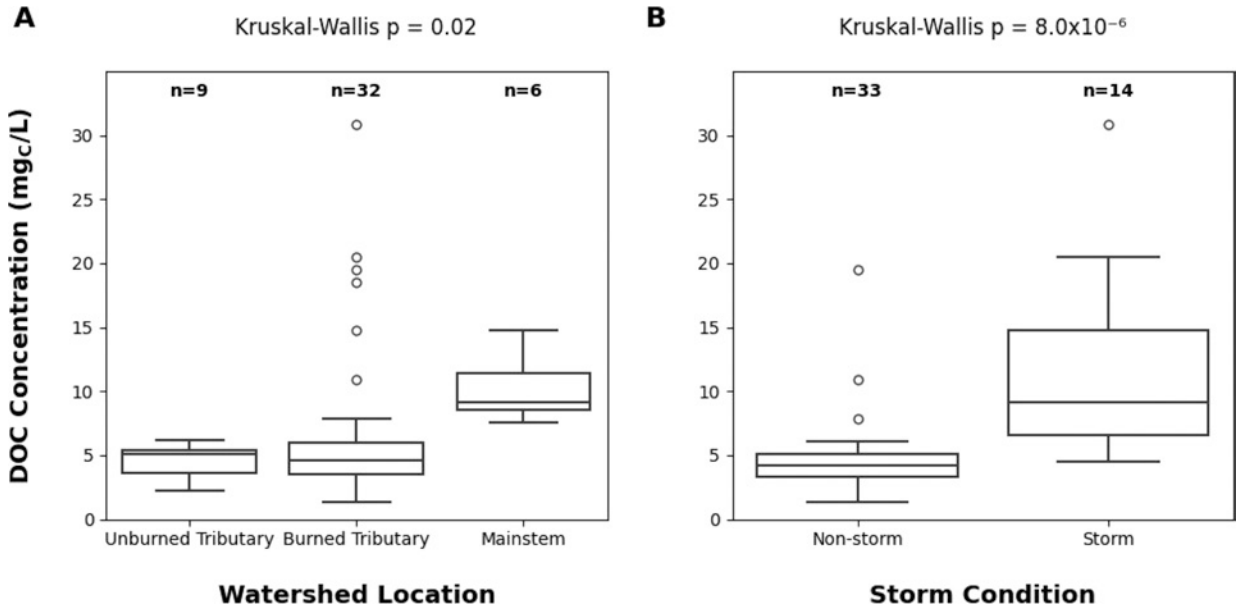

Figure 2. DOC concentration (mg/L) in all CLP streamwater samples by watershed location (A) or storm condition (B). Boxplots display the 10th, 25th, 50th, 75th, and 90th percentiles, as well as outliers (circles). Sample size is listed above each box.

The eluent was further evaporated to 0.5 mL under a flow of nitrogen for analysis by LC/QTOF-MS.

Streamwater samples were analyzed for DOC; a subset of 22 samples, including one ash aqueous leachate sample, was selected for additional screening for specific BPCAs. Samples for both DOC and BPCA analysis were collected in precombusted (heated for 3 h at 500 °C) amber glass bottles and stored at 4 °C throughout the analysis process. DOC samples were filtered through 0.7 μm-pore glass fiber filters (Millipore Corp.; Burlington, MA, USA) within 24 h of collection. DOC concentrations were determined via a high-temperature catalytic oxidation method[17] using a Shimadzu TOC-VCPN total organic carbon analyzer (Shimadzu Corporation, Columbia, MD, USA). Prior to analysis, samples were treated with a 2 M HCl addition to remove mineral carbon. The lower limit of detection for DOC was 50 μg/L.

LC/QTOF-MS Analysis for BPCAs. The samples of streamwater were processed following the methods described in recent studies.[1,18] Briefly, 14 standards (Table S2) were obtained from Sigma-Aldrich (Allentown, PA, USA) and used for sample recovery and analysis. Samples were filtered in the laboratory (0.7 μm-pore glass fiber), stored at 4 °C, and analyzed within 14 days of collection. SPE was used with 500 mg HLB cartridges after acidification to pH 2.5 with formic acid. See Ferrer et al.[1] and Ferrer and Thurman[18] for complete details.

Briefly, the LC/QTOF-MS method used an ultrahigh-performance liquid chromatography (UHPLC) system with a thermostated autosampler, column compartment, and a binary pump (Agilent Series 1200, Agilent Technologies, Inc.; Santa Clara, CA, USA) equipped with a reversed-phase C8 analytical column of 150 mm × 4.6 mm with 3.5 mm particle size (Zorbax Eclipse XDB-(8)). The column temperature was maintained at 25 °C, and the injection volume was 20 μL. Mobile phases A and B were water with 0.1% formic acid and acetonitrile, respectively, with a flow rate of 0.6 mL/min. The chromatographic method held the initial mobile phase composition (10% B) constant for 5 min, followed by a linear gradient to 100% B after 30 min. The column was connected to a quadrupole time-of-flight mass spectrometer (QTOF-MS; Agilent model 6546) with an Agilent Jet Stream Technology electrospray source in negative ion mode.

Statistical Analysis. Storm conditions were compared within the CLP watershed to evaluate whether the DOC mobilized by precipitation events differed from that mobilized under baseline conditions. Watershed locations, including burned and unburned tributaries and mainstem locations, were also compared independently of storm conditions to assess spatial variability in DOC exports (Figure 2). A nonparametric approach was used to account for nonnormal data and unequal sample sizes while evaluating DOC concentrations across both sampling sites and flow conditions. These analyses were performed by using a Kruskal–Wallis test (Sci.Py v1.11.1). Statistical significance is reported at $\alpha = 0.05$. For BPCA analysis, BPCA concentrations below the detection limit were considered to be negligible (Table 1).

RESULTS AND DISCUSSION

Dissolved Organic Carbon in Streamwater. Figure 2 shows boxplots of DOC concentrations in the CLP, plotting DOC separately as a function of either watershed location or storm condition. Postfire spatial differences in DOC concentrations in the CLP watershed were statistically significant ($p < 0.05$). Average postfire DOC concentrations were lower in all samples collected in the tributaries (mean = 6.98 mg_C/L for burned tributaries and mean = 4.68 mg_C/L for unburned tributaries) than they were in the CLP mainstem samples (mean = 10.2 mg_C/L), despite measured DOC concentrations as high as 30.8 mg_C/L recorded in burned tributaries. With respect to storm conditions, DOC exhibited significantly higher concentrations ($p < 0.001$) following storm events (mean = 12.0 mg_C/L) than during nonstorm conditions (mean = 4.79 mg_C/L), independent of sampling location.

The observed increases in DOC levels as a function of both watershed location and storm condition in this study are consistent with findings in previous studies,[7,8,19] which suggests that intense rainstorm events are the primary drivers of postfire DOC exports into stream catchments. This is likely

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Table 1. Concentrations of Individual BPCAs (μg/L) in Select Streamwater Samples from the CLP Watershed

	3,5-PCA	1,2,4-BPCA	1,2,3-BPCA	1,3,5-BPCA	1,2-BPCA	1,4-BPCA	1,3-BPCA	3-methylphthalic acid	1,4-napthalene dicarboxylic acid	2,6-napthalene dicarboxylic acid	4,4′-napthalene dicarboxylic acid	2,2′-napthalene dicarboxylic acid
LOQ (μg/L)	0.05	0.20	0.10	0.05	0.50	0.50	0.10	0.10	0.10	0.10	0.10	0.05
Burned Tributaries												
Bennett 0512	<0.05	**0.32**	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Bennett 0804	<0.05	**0.60**			<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	**0.06**	<0.05
Black Hollow 0512	<0.05	**0.24**	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Black Hollow 0518	<0.05	**0.20**	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Black Hollow 0811	<0.05	**0.94**	**0.46**	**0.30**	<0.50	<0.50	<0.10	**0.08**	<0.10	<0.10	<0.10	<0.05
Sheep 0512	<0.05	**0.29**	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Sheep 0518	<0.05	**0.33**	**0.06**	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Sheep 0629	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Sheep 0804	<0.05	**0.39**	**0.16**	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	**0.13**	<0.10	<0.05
Sheep 0811	<0.05	**1.13**	**0.84**	**0.26**	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Little Beaver 0701	<0.05	**0.40**	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Kyle 0701	**2.00**	**174**	**67.0**	**20.0**	**43.0**	**13.0**	**28.0**	**2.30**	<0.10	**0.38**	<0.10	**0.22**
Fish 0701	**0.12**	**3.6**	**1.00**	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Unburned Tributaries												
Poudre North Fork 0518	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Poudre North Fork 0629	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Poudre North Fork 0810	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Mainstem												
South Fork 0701	<0.05	**0.86**	**0.17**	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Below South Fork 0701	**0.08**	**1.57**	**0.30**	<0.05	<0.50	<0.50	<0.10	<0.10	**0.20**	<0.10	<0.10	<0.05
Below Rustic 0721	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	**0.08**	<0.05
Below Rustic 0804	<0.05	<0.20	<0.10	<0.05	<0.50	<0.50	<0.10	<0.10	<0.10	<0.10	<0.10	<0.05
Whitewater 0723	**0.05**	**7.50**	**1.55**	**0.39**	**1.51**	**0.26**	**0.64**	**0.06**	<0.10	<0.10	**0.05**	<0.05

because water slowly infiltrates into the soil and ash layers in the burned catchments during snowmelt and nonstorm conditions, while storms deliver precipitation at rates that exceed infiltration, thereby increasing overland flow and the subsequent mobilization of pyrogenic compounds into stream channels.

Identification of BPCAs in Ash and Streamwater. Table S2 shows the chemical structures and accurate mass ions used for the identification of BPCAs in ash aqueous leachate and streamwater. Select compounds were identified previously in runoff from burned areas following the Camp Fire in California,[1] which informed their priority for further investigation in this set of postfire samples. The 14 carboxylated compounds for which commercial standards exist include dicarboxylated benzoic acids, tricarboxylated benzoic acids, pyridine acid, dicarboxylated naphthenic acids, and dicarboxylated biphenyl acids. These compounds have similar MS−MS fragmentation patterns, which involve the loss of 44 mass units (CO_2), as the molecule decarboxylates in the fragmentation cell of the mass spectrometer.

Figure 3 shows both the mass spectrum (MS−MS of the 209.0092 m/z ion in the Black Hollow ash aqueous leachate) and the fragmentation tree for the identification of 1,2,4-BPCA with sequential losses of CO_2 to form definitive fragment ions of m/z 165.0193, 121.0295, and 77.0397 (calculated exact mass). This fragmentation pattern (i.e., the loss of carbon dioxide) is similar for all 14 BPCA compounds and makes the identification straightforward. The final fragment ion is the core structure of the BPCA; for example, for 1,2,4-BPCA, this fragment is the benzene negative ion at m/z 77.0397. The associated qualitative analysis of mass spectra and fragmentation patterns enabled the identification of individual compounds present in ash aqueous leachate, which in turn was used to inform the targeted quantitative analysis of specific compounds present within streamwater samples.

Figure S1 shows an extracted ion chromatogram for Kyle Creek, a tributary within the burned watershed and feeds into the Poudre River (Figure 1), sampled on July 1, 2021, during a blackwater-producing storm event. The extracted ions are m/z 209.0092 and 165.0193, which are the deprotonated molecule and fragment ion, respectively, for the benzene tricarboxylated

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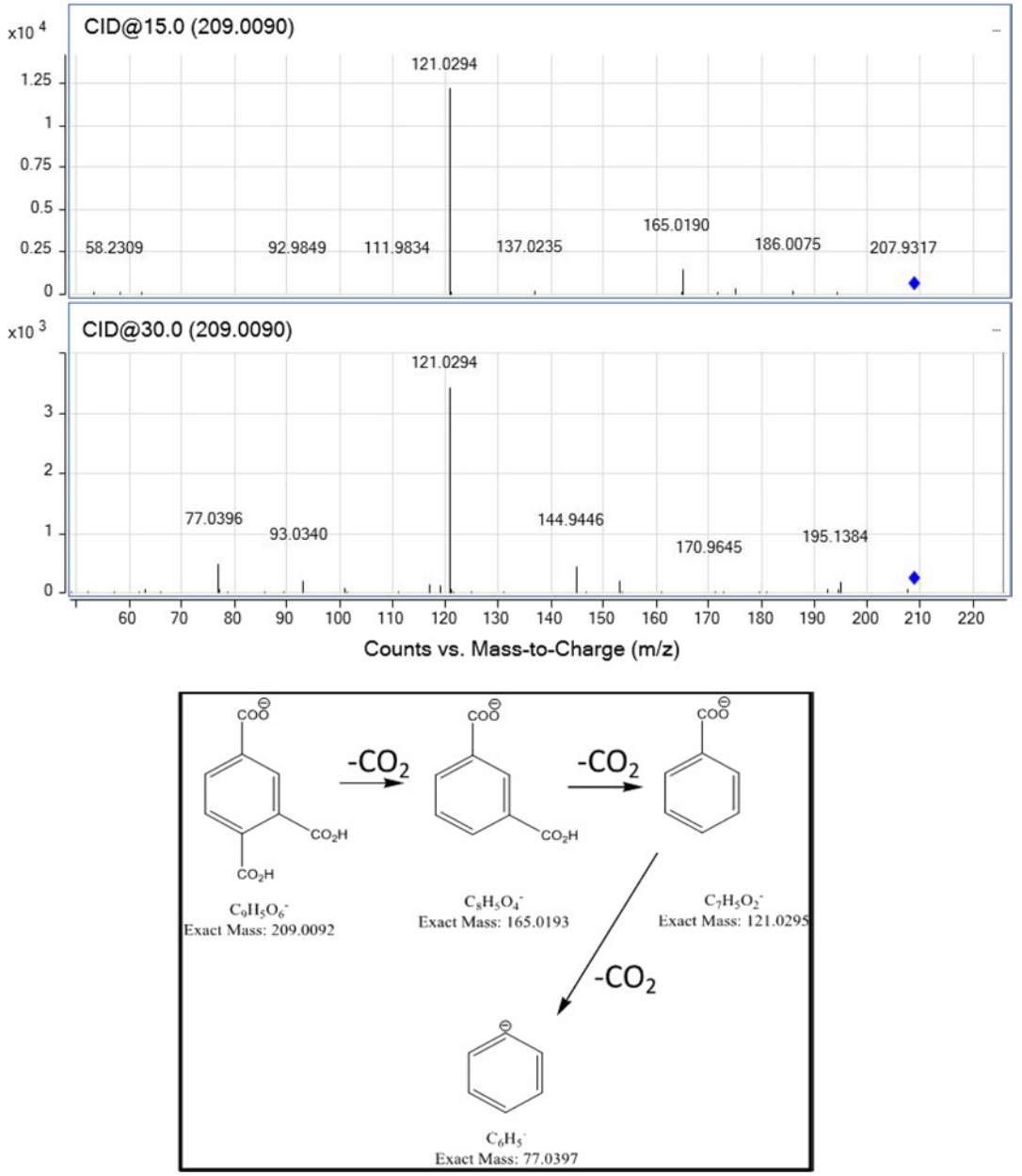

Figure 3. Mass spectrum (top) and the MS−MS fragmentation tree (bottom) for 1,2,4-BPCA in the Black Hollow Creek ash aqueous leachate. The mass values shown in the spectrum are the measured values.

acid. The separation of the seven distinct classes of BPCAs in this study follows the number of carboxyl groups present with the tricarboxylated compounds eluting before the dicarboxylated analogues. Subtle differences in the pK_a values of each compound affect water solubility and retention of the compound within its class. For example, 1,2-BPCA has a lower pK_{a1} than its isomers, 1,4- and 1,3-BPCA and therefore elutes slightly ahead of these compounds. The grouping of isomers as a result of subtle differences in chemical properties is also characteristic of the naphthenic and biphenyl acids and further helps in the identification of these compounds.

When the extracted ion chromatogram for naphthenic acids within the aqueous leachate of Black Hollow ash is compared to that of the Kyle Creek blackwater storm sample, unique profiles are observed (Figure S2). The extracted ion of m/z 215.0350 in the Black Hollow chromatogram shows nine peaks, all with the same accurate mass (±0.0005 m/z). Standards were only available for three of the nine identified isomers in the aqueous leachate of Black Hollow ash (1,4-, 2,6-, and 2,3-naphthalene dicarboxylic acid), but all of the observed compounds had a similar fragmentation pattern that indicated they are isomers of dicarboxylated naphthenic acid. Dicarboxylated naphthenic acid exists within nine possible combinational patterns, and all appear to be present in the aqueous leachate of Black Hollow ash. Conversely, the Kyle Creek sample has only seven identified isomers, two of which are confirmed by standards as the 2,6-naphthalene dicarboxylic acid and 2,3-naphthalene dicarboxylic acid isomers. The differences in the observed numbers of isomers present in each sample are likely due to the preferential formation of organic−inorganic metal−ligand complexes between specific naphthenic acids and metallic ions[20] present within the stream channels. The complexation process causes these compounds, which are initially present only at low concentrations, to precipitate out

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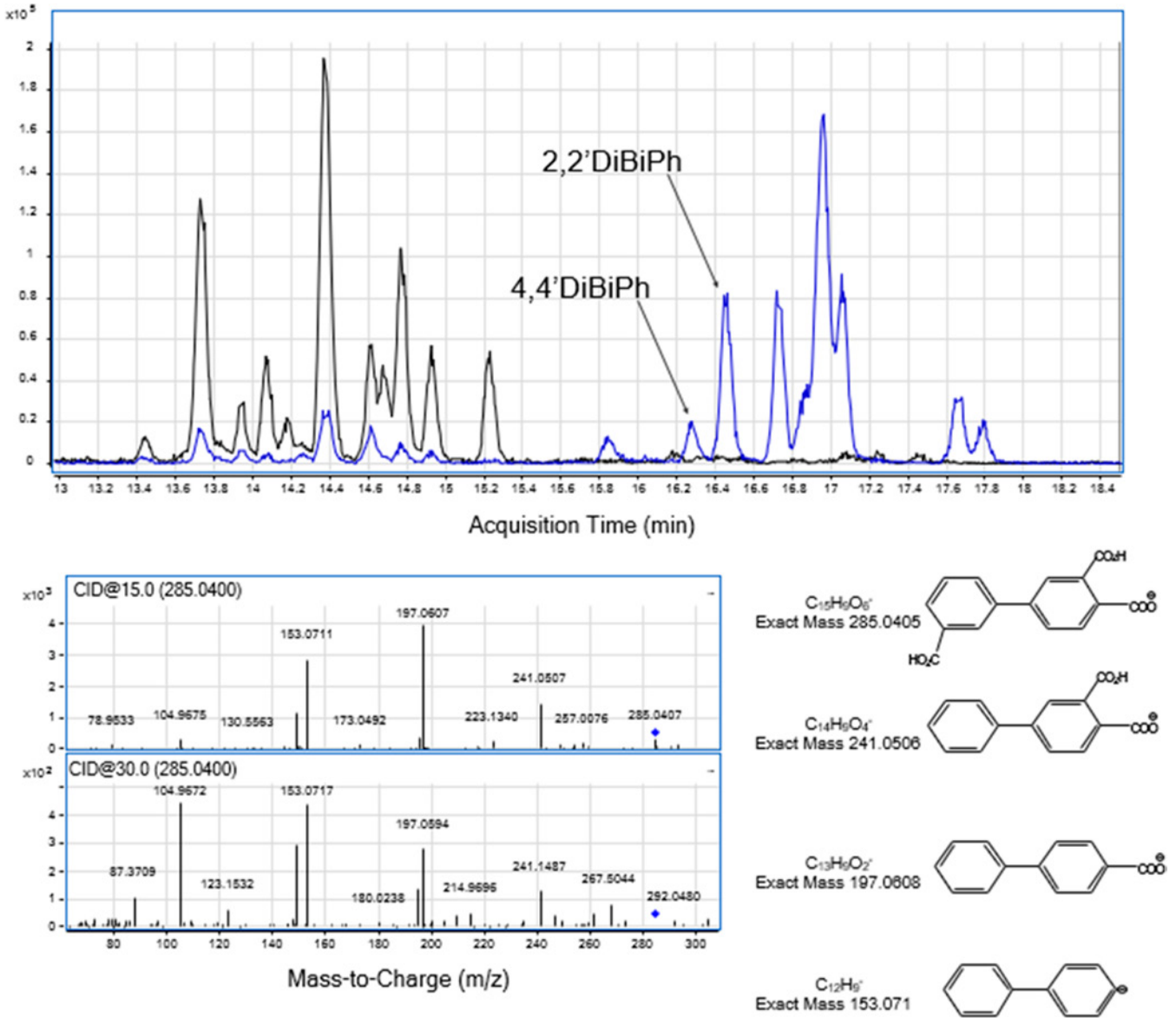

Figure 4. Chromatographic separation and MS−MS identification in negative ion mode for biphenyl dicarboxylated acids (blue) and tricarboxylated acids (black) in the aqueous leachate from Black Hollow ash. The peaks denoting commercial standards are highlighted for the dicarboxylated acids. The mass spectrum shows the measured values.

of the dissolved form, which is why they appear to be absent from the Kyle Creek sample but present within the ash aqueous leachate.

As with the naphthenic acid isomers, a similar pattern of isomer results was noted for the dicarboxylic acids of biphenyl in the Black Hollow ash aqueous leachate (Figure 4), for which there are two standards: 4,4′-biphenyl dicarboxylic acid and 2,2′-biphenyl dicarboxylic acid. Dicarboxylic acids of biphenyl exist within 14 possible different combinations of isomers with two carboxyl groups. Of these 14, eight separated isomers and an envelope of several isomers between 16.8 and 16.9 min are observed in the chromatogram. In addition to the dicarboxylic acid form, the extracted ion chromatogram for the Black Hollow ash aqueous leachate at m/z 285.0405, which corresponds to the tricarboxylic acid of biphenyl, is also included in Figure 4. The MS−MS of this mass is consistent with three losses of CO_2, giving the base peak ion of biphenyl at m/z 153.0710. The chromatography and retention times also fit the more hydrophilic nature of a tricarboxylic acid since the entire family of isomers elutes prior to the dicarboxylic acids of biphenyl.

Six major isomers of methylbenzene dicarboxylic acid and four isomers of hydroxybenzene dicarboxylic acids were also detected in both the Kyle Creek blackwater storm sample and the aqueous leachate of Black Hollow ash (Figure 5). One standard was available for each set of isomers: 3-methylphthalic acid for the methylbenzene dicarboxylic acids and 4-hydroxyisophthalic acid for the hydroxybenzene dicarboxylic acids, respectively. MS−MS fragmentation for all isomers confirmed the identification of both sets of compounds. The peak intensity suggests that although the compounds are present in both ash and streamwater, the relative concentrations of both the methylbenzene and hydroxybenzene isomers are higher in the streamwater than in the ash aqueous leachate.

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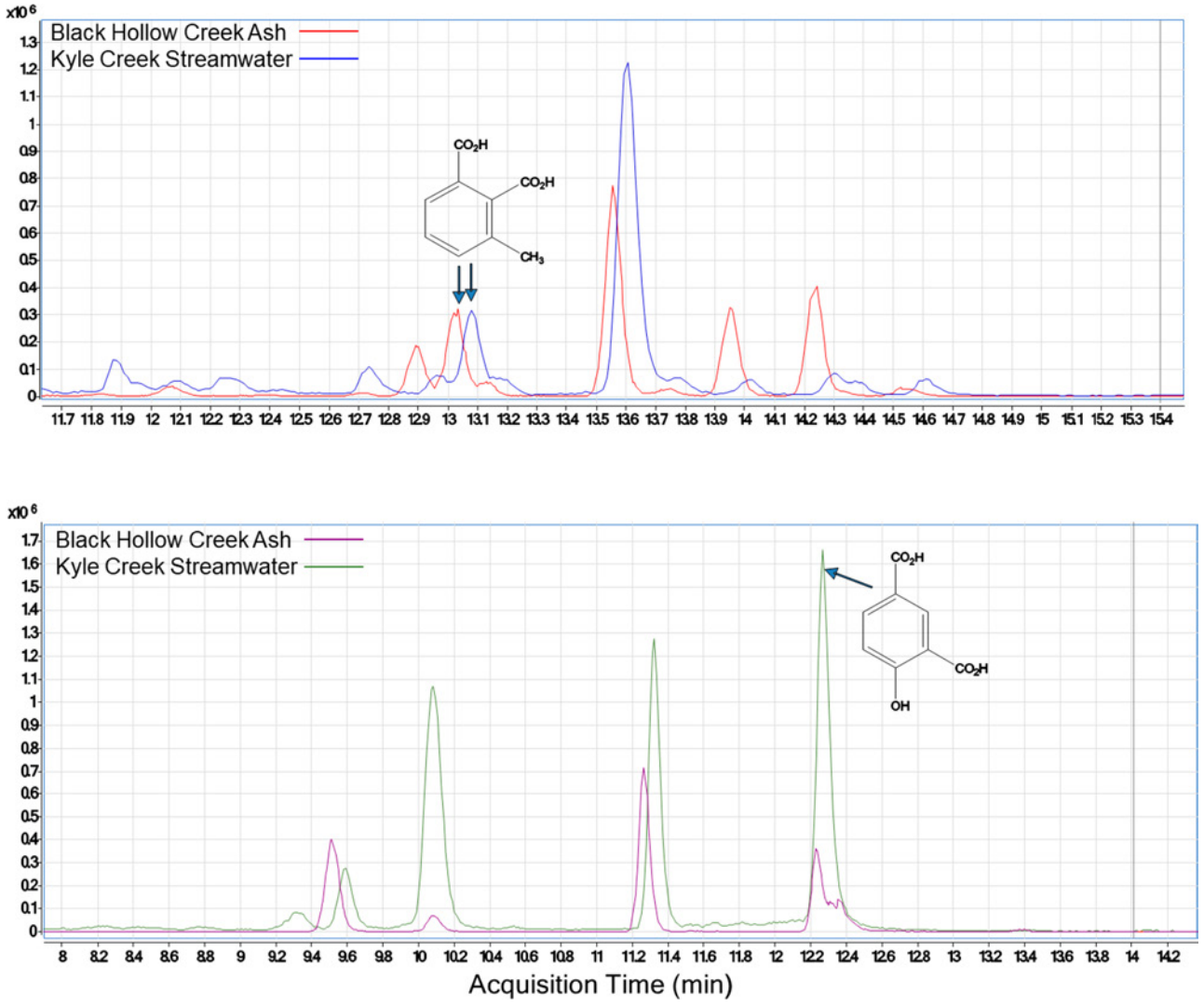

Figure 5. Isomers of methylbenzene dicarboxylic acid in the Black Hollow ash aqueous leachate (red trace) and Kyle Creek streamwater sample (blue trace), as compared to isomers of hydroxybenzene dicarboxylic acid in the Black Hollow ash aqueous leachate (purple trace) and Kyle Creek blackwater storm sample (green trace).

Notably, the aqueous leachate of the Black Hollow ash yields the occurrence of the 14 standard compounds shown in Table S2 apart from 3,5-pyridine dicarboxylic acid, which was present only in trace amounts in streamwater samples and entirely absent in ash aqueous leachate samples. One explanation for this absence is that 3,5-pyridine dicarboxylic acid is derived from nitrogen-rich organic material in the upper layer of soil and is not associated with the ash from the burning of relatively low-N lignocellulosic materials. This pattern is consistent with previous work,[1,5] which showed high levels of 3,5-pyridine dicarboxylic acid when laboratory experiments were performed with representative soil that was muffled at temperatures similar to those produced by wildfires, but low levels of the compound in postfire ash and streamwater samples.

Quantification of BPCAs in Storm and Nonstorm Streamflow. BPCAs were measured in both burned and unburned portions of the CLP watershed during high streamflow conditions, during peak snowmelt, and following intense rainstorms, as well as during low-flow baseline conditions (Figure 6 and Table 1). Postfire spatial differences in BPCA concentrations exhibited a borderline significance (p = 0.052). Average postfire total BPCA concentrations in burned tributaries (mean = 27.8 μg/L) were higher than those in the mainstem (mean = 3.01 μg/L), though the distribution of BPCAs in the burned tributaries was highly influenced by the measured BCPAs in Kyle Creek (350 μg/L) due to the ephemeral nature of the stream. Concentrations of all BPCAs were higher during high-flow, storm conditions (i.e., μg/L concentration range, mean = 28.62 μg/L) as compared to low-flow, nonstorm conditions (i.e., ng/L concentration range, mean = 0.608 μg/L), although this difference was not statistically significant (Kruskal–Wallis, p = 0.19).

There was no observed correlation between measured DOC and 1,2,4-BPCA concentrations in the streamwater samples, which suggests that DOC is not a specific indicator of BPCAs in this watershed. This is likely because the combustion of vegetative fuels is not the sole source of DOC within forested watersheds. Rather, snowmelt, flooding, and other processes mobilize both nonpyrogenic soil organic carbon and pyrogenic compounds into stream channels. Accordingly, the DOC alone does not control BPCA concentrations since it is not solely composed of compounds of pyrogenic origin.

Tricarboxylated benzoic acids (1,2,4-BPCA and 1,2,3-BPCA) comprised the majority of the observed BPCAs

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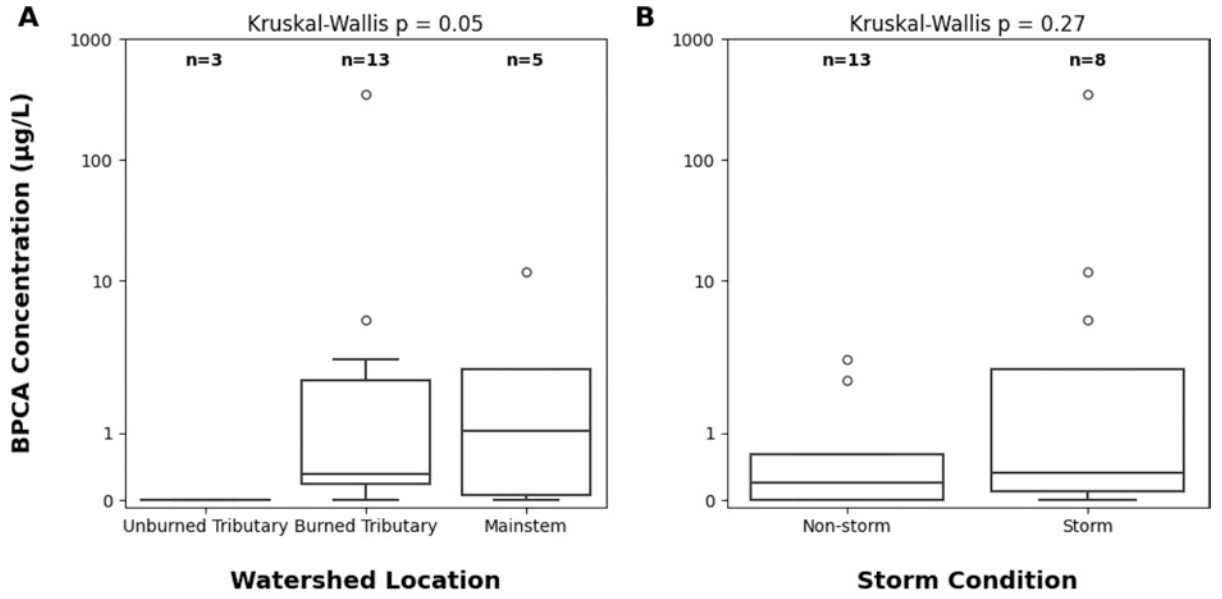

Figure 6. BPCA concentration (μg/L) in all CLP streamwater samples by watershed location (A) or storm condition (B). Boxplots display the 10th, 25th, 50th, 75th, and 90th percentiles as well as outliers (circles). Sample size is listed above each box.

regardless of sampling date, location, or flow conditions (Figure S4). Additionally, 1,2,4-BPCA exhibited higher measured concentrations than the 1,2,3-BPCA isomer across all samples. The blackwater storm sample collected from Kyle Creek following a midsummer monsoonal rain event exhibited the highest concentration of 1,2,4-BPCA measured during the study (174 μg/L). In comparison, a later storm event on July 21st, 2021, generated the second-highest concentration of 1,2,4-BPCA (7.5 μg/L) in a streamwater sample from the mainstem of the CLP. For the high-flow storm events in the burned areas of the CLP watershed, 1,2,4-BPCA represented up to 0.6% of the total measured DOC, a considerable proportion of the overall organic carbon concentration within the streamwater.

With the exception of the peak BPCA concentrations in the two aforementioned high-flow storm samples, the concentration of 1,2,4-BPCA ranged from <0.025 to 3.6 μg/L across the sample sites; median 1,2,4-BPCA concentrations during storm conditions were 0.4 vs 1.22 μg/L for burned tributary and mainstem sites, respectively. Although 1,2,4-BPCA and 1,2,3-BPCA are present under both storm and nonstorm conditions, the bulk of their export is expected to occur during high-flow rain events. For example, a hypothetical 6 h rain event with 174 μg/L of BPCAs would export a similar amount of the constituent as that transported during nearly 3 months at low baseflow and a 0.5 μg/L concentration.

The next most abundant class of BPCAs observed was the dicarboxylated benzoic acids, of which 1,2-BPCA (phthalic acid) was the most prevalent in the Kyle Creek and CLP mainstem storm samples (1.5−43 μg/L). Phthalic acid is used in the manufacture of plastics and therefore may be traced to a manmade source via potential contamination from plastic products employed during sampling.[21] However, none of the blank samples used for the analysis of either ash or water contained 1,2-BPCA, which supports the conclusion that this compound was not introduced during sampling or processing, but rather was a product of wildfire-induced combustion. The other two possible isomers of benzene dicarboxylated acid, 1,3-BPCA and 1,4-BPCA, were also present at 0.64−28 and 0.26−13 μg/L, respectively, in the Kyle Creek and CLP mainstem storm samples but below the detection limit in all nonstorm samples.

Lignin, an important structural component of conifer forests, is the most likely source for 1,2,4-BPCA, 1,2-BPCA, and the overall classes of tri- and dicarboxylated compounds produced during wildfires.[1,3,5] As highlighted in Figure S5, which depicts the stylized molecular structure of a lignin molecule, lignin has the appropriate substitution patterns to give rise to both tricarboxylic and dicarboxylic acids via condensation and oxidation reactions. However, 1,3,5-BPCA is related to a substitution pattern not commonly seen in lignin,[1] which suggests that it may be derived from an alternative material than its tricarboxylated isomers.

Two other classes of BPCAs considered in this study, naphthenic and biphenyl dicarboxylic acids, were both present in low concentrations under high-flow conditions (e.g., 0.22−0.38 μg/L in the Kyle Creek storm sample). The low solubility, potential sorption to soil, and low production of these compounds within wildfire may explain their relatively low concentrations in storm samples. They are less likely to originate from lignin but rather can form as a condensation product of benzene rings and subsequent carboxylation processes. Fused three- and four-member rings, such as anthracene and pyrene, form during combustion,[10] and naphthalene and biphenyl acids may form as condensation products of this black carbon.

CONCLUSIONS

The results from this study showcase the complex impacts that wildfires can have on water quality. The accurate mass analysis confirms the presence of 14 BPCAs that have commercial standards, along with associated isomers of these compounds. Ash and partially burned lignocellulosic materials are a major source of BPCAs in the impacted watershed; these compounds represent a significant portion of the DOC that is exported in the aftermath of a wildfire. In addition to the targeted compounds, several hundred other compounds known to be associated with combustion processes are likely to be present

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in these samples and may further affect postfire water quality. Although BPCAs may be present at high postfire concentrations in aqueous systems, there is no current evidence that they are toxic to humans. Nevertheless, additional work to better understand the potential human and environmental health effects of postfire BPCAs in surface water is warranted.

Tricarboxylated benzoic acids are the major class of compounds quantified, and 1,2,4-BPCA, specifically, predominated in burned tributaries and mainstem streamwater throughout the CLP. In general, BPCAs have been shown to comprise over 1.2% of the DOC in postfire streamwater samples, with as much as 0.6% of the DOC comprised of a single compound. Therefore, postfire event-based monitoring and analysis remain critical to identifying and confirming spatial and temporal trends associated with the production and mobilization of novel pyrogenic compounds; such studies may further enable the practical use of BPCA analysis as a quantitative tracer of postfire effects on surface water quality.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.3c00246.

Table of sample sites and DOC values, table of analytical standards, extracted chromatograms for benzene polycarboxylic acids, extracted chromatogram for naphthenic dicarboxylated acids, visualized concentrations of BPCAs, stylized molecular structure of lignin (PDF)

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Notes

The authors declare no competing financial interest.

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