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1. REPORT DATE (DD-MM-YYYY) 09-01-2023	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 1-May-2021 - 31-Oct-2022
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4. TITLE AND SUBTITLE Final Report: Chemical contamination in watersheds after wildfires	5a. CONTRACT NUMBER W911NF-21-1-0177
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102

6. AUTHORS	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES University of Colorado - Boulder 3100 Marine Street, Room 481 572 UCB Boulder, CO 80303 -1058	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 78577-BB-II.1

12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Fernando Rosario-Ortiz
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	19b. TELEPHONE NUMBER 303-492-7607

RPPR Final Report

as of 10-Jan-2023

Agency Code: 21XD

Proposal Number: 78577BBII

Agreement Number: W911NF-21-1-0177

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DUNS Number: 007431505

EIN: 846000555

Report Date: 30-Nov-2022

Date Received: 09-Jan-2023

Final Report for Period Beginning 01-May-2021 and Ending 31-Oct-2022

Title: Chemical contamination in watersheds after wildfires

Begin Performance Period: 01-May-2021

End Performance Period: 31-Oct-2022

Report Term: 0-Other

Submitted By: Ph.D. Fernando Rosario-Ortiz

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Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees:

STEM Participants:

Major Goals: The main objective of this project was to investigate potential for contamination of water supplies after wildfires, due to the formation and mobilization of organic contaminants from the combustion of biomass. Specifically, through this short-term funding request, the PI and his team conducted preliminary work on the quantification of organic contaminants from samples collected from recent wildfires near Boulder, CO. The proposed work represents an opportunity to advance the knowledge regarding impact of wildfires on water quality, specifically focusing on contamination by organic compounds.

Accomplishments: During the project, the PI and his team were able to:

1. Finalize the analytical methods for the detection and quantification of 14 organic compounds, including a series of aromatic polycarboxylic acids.
2. During the summer of 2021, we samples extensively the runoff from the Cameron Peak fire, which impacted Northern Colorado.
3. We analyzed several water quality parameters including the aforementioned 14 organic compounds. We also obtained total ion chromatograph showing numerous other yet-to-be-identified compounds.
4. We analyzed all data and are working on submitting a manuscript for EST.

Training Opportunities: The following folks participated in the project:

1. Cresten Mansfeldt, assistant professor at CU Boulder.
2. Taylor Motley, PhD student who led the sampling and water quality analysis. Unfortunately, Taylor decided to leave the PhD program to pursue a career in the medical field.
3. Mackenzie Bowden, a new PhD student who is supporting the completion of the project.
4. Mike Thurman, senior scientist at CU Boulder, who co-led the MS work.
5. Imma Ferrer, senior scientist at CU Boulder, who co-led the MS work.
6. Chuck Rhoades from the US Forest service, who supported the sampling campaign.
7. Timothy S. Fegel from the US Forest service, who supported the sampling campaign.

Results Dissemination: We are near completion for a manuscript describing the results from the project. This manuscript will be submitted to EST Letters. Part of the results from this project were also included in a recent National Academies Report.

Honors and Awards: Nothing to Report

RPPR Final Report
as of 10-Jan-2023

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)

Participant: Taylor Motley

Person Months Worked: 6.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: PD/PI

Participant: Fernando Rosario-Ortiz

Person Months Worked: 15.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Co-Investigator

Participant: Cresten Mansfeldt

Person Months Worked: 6.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Taylor Motley

Person Months Worked: 4.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Graduate Student (research assistant)

Participant: Mackenzie Bowden

Person Months Worked: 3.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Staff Scientist (doctoral level)

Participant: Mike Thurman

Person Months Worked: 12.00

Funding Support:

Project Contribution:

National Academy Member: N

Participant Type: Staff Scientist (doctoral level)

Participant: Imma Ferrer

Person Months Worked: 12.00

Funding Support:

Project Contribution:

RPPR Final Report
as of 10-Jan-2023

National Academy Member: N

Partners

Chuck Rhoades
Fort Collins, CO USA

4
Support from US Forest Service

Tim Fegel
Fort Collins, CO USA

4
Support from US Forest Service

I certify that the information in the report is complete and accurate:

Signature: Fernando Rosario-Ortiz

Signature Date: 1/9/23 11:09AM

Chemical Contamination in Watersheds After Wildfires

Final Report Submitted by:

Fernando Rosario-Ortiz (PI)

Professor, Department of Civil, Environmental, and Architectural Engineering

Director, Environmental Engineering Program

University of Colorado Boulder

Abstract and Objectives

The threat of wildfires to infrastructure continues to grow as the frequency and intensity of fires also accelerates. Higher temperatures and prolonged droughts during recent decades have extended fire season lengths worldwide and have generated larger, more intense wildfires. For example, 2020 was a significant year in terms of both number and burned area by wildfires, starting in Australia earlier and then following in the summer in the US. The US states of California and Colorado reported some of the largest fires ever recorded during the summer of 2020. Earlier work by the PI has identified the presence of benzoic acids and other organic compounds in aqueous samples after wildfires. These findings are concerning as they raise the possibility of potential exposure of communities to these compounds in water after wildfires, a situation that can also be extrapolated to Army bases which have their own drinking water facilities and are also at potential risk of wildfires. The main objective of this project was to investigate potential for contamination of water supplies after wildfires due to the formation and mobilization of organic contaminants from the combustion of biomass. Specifically, through this short-term funding request, the PI conducted work on the quantification of organic contaminants from samples collected from recent wildfires near Boulder, CO.

Specifically, 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 aromatic polycarboxylic acids (APCAs) were measured in these samples. Benzene, naphthalene, and biphenyl polycarboxylic acids were quantitatively monitored for their occurrence in the watersheds, and numerous isomers also were detected. High-flow events, containing high concentrations of charred organic matter and ash, were sampled during storm runoff (typically high intensity rainfall > 5 cm/hr). High flow events contained concentrations of APCAs ranging from 1 to greater than 100 $\mu\text{g/L}$ but were absent from unburned watersheds and occurred at much lower levels (ng/L) during non-storm conditions. The most concentrated and abundant APCA in burned samples (1,2,4-benzene tricarboxylic acid) rarely occurred in unburned samples and thus may serve as a tracer of wildfire impacts on water quality. Ash collected immediately following the fire contained the same suite of compounds ($\mu\text{g/g}$ concentration range) as water samples. These results suggest that these APCAs constitute an important proportion of the organic matter exports after wildfires.

Background

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 wildfires.¹⁻³ During the 2020 fire season, the U.S. states of California and Colorado both reported the largest within-state fires on record. Fueling these wildfires are combustion reactions that create a suite of organic compounds which are frequently detected in air^{1,3}, ash^{2,3}, soil⁴⁻⁵, and water samples.²⁻⁶ Understanding the source and fate of combustion-related compounds requires an evaluation of chemical constituents that are both dissolved and mobilized by water in storm events.⁷⁻⁸

Combustion of vegetation and surface organic soil layers by severe wildfires expose burned landscapes to soil erosion and alter how watersheds regulate water supplied to both aquatic habitats and downstream uses.⁶ In addition to short-term post-fire responses, loss of upland and riparian vegetation and rearrangement of stream and floodplain geomorphology alter biogeochemical processes that regulate nutrient (N and P), metal, 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 post-fire changes.⁹⁻¹² However, highly variable wildfire behavior, coupled with spatially complex vegetation, landscape, and hydrologic factors, complicate understanding and expectations regarding post-fire surface water and drinking water quality. Further, convergence of intense rainstorms over recently burned areas, though highly unpredictable, determines the occurrence of significant hillslope, watershed, and water quality responses.

Combustion of vegetation also impacts the concentration and reactivity of the dissolved organic matter (DOM) exports into surface waters.⁷⁻⁸ For example, the concentration of DOM in surface streams can increase after a wildfire, and that increased DOM is more aromatic and has lower molecular weight.⁴ There is significant interest in better understanding the specific composition of DOM exported after wildfires. It has also been reported that wildfires increase the export of black carbon. In previous laboratory work, Cawley et al. (2018) demonstrated that an increase in combustion temperature moved the composition of the DOM towards a higher proportion of oxygen and nitrogen containing moieties.¹³ In a more recent laboratory study, Thurman et al. (2020) reported the occurrence of aromatic polycarboxylic acids (APCAs) as a major component of the DOM in water leachate from burned soils using high resolution mass spectrometry (LC-QTOF-MS) and carbon-13 NMR.⁴ On the same set of samples, Bahureksa et al. (2022)¹⁴ used Fourier transform high resolution mass spectrometry to show a clear movement of organic compounds toward formation of polycarboxylic acids. Ferrer et al. (2021) showed clear evidence of the formation of APCAs in field samples from a wildfire in California, including ash samples collected in the field. However, the recent work by Ferrer and Thurman focused on qualitative identification of some of the major APCAs, with limited quantitative information or concentration profiles over time.

The objective of this study was to further our understanding of the concentrations and distribution of APCAs collected from surface waters after a wildfire. Specifically, baseflow and storm samples were collected approximately 5-12 months after the Cameron Peak Fire in Colorado. Sampling included high and low flow at both impacted and control sites. Samples were analyzed for dissolved organic carbon and for the concentrations of APCAs, using LC-QTOF-MS.

Materials and Methods

Site Description

The Cameron Peak Fire (August to December 2020) was the largest fire in Colorado history (844 km²). Combined with the 2012 High Park Fire, more than 60% of the forested portion of the Cache La Poudre (CLP) watershed has burned in recent years (Fig 1). The CLP is the primary drinking water source for the cities of Fort Collins, Greeley, and Thornton (approximate population of 200,000) and irrigation source for much of the agricultural land of the Northern Front Range of Colorado. The fire ignited in subalpine forests near the CLP's headwaters and was driven east and down elevation by wind events into lodgepole and ponderosa pine forest zones.

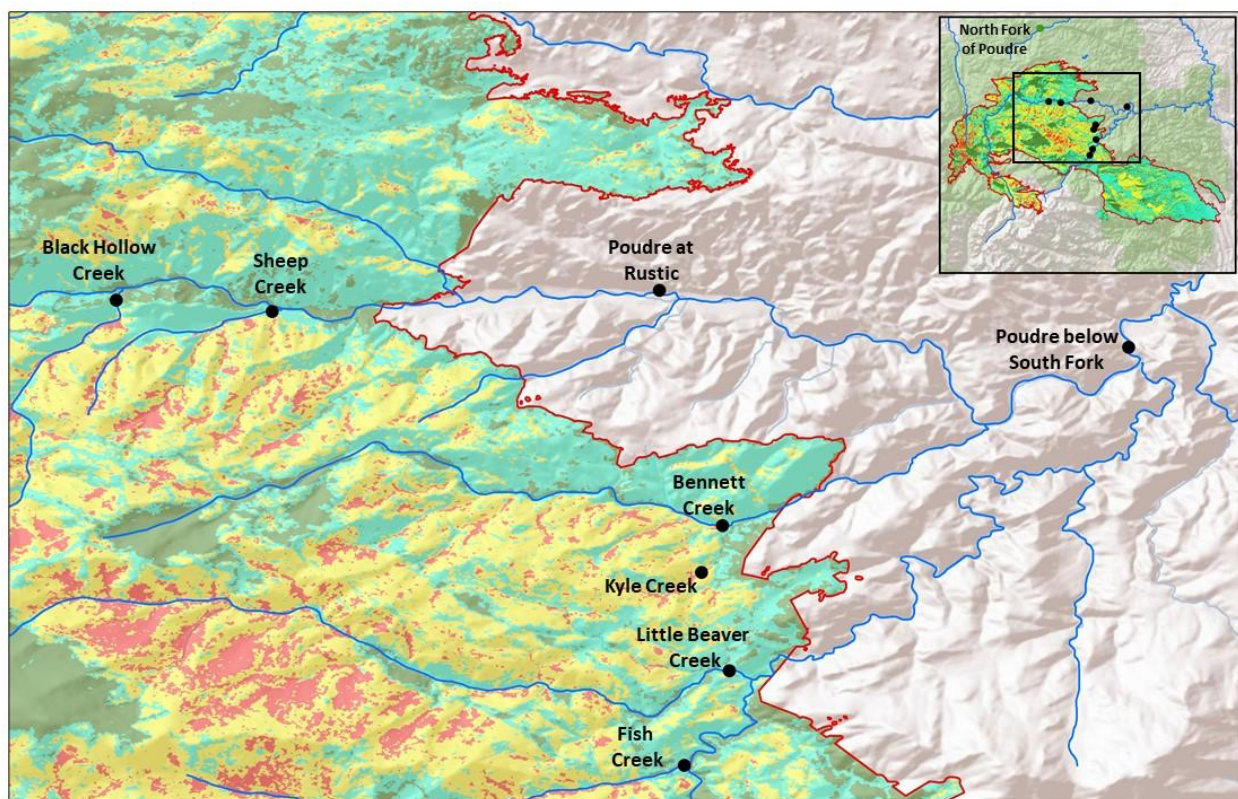


Figure 1. Map of Cameron Peak Fire and sampling sites with related to relative burn severity.

Sampling and Water Quality Analysis

To analyze the first-year effects of the fire on water quality, 27 water samples were collected from the mainstem of the CLP, along with six tributary streams (five burned, one unburned control) roughly biweekly through the summer of 2021. Two samples were also collected immediately following intense monsoonal rainstorms. Samples were analyzed for dissolved organic carbon (DOC) and specific APCAs. Samples for DOC and specific APCA analysis were collected in pre-combusted (heated for 3 hours at 500 °C) amber glass bottles and stored at 5 degrees C until analysis. DOC/TDN samples were filtered through 0.7 µm pore-size glass fiber filters (Millipore Corp, Burlington, MA) within 24 hours of collection and concentrations were determined using a Shimadzu TOC-VCPN total organic carbon analyzer, with 2 M HCl addition

before analysis to remove mineral C (Shimadzu Corporation Columbia, MD). The detection limit for DOC was 50 $\mu\text{g/L}$.

LC/QTOF-MS Analysis for APCAs

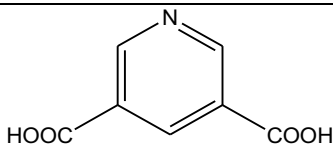
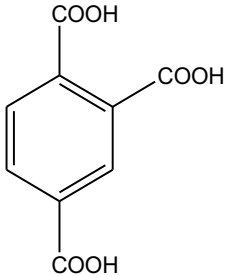
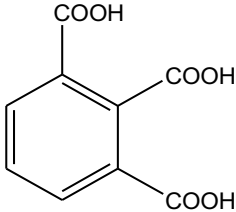
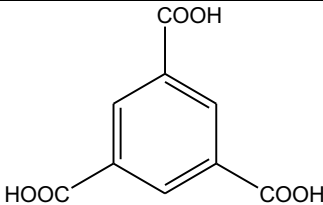
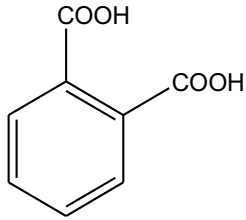
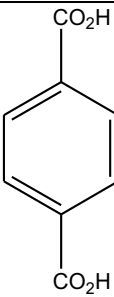
Eighteen of the samples of ash and water were processed following the methods described in previous work (Ferrer et al., 2021) and are summarized in the Supplemental Information below.

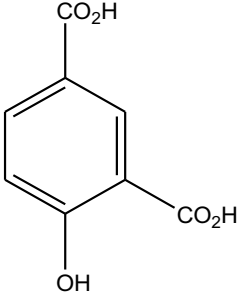
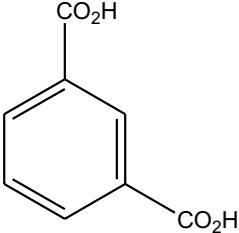
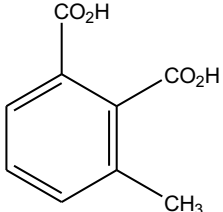
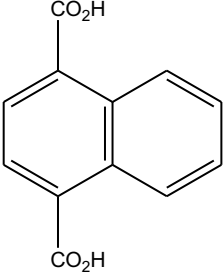
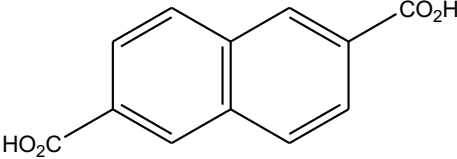
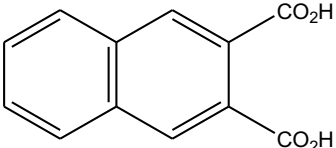
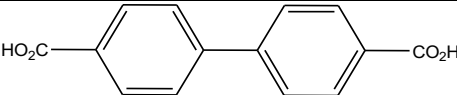
Results and Discussion

APCAs in Stream Water and Ash.

Table 1 shows the chemical structures and accurate mass ions used for the identification of APCAs in water samples collected as part of the current study. Some of these compounds were also found in runoff from burned areas following the Paradise Fire in California (Ferrer et al., 2021). The 14 compounds, for which commercial standards exist, include the following: dicarboxylated benzoic acids, tricarboxylated benzoic acids, pyridine acid, dicarboxylated naphthalene acids, and dicarboxylated biphenyl acids. These compounds have similar MS-MS fragmentation patterns, which involves the loss of 44 mass units (CO_2), as the molecule decarboxylates in the fragmentation cell of the mass spectrometer. Figure S1 shows both the mass spectrum (MS-MS of the 209.0118 m/z ion in the Black Hollow ash aqueous-leachate) and the fragmentation tree for the identification of 1,2,4-BPCA with the 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 compounds and makes identification straightforward. The final fragment ion is the core structure of the APCA; for example, for 1,2,4-BPCA, this fragment is the benzene negative ion at m/z 77.0397.

Table 1. Compounds targeted during water and ash analysis following the 2020 Cameron Peak Fire, Colorado.

Compound	Ret. time (min)	Chemical Structure	-Ion	Calculated Accurate Mass of <i>m/z</i> ion
3,5-Pyridine carboxylic acid	4.0		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	166.0146 122.0248 78.0349
1,2,4-Benzene tricarboxylic acid (1,2,4-BPCA)	6.2		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	209.0092 165.0193 121.0295
1,2,3- Benzene tricarboxylic acid (1,2,3-BPCA)	9.1		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	209.0092 165.0193 121.0295
1,3,5- Benzene tricarboxylic acid (1,2,5-BPCA)	10.0		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	209.0092 165.0193 121.0295
1,2- Benzene dicarboxylic acid	11.4		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	165.0193 121.0295 77.0397
1,4- Benzene dicarboxylic acid	11.6		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	165.0193 121.0295 77.0397

4-Hydroxy- Isophthalic Acid	12.3		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	181.0142 137.0244 93.0345
1,3- Benzene dicarboxylic acid	12.5		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	165.0193 121.0295 77.0397
3-Methylphthalic Acid	13.1		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	179.0350 135.0452 91.0553
1,4-Naphthalene Dicarboxylic Acid	14.6		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	215.0350 171.0452 127.0553
2,6-Naphthalene Dicarboxylic Acid	15.1		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	215.0350 171.0452 127.0553
2,3-Naphthalene Dicarboxylic Acid	15.8		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2CO ₂] ⁻	215.0350 171.0452 127.0553
4,4'-Biphenyl Dicarboxylic Acid	16.3		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	241.0506 197.0608 153.0709

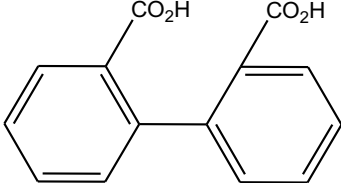
2,2'-Biphenyl Dicarboxylic Acid	16.5		[M-H] ⁻ [M-H-CO ₂] ⁻ [M-H-2 CO ₂] ⁻	241.0506 197.0608 153.0709
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Figure S2 shows an extracted ion chromatogram for Kyle Creek, a tributary to the south fork of the CLP sampled on July 1st 2021 during a black water-producing storm event (Fig. 1). The ions extracted are: 209.0092 and 165.0193 m/z , which are the deprotonated molecule and fragment ions for the benzene tricarboxylated acid. The deprotonated molecule for the benzene dicarboxylic acid is the 165.0193 m/z ion. The separation of the six APCAs follows the number of carboxyl groups present, with the tricarboxylated compounds eluting before the dicarboxylated analogues. Subtle differences in the pKa of each compound affects water solubility and retention of the compound within its class. For example, 1,2-benzene dicarboxylic acid elutes slightly ahead of its isomers of 1,4- and 1,3-benzene dicarboxylic acid isomers. The grouping of isomers is also characteristic of the naphthalene and biphenyl acids and further helps in the identification of these compounds and their isomers.

Figure 2 shows the extracted ion chromatogram for a leachate of Black Hollow ash aqueous-leachate compared with the Kyle Creek black water storm event sample. Note the extracted ion of m/z 215.0350 shows nine peaks all with the same accurate mass ($\pm 0.0005 m/z$). Standards were only available for three of the isomers, but all the compounds had a similar fragmentation that indicated they are dicarboxylated naphthalenic acids isomers. There are nine possible combinational patterns for the dicarboxylated naphthalenic acid, and all appear to be present in the ash sample. Conversely, the Kyle Creek sample has only seven isomers, two of which are confirmed by standards as the 2,6-dicarboxynaphthenic acid and the 2,3-dicarboxynaphthenic acid isomers.

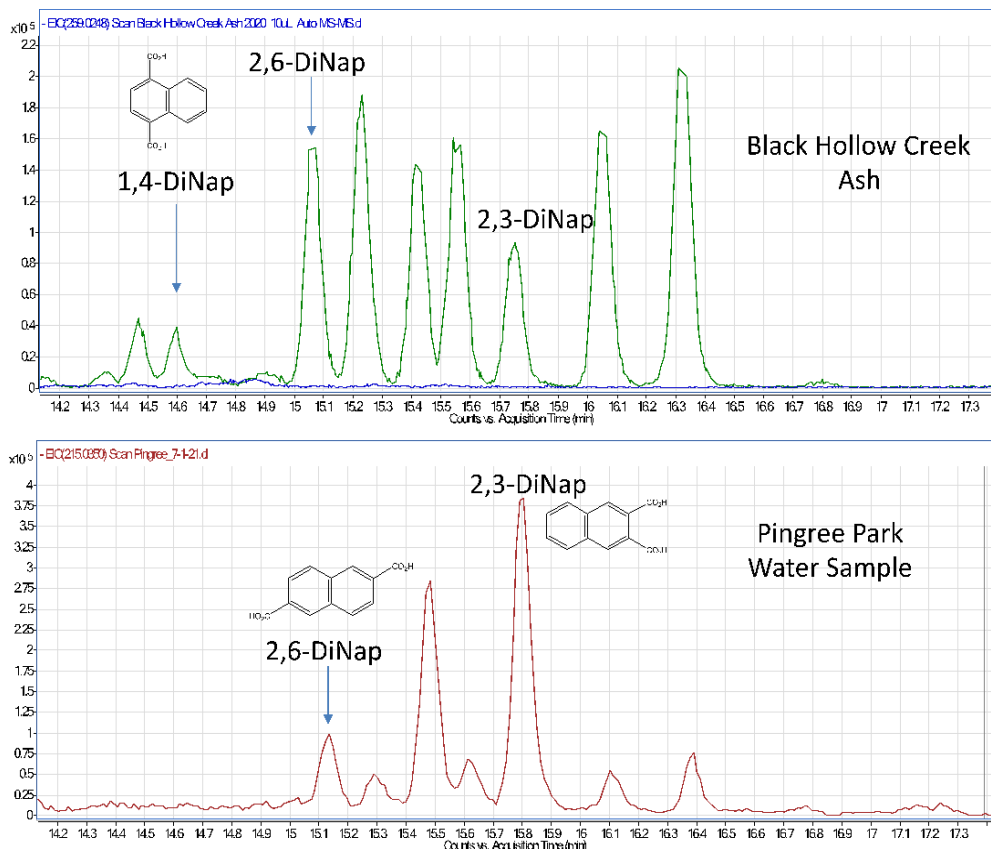


Figure 2. Extracted ion chromatogram for a leachate of the Black Hollow ash aqueous-leachate compared with the Kyle Creek blackwater storm sample

Figure 3 shows a similar pattern of isomer results for the dicarboxylic acids of biphenyl in the Black Hollow ash aqueous-leachate, for which there are two standards: 4,4'-biphenyl dicarboxylic acid and 2,2'-biphenyl dicarboxylic acid. There are eight separated isomers and an envelope of several isomers between 16.8 to 16.9 minutes in the chromatogram. There are 14 possible, different combinations of isomers with two carboxyl groups, of which we have the two standards (Figure 3). Also shown in Figure 3 is the extracted ion chromatogram at m/z 285.0405, which corresponds to the tricarboxylic acid of biphenyl. 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 time fit the more hydrophilic nature of a tricarboxylic acid since the entire family of isomers elute prior to the dicarboxylic acids of biphenyl.

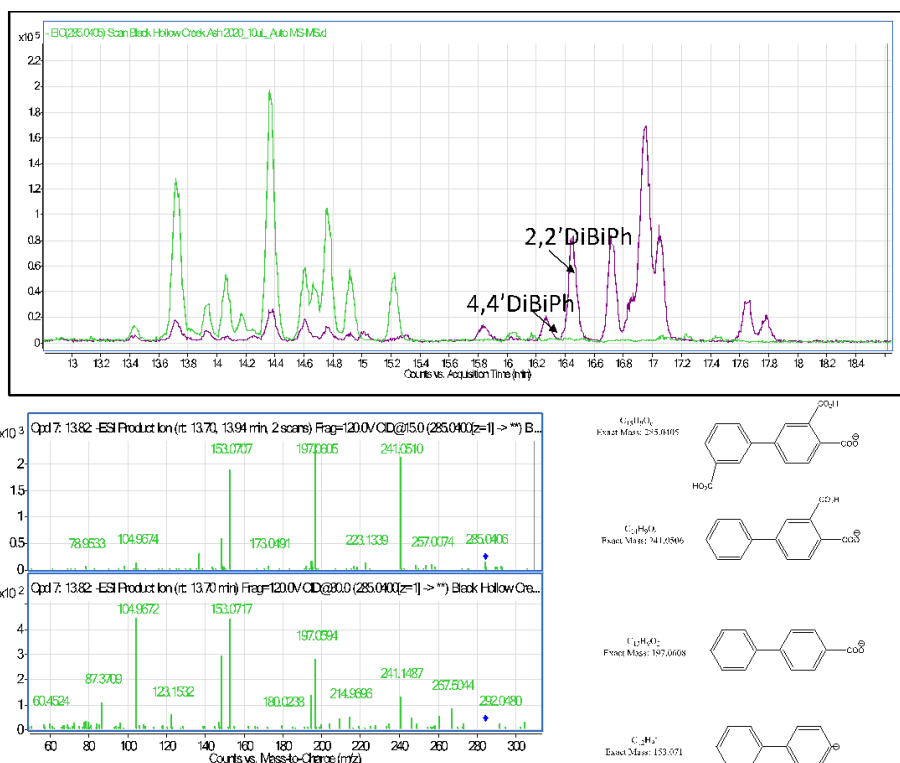


Figure 3. Black Hollow ash aqueous-leachate for which there are two standards: 4,4'-biphenyl dicarboxylic acid and 2,2'-biphenyl dicarboxylic acid

Figure S3 shows six major isomers of methylbenzene dicarboxylic acid and four isomers of hydroxybenzene dicarboxylic acid from both the Kyle Creek blackwater storm sample and Black Hollow ash aqueous-leachate samples. One standard was available for each set of isomers. MS-MS fragmentation for all isomers confirmed the identifications of both sets of compounds. Notably, the aqueous leachate of the ash gives similar compounds and distributions of the 14 compounds shown in Table 1 with one exception: 3,5-pyridine dicarboxylic acid, which was only present in trace amounts in water samples and absent in ash samples. One explanation for this absence is that this compound is being derived from nitrogen-rich organic material in the upper layer of soil and not associated with the ash from burning of relatively low-N woody materials. This pattern is consistent with our previous work which showed high levels of 3,5-pyridine dicarboxylic acid when laboratory experiments were performed with soil that was muffled at temperatures similar to wildfires.⁴

Concentration of APCAs in Storm and non-Storm Streamflow

APCAs were measured under different flow conditions in the burned watersheds that included high (intense rainstorm events, >5 cm/hr of precipitation) and low (non-storm events) stream flow. The water sample collected following an early spring rain event in Kyle Creek had the highest concentration of 1,2,4-BPCA measured during the study (174 $\mu\text{g/L}$). In comparison, a later high intensity rain event generated the second highest concentration of a 1,2,4-BPCA within the main stem of the CLP (7.5 $\mu\text{g/L}$). The remainder of the samples were collected during non-storm conditions. Table 2 also shows the total concentration of APCAs, the DOC values, and the parts per thousand of the overall DOC which was represented by the individual APCA compounds.

For the high flow events on the South Fork of the CLP mainstem, 1,2,4-BPCA represented approximately 3.1% of the overall DOC, a significant proportion of the overall organic carbon concentration. Overall, the concentration of 1,2,4-BPCA ranged from <0.025 to 1.57 µg/L. The median concentration during low-flow events was 0.32 µg/L.

Table 2. APCA concentrations in high flow events.

Compound (µg/L)	SFM Storm Event 7-21-21	% of total DOC	Kyle Creek Blackwater Event 7-1-21	% of total DOC
3,5-PCA	0.05	0.00	2	0.03
1,2,4-BPCA	7.5	0.49	174	3.09
1,2,3-BPCA	1.55	0.10	67	1.19
1,3,5-BPCA	0.39	0.03	20	0.35
1,2-BPCA	1.51	0.11	43	0.86
1,4-BPCA	0.26	0.02	13	0.26
1,3-BPCA	0.64	0.05	28	0.56
3-Methylphthalic Acid	0.06	0.00	2.32	0.05
1,4-Naphthalene Dicarboxylic Acid	<0.05	na	<0.05	na
2,6--Naphthalene Dicarboxylic Acid	<0.05	na	0.38	0.01
4,4'-Biphenyl Dicarboxylic Acid	0.05	0.00	<0.05	na
2,2'-Biphenyl Dicarboxylic Acid	<0.05	na	0.22	0.01
DOC (mg/L)	7.8	na	29	na
Total APCAs (ug/L)	12.01	na	349.9	na

The next most abundant class of APCAs we observed were dicarboxylated benzoic acids of which 1,2-BPCA (phthalic acid) was the most abundant. Phthalic acid is used in the manufacture of plastics and has a man-made source. However, based on our previous study of fireplace ash, we are confident this compound was not introduced during sampling but was a product of wildfire.⁴ Lignin is most likely source for 1,2-BPCA and this overall class of compounds.²⁻⁴ For example, the other two possible isomers, 1,3-BPCA and 1,4-BPCA, were also present at 13-28 µg/L and 0.26-0.64 µg/L in the Kyle Creek and Poudre River storm samples, respectively.

Two other classes of APCAs considered are the naphthalene and the biphenyl dicarboxylic acids which were both present in low concentrations (e.g., 0.22-0.38 µg/L in the Kyle Creek sample). The low solubility, potential sorption to soil and low production of these compounds within wildfire may explain their relatively low concentration. They are less likely to originate from lignin, but 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 combustion¹⁰, and naphthalene and biphenyl acids may form as condensation products of black carbon.

The bar chart in Figure 4 depicts the overall distribution of APCAs in select samples for both high (7-1 and 7-21) and low (all dates excluding July) flow events. The results indicate that

of the APCAs detected in each sample, 1,2,4-BPCA and 1,2,3-BPCA are the dominant components, regardless of precipitation, streamflow, or sample location.

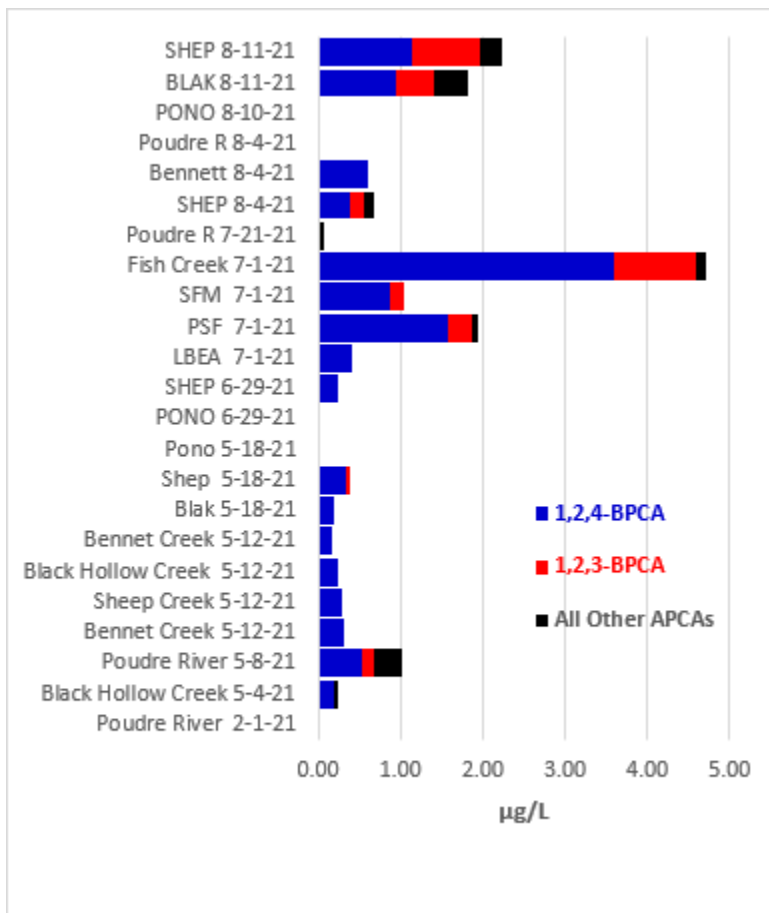


Figure 4. Concentration of APCAs for all samples and sites.

The results from this project showcase the complex impacts that wildfires can have on water quality. Ash and partially burned woody materials are a major source of APCAs in the impacted watershed, and these compounds represent a significant portion of the DOC which is exported in the aftermath of a wildfire. Our accurate mass analysis confirms the presence of 14 APCAs that have commercial standards along with isomers of all of these compounds. In addition to the target compounds, several hundred other compounds known to be associated with combustion processes are likely to be present in these samples. Lastly, although these compounds are present at high concentrations, there is no evidence that they are toxic for humans, although more work is needed to better understand potential public health effects.

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Supplemental Information

Liquid-Chromatography Quadrupole Time-of-Flight Mass Spectrometry (LC/QTOF-MS) Analysis for APCAs

The samples of ash and water were processed following the methods described in our previous study (Ferrer et al., 2021). Briefly, the method used an ultra-high pressure liquid chromatography (UHPLC) system with a thermostated autosampler, column department, and a binary pump (Agilent Series 1200, Agilent Technologies, Inc.; Santa Clara, CA) equipped with a reversed-phase C8 analytical column of 150 mm x 4.6 mm with 3.5mm particle size (Zorbax Eclipse XDB-(8). Column temperature was maintained at 25°C and injection volume was 20 mL. 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 UHPLC 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 (See Ferrer et al. 2021, for details).

Fourteen standards were obtained (Table 1) from Sigma Aldrich (PA) and used for sample recovery and analysis (Ferrer et al. 2021). Samples were filtered in the field (see above), stored in the refrigerator, and analyzed within 14 days of collection. Solid phase extraction was used with 500 mm HLB (Waters Corporation, MA) after acidification to pH 2.5 with formic acid. See Ferrer et al. (2021) for complete details.

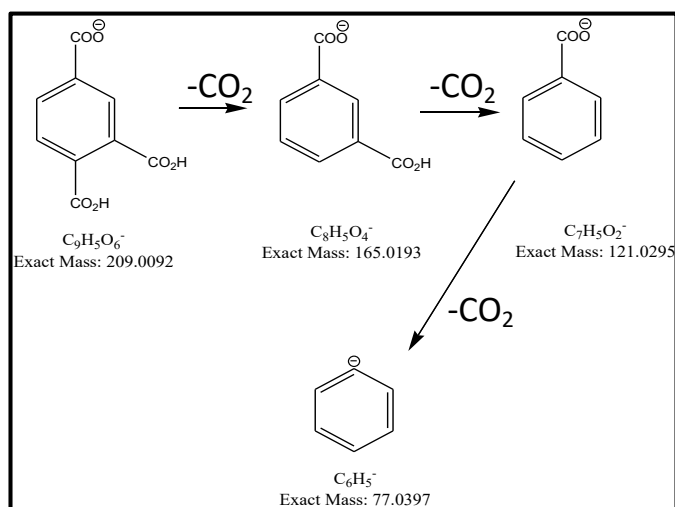
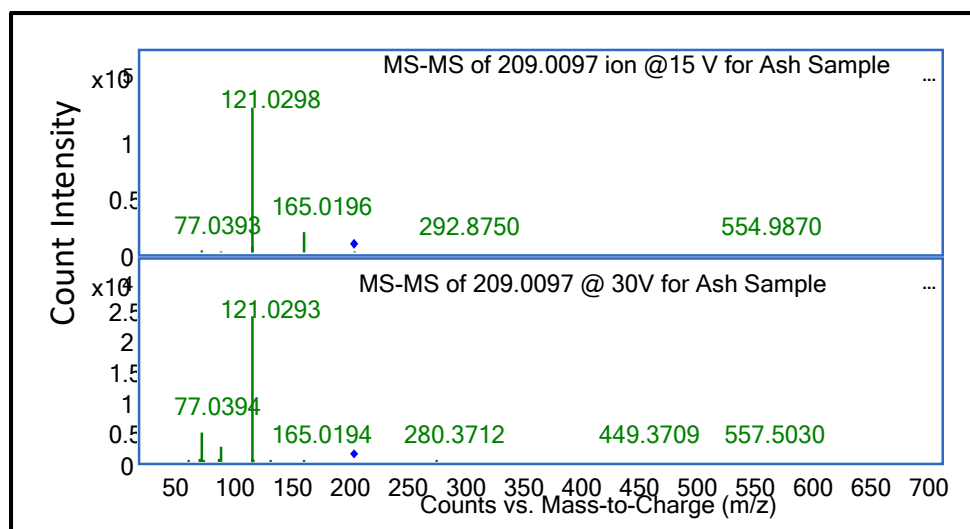


Figure S1. (Top) shows the mass spectrum and the bottom part shows the MS-MS fragmentation tree for 1,2,4-BPCA. The mass values shown are the measured values.

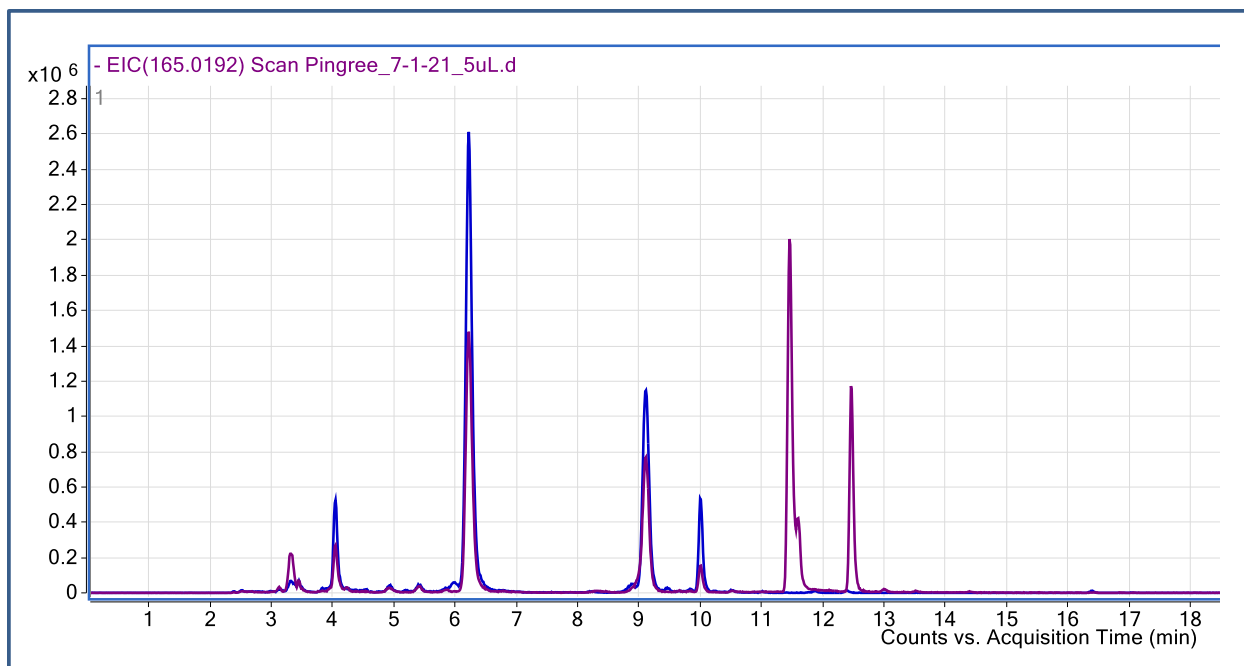


Figure S2. Extracted Ion Chromatogram of 209.0092 and 165.0193 m/z for BPCAs.

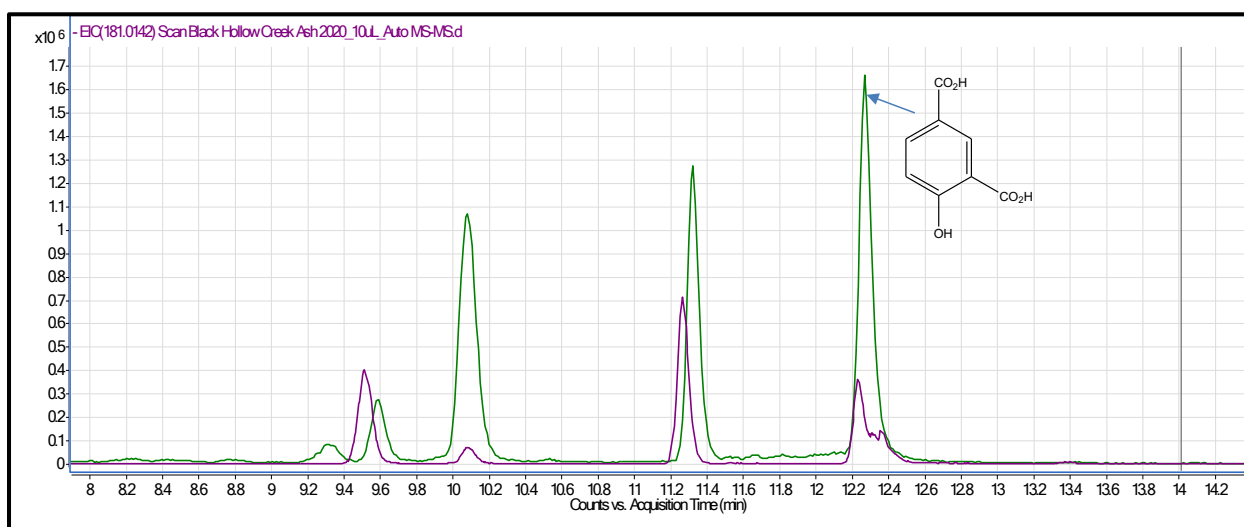
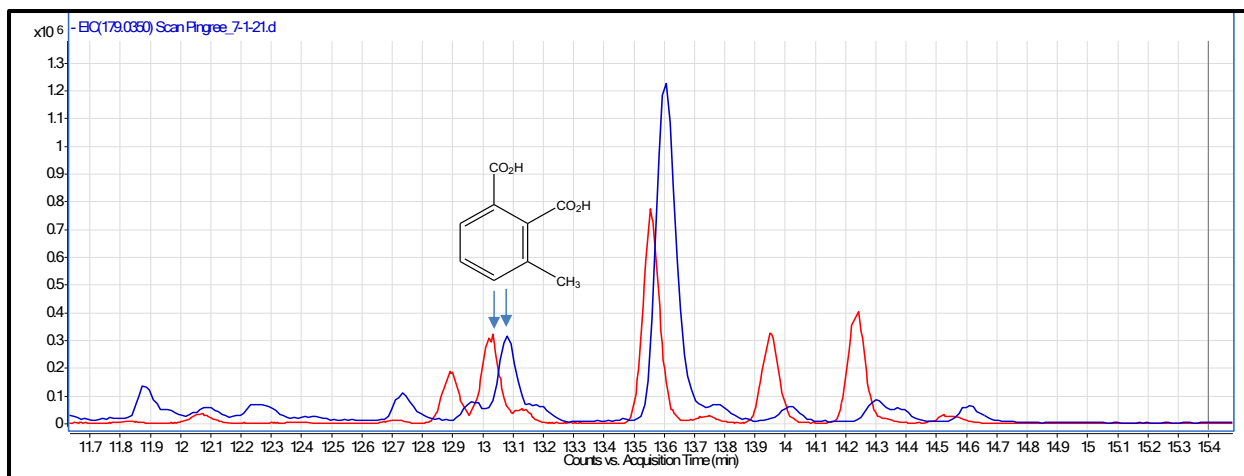


Figure S3. Isomers of Methybenzene dicarboxylic acid and Hydroxybenzene dicarboxylic acid.