Poster Reprint

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MP 102

Non-Target Analysis of Runoff Waters from Urban Fires Using LC/QTOF-MS "Finding Nylon Degradation Products in Drinking-Water Sources"

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Introduction

Novel Aspect: Non-Target analysis of runoff water from fires found nylon degradation products that are unique to urban fires.

Urban fires are more frequent now as wildfires meet urban environments. They are commonly known as wildland-urban interface (WUI). Our recent research using ESI negative LC/QTOF-MS has reported the importance of benzene polycarboxylic acids (BPCAs), including benzene sulfonic-acids (BSAs). These compounds are widespread and occur at ng/L concentrations in runoff waters. They are analyzed in negative ion ESI. But, what about ESI positive? What does non-target ESI positive analysis show for urban samples?

Two urban fires (WUI) were investigated in this study:

- The Marshall Fire (December 30-31, 2021)
- The Nederland Fire (October 19, 2025).

A total of 1064 homes burned in the Marshall Fire, near the University of Colorado in Boulder.

Marshall Fire (2021)

The Nederland Fire burned 20 businesses on a strip mall and was put out with 4-million liters of tap water. The water then ran into a stream that drained directly into a Reservoir and ultimately serves as a drinking-water source for the City of Boulder. Our laboratory is supplied with drinking water from the City of Boulder, making this a relevant home-town study.

Nederland Fire (2025)

Experimental

Sample Collection and Experimental Analysis

Samples were collected the day of the Nederland fire by the City of Boulder from the contaminated stream (location 2), a nearby drinking-water reservoir impacted by the fire (location 3, Barker reservoir), and an upstream uncontaminated site (location 1). See Figure 1 for sampling sites.
The Marshall Fire samples were collected 3 days after the fire was extinguished.

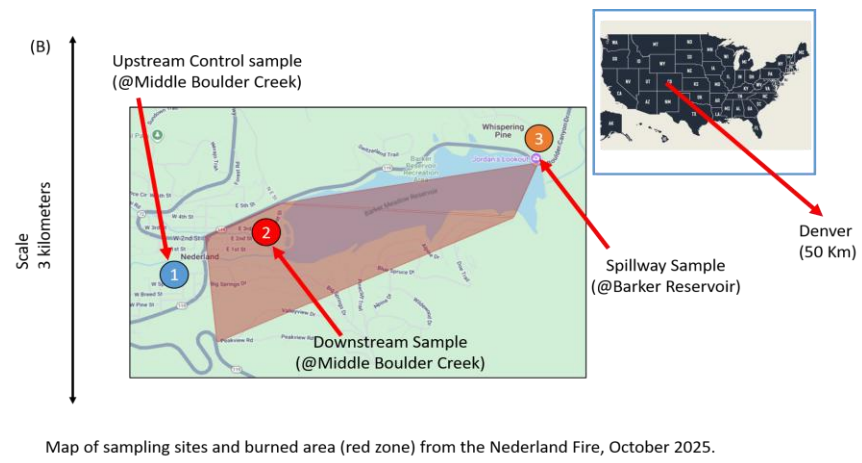


Figure 1. Map of the burned area and sampling sites for the Nederland, Colorado Fire, in October 2025. A strip mall burned and ash and debris and water ran into Middle Boulder Creek and into Barker Reservoir, a drinking-water source.

Water samples (100 mL) were concentrated by solid phase extraction) and analyzed by LC/QTOF-MS-MS (Agilent Model 6546) performing at less than 2-ppm mass accuracy and >50,000 resolving power. Mobile phases were 0.1% formic acid/water and acetonitrile using Zorbax Eclipse XDB-C8. The chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A after 30 min. Both auto MS-MS (data dependent) and data independent analysis were acquired. MassHunter (MH) Explorer 2.0 was used for data analysis.

Figure 2. LC/QTOF-MS, Agilent 6546 with 1290 Infinity UHPLC.

Results and Discussion

Separation and Identification of Target Benzene Polycarboxylic Acids (BPCAs) and Benzene Sulfonic Acids (BSAs) in Negative Ion Electrospray.

A suite of BPCAs and their chlorinated and sulfonated analogues were identified with automated NTA (Suspects) and libraries from a previous study using MassHunter and ChemVista [1-3]. In total, 30 BPCAs and several emerging contaminants (pesticides and pharmaceuticals) were identified and confirmed in the Nederland fire with these analyses.

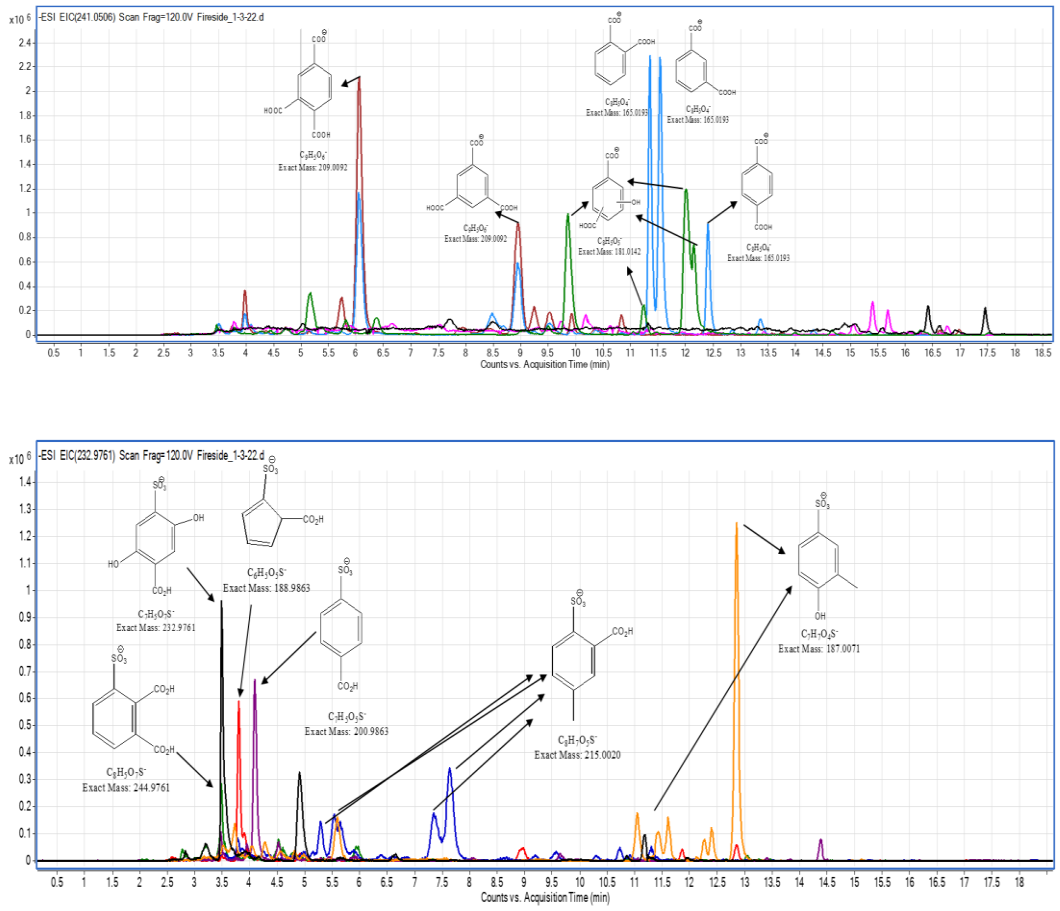


Figure 3. Targeted analysis of benzene polycarboxylic acids and benzene sulfonic acids in both the Nederland Fire and the Marshall Fire. All analyses were performed in Negative ion. MassHunter Qual was used.

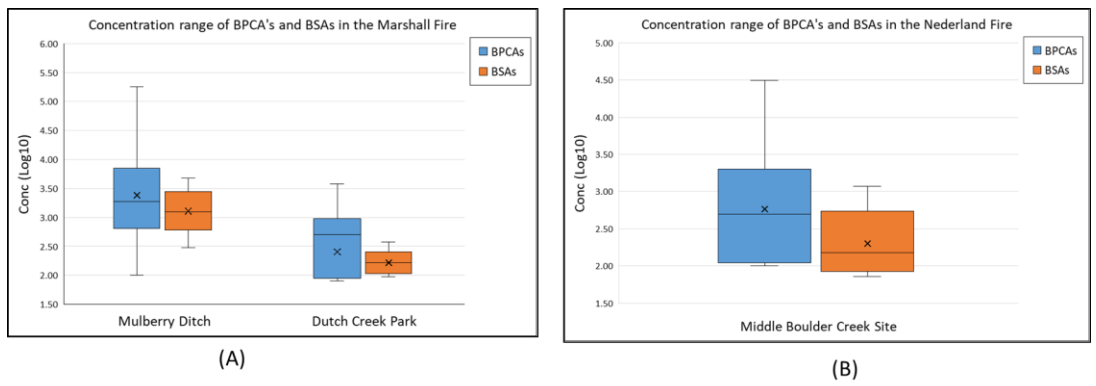


Figure 4. Range of Concentrations (ng/L) as Log 10 for BPCAs (blue) and BSAs (orange) in (A) two sites downstream of the Marshall Fire, and (B) the Nederland Fire. MassHunter Quant was used.

Separation and Identification of Nylon Degradation Products in Positive-Ion Electrospray.

A different approach was applied for complete unknown analyses for fire compounds with positive ESI rather than negative ESI, which resulted in a new suite of fire compounds, never reported before . The compounds did not match any database of known compounds, although a major ion at *m/z* 114.0913 was found that matched a caproic amide formula (Figure 5).

This ion at *m/z* 114.0913 appeared in other peaks in the ion chromatogram, suggesting a relationship. The major peaks included nominal masses at *m/z* 114, 227, 340, 453, and 566. The masses are associated by a difference of 113 mass units. This suggested a polymeric structure containing a single N atom, when the N rule is applied for even electron ions. The formulas gave rise to a caproic-amide polymeric structure ($C_6H_{11}NO$). A quick Wikipedia search shows that the caproic amide is the basic building block of Nylon 6. MS-MS analysis of one of the largest peaks (453) showed that, indeed, all the individual compounds are related to one another as fire-degradation products of Nylon 6, which is used in carpet, plastics, clothing, and many other products.

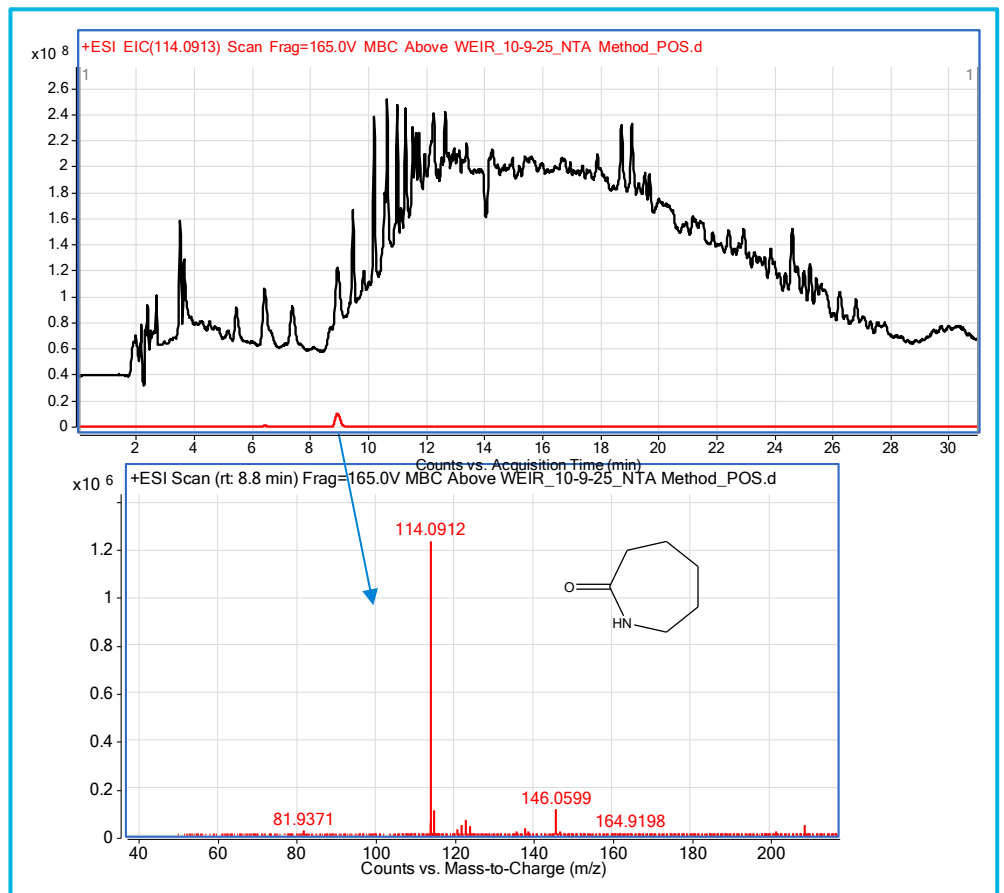


Figure 5. Full scan chromatogram of the water sample from the Nederland fire and spectrum of m/z 144 peak.

Results and Discussion

Separation of Nylon Polymers

Nylon 6 is widely used in plastics and fibers. The conversion of caprolactam into Nylon products entails a ring-opening polymerization.

The Figure below shows the chromatographic separation of polymers from 1 to 5 units long of the repeating unit, 113.084 mass units, which is the caprolactam unit minus a hydrogen atom.

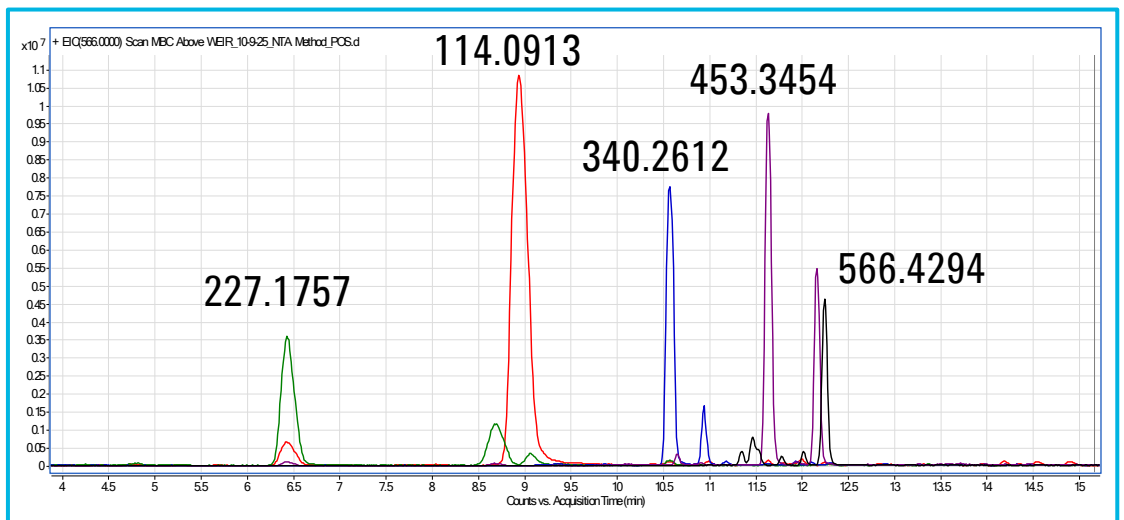


Figure 6. Chromatographic separation and accurate mass identification of polymeric fragments of Nylon 6, from 1 to 5 units long.

MassHunter Explorer 2.0 revealed unique features that are present mainly in downstream samples. Figure 7 shows the volcano plot obtained after comparison of downstream samples to upstream samples. Also shown is a Venn diagram (another way to represent the differences) comparing both set of samples and their unique compound groups.

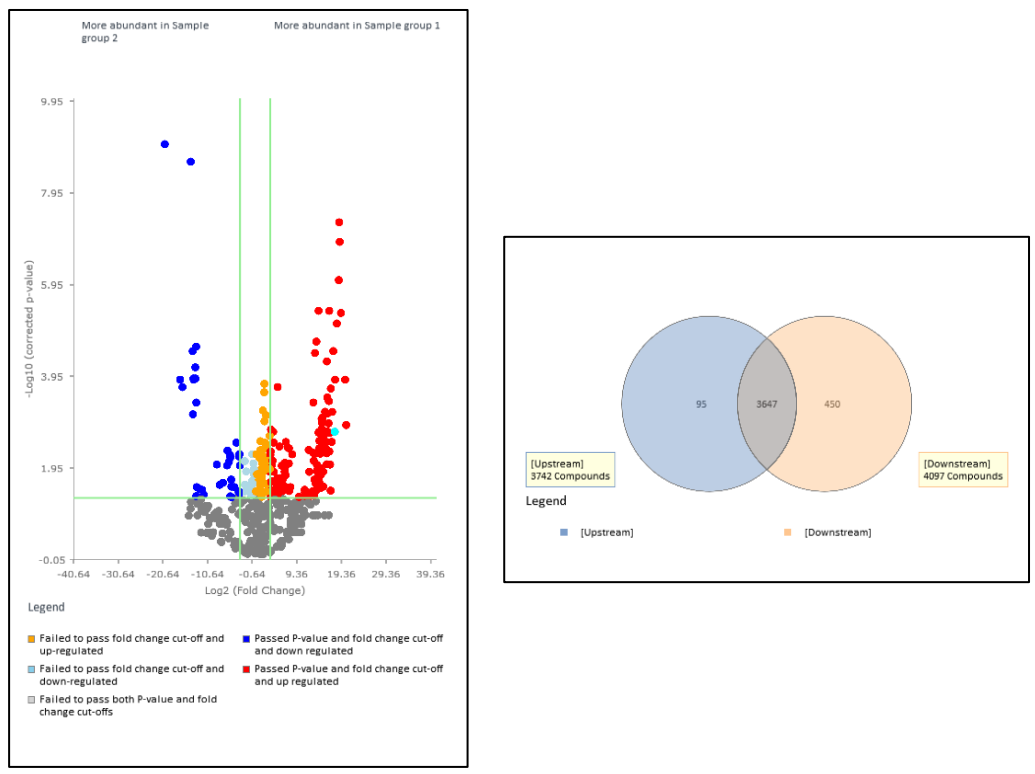


Figure 7. MassHunter Explorer results for a set of samples from the Marshall Fire.

MS-MS Analysis of m/z 453 ion

Figure 8 shows the MS-MS spectrum of the m/z 453 ion showing major fragment ions, which was hypothesized to be the Nylon 6 polymer of 4 units long. The ions at m/z 114.0916 and 227.1763 are the single and double units of the caprolactam structure, which is shown below.

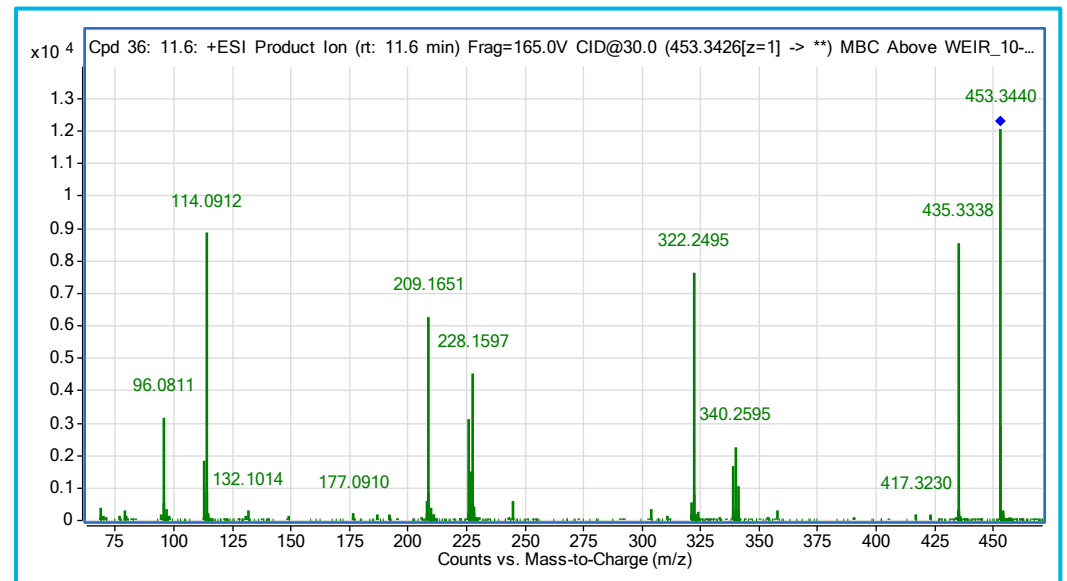
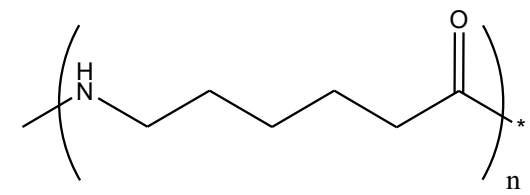


Figure 8. MS-MS spectrum of m/z 453.3454 at 30V.



Linear caprolactam repeating unit

Conclusions

1. Accurate mass is necessary at the <2 ppm error for robust unknown analysis.
2. Tools include software programs and insights gleaned from the sample and scientific intuition, including diagnostic ions, noting the odd-even relationship in this case and the large even mass defect increasing by 0.08 mass units, suggesting a linear CH2-CH2 repeating unit.
3. Future work is to dig deeper into other nylon products and prospect the samples for more related unknowns. Retrospective analysis is powerful when using accurate mass spectrometry.

References

1. Ferrer, I. et al., Wildfires: Identification of a New Suite of Aromatic Polycarboxylic Acids in Ash and Surface Water. Sci. Total Environ. 2021, 770.

2. Ferrer, I. and Thurman, E. M. Chemical Tracers for Wildfires–Analysis of Runoff Surface Water by LC/Q-TOF-MS. Chemosphere 2023, 339.

3. Thurman, E. M. et al., Occurrence of Benzene Polycarboxylic Acids in Ash and Streamwater after the Cameron Peak Fire. ACS ES T Water 2023, 3 (12).

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