

Rapid screening of volatile chemicals in surface water samples from the East Palestine, Ohio chemical disaster site with proton transfer reaction mass spectrometry

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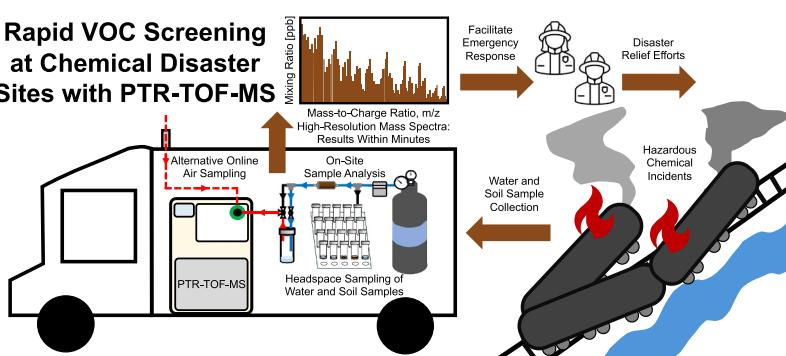
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HIGHLIGHTS

- Surface water samples collected from the East Palestine, Ohio chemical disaster site.
- Novel headspace sampling method developed to support disaster response efforts.
- PTR-TOF-MS enabled rapid screening of VOCs in surface water samples from East Palestine, Ohio.
- Hundreds of VOCs were detected in surface water samples near the chemical disaster site.
- The method can be applied to facilitate emergency response to chemical spills and burns.

GRAPHICAL ABSTRACT

Rapid VOC Screening at Chemical Disaster Sites with PTR-TOF-MS



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ABSTRACT

The increasing prevalence of hazardous chemical incidents in the United States necessitates the implementation of analytically robust, rapid, and reliable screening techniques for toxicant mixture analysis to understand short- and long-term health impacts of environmental exposures. A recent chemical disaster in East Palestine, Ohio has underscored the importance of thorough contamination assessment. On February 03, 2023, a Norfolk Southern train derailment prompted a chemical spill and fires. An open burn involving over 100,000 gal of vinyl chloride was conducted three days later. Hazardous compounds were released into air, water, and soil. To provide time-sensitive exposure data for emergency response, this study outlines a novel methodology for rapid characterization of chemical contamination of environmental media to support disaster response efforts. A controlled static headspace sampling system, in conjunction with a high-resolution proton transfer reaction time-of-flight mass spectrometer (PTR-TOF-MS), was developed to characterize volatile organic compounds (VOCs) in surface water samples collected near the East Palestine train derailment site. Spatial variations were observed in the chemical composition of surface water samples collected at different locations. Hydrocarbons were found to be the most abundant chemical group of all surface water samples, contributing 50 % to 97 % to the total headspace VOC mass. Compounds commonly detected in surface water samples, including benzene, styrene, xylene, and

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methyl *tert*-butyl ether (MTBE) were also observed in most surface water samples, with aqueous concentrations typically at ng/L levels. This study demonstrated the potential of the proposed methodology to be applied for rapid field screening of volatile chemicals in water samples in order to enable fast emergency response to chemical disasters and environmental hazards.

1. Introduction

In the United States (U.S.), hazardous chemical incidents, including fires, explosions, and chemical releases, are a common occurrence. On average, these incidents occur once every two days (Coalition to Prevent Chemical Disasters, 2023; Gillam, 2023). In the U.S., there were approximately 172,000 chemical spills that affected waterbodies between 2004 and 2014 (Weidhaas et al., 2016). Approximately 2 % to 16 % of unconventional oil and gas wells in four states of the U.S. report a spill each year, resulting in chemical release to air and water, and subsequently infiltration of emulsions into soil (Patterson et al., 2017). Over the past 20 years, hundreds of thousands of chemical incidents have impacted drinking water sources (Weidhaas et al., 2016; Whelton et al., 2017; U.S. EPA, 2021). In response to hazardous chemical incidents, the Emergency Response Guidebook (ERG) provides guidelines that can help first responders in these events, with procedures on recommended evacuation distances, personal protective equipment, first aid, and isolation practices (U.S. DOT, 2024). Depending on the complexity of an incident, experts from outside the area may be consulted, but response is always initiated by local emergency services. Should a disaster exceed local capabilities, assistance from state and federal agencies may be requested. Rapid evaluation of air, water, and soil contamination and human exposure risks is critical to decision making. This helps officials minimize population exposures and environmental harm. An effective and reliable approach to assess air, water, and soil contamination, and subsequent human exposures, is urgently needed.

Hazardous chemical incidents and spills, such as the 2023 East Palestine, Ohio train derailment, are a frequent occurrence in the U.S. that put communities at risk of exposure to complex mixtures of volatile and semi-volatile chemicals. On February 03, 2023, a Norfolk Southern train derailed in East Palestine, Ohio (40.8360°N, 80.5227°W) due to an overheated wheel bearing. Eleven derailed train cars carried hazardous chemicals, including vinyl chloride (C_2H_3Cl), isobutylene (C_4H_8), butyl acrylate ($C_7H_{12}O_2$), 2-ethylhexyl acrylate ($C_{11}H_{20}O_2$), 2-butoxyethanol ($C_6H_{14}O_2$), and benzene (C_6H_6). Notably, over 100,000 gal of vinyl chloride, a human carcinogen, were released into the environment following the train derailment (NTSB, 2023). This derailment was followed by a deliberate chemical burn, resulting in the transformation of chemical constituents due to combustion and pyrolysis (Marx and Niarchos, 2023). Residents of East Palestine reported visual and olfactory signs of exposure to contamination as well as symptoms such as headaches, anxiety, coughing, fatigue, tiredness, irritation, and pain or burning of skin (Ohio EPA, 2023a; Oladeji et al., 2023). Health concerns due to the volatile nature of spilled chemicals underscore an urgent need for enhanced contaminant detection methods to assess environmental and health hazards effectively and reliably and to ensure the well-being of affected residents.

Historically, several techniques have been used to monitor air and water composition after chemical incidents. Photoionization detectors (PIDs) are sometimes used for volatile organic compound (VOC) sampling due to their low cost, portability, and relatively expansive range. In Ohio, air sampling was conducted using PIDs by the U.S. Environmental Protection Agency (EPA) (U.S. EPA, 2023a). However, PIDs do not provide reliable data on chemical loadings in an environment as they fail to speciate chemical compounds, can underestimate volatile chemical concentrations by one to two orders of magnitude, and are prone to signal interferences due to ambient moisture (Barsky et al., 1985; Ding et al., 2023b). In addition, PIDs respond to different VOCs with different sensitivities (Barsky et al., 1985; Coy et al., 2000), and PID performance

has only been evaluated for a limited number of VOCs (Lee et al., 1987; Mergemeier et al., 1998; Noh et al., 2023; Rezende et al., 2019; Xu et al., 2021). PID readings can be challenging to interpret, especially following chemical spill events where a complex mixture of compounds can be released. A second approach to air sampling is to utilize sorbent tube and canister sampling, followed by offline analysis via thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) or GC-flame ionization detection (GC-FID). Such techniques generally offer poor time-resolution, can result in long delays in sample processing and analysis, and cannot be scaled to achieve multi-media environmental sampling in the field.

GC-MS and GC-FID are commonly used to analyze VOCs in water samples (Chary and Fernandez-Alba, 2012), including drinking water (Kavcar et al., 2006; Niri et al., 2008), wastewater (Antoniou et al., 2006; Zhang et al., 2024), groundwater (Aeppli et al., 2008; Yang et al., 2004), and surface water (Furtula et al., 2004; Huybrechts et al., 2005; Regueiro et al., 2009; Schmidt et al., 2004). Following the 2023 East Palestine, Ohio train derailment, air, water, and soil samples were collected by responding organizations and the VOC composition of the samples was analyzed by laboratories using U.S. EPA Method TO-15 for the air samples and Method 8260D for the water and soil samples (U.S. EPA, 2023b). Both methods use a GC-MS to examine the VOC loadings in the samples. Such techniques often require sample preparation and a relatively long sample analysis time ranging from 20 min to >1 h for each sample. While GC-MS and GC-FID can precisely characterize the chemical composition of water samples, such techniques, coupled with sample preparation, may slow down chemical disaster emergency response and decision making by public health officials.

To identify environmental and public health risks more rapidly at a chemical disaster site, improved sampling and analysis approaches are needed. Here, novel online mass spectrometry was applied for rapid characterization of the chemical contamination of surface water samples collected near the East Palestine train derailment site. Specifically, proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS) with hydronium (H_3O^+) as the reagent ion was used. PTR-TOF-MS is a form of chemical ionization mass spectrometry (CIMS) that has been used for online monitoring of VOC concentrations in atmospheric environments. The PTR-TOF-MS can be expanded to other forms of CIMS when configured with different reagent ions, such as NH_4^+ , O_2^+ , and NO^+ , to improve detection of different categories of VOCs (Wu et al., 2021; Guimbaud et al., 2007; Koss et al., 2016; Lee et al., 2024; Xu et al., 2022). PTR-TOF-MS enables detection of VOCs at concentrations as low as a few ppt with high sensitivity, fast response (<100 ms), and high mass resolution (>6000 m/Δm) (Coggon et al., 2021; Jiang et al., 2023, 2021b, 2021a; Jordan et al., 2009; Liu et al., 2024; Müller et al., 2014; Rosales et al., 2022; Tang et al., 2016, 2015; Wu et al., 2020; Wu et al., 2024).

To characterize the VOC composition of liquid and solid samples, PTR-TOF-MS has the advantage that sample pretreatment is not necessary compared to conventional analytical methods including GC-MS or GC-FID. VOCs that vaporize into the headspace of the sample can be directly analyzed by the PTR-TOF-MS. Real-time headspace sampling with PTR-TOF-MS has been previously applied in food and flavor analysis, including for wine, fruits, and coffee, to determine their aroma or origin (Berbegal et al., 2020; Campbell-Sills et al., 2016; Cappellin et al., 2012; Farneti et al., 2015; Gloess et al., 2014; Li et al., 2021; Liu et al., 2018; López et al., 2016; Masi et al., 2015; Romano et al., 2014; Sánchez-López et al., 2014; Yener et al., 2014; Zardin et al., 2014). PTR-TOF-MS has also been used for solid material analysis by sampling VOCs

in the headspace of soil samples (Danner et al., 2012; Mancuso et al., 2015) and polymer 3D printing materials (Wojnowski et al., 2022). Real-time headspace VOC monitoring via PTR-TOF-MS has been applied to understand the multiphase partitioning of specific compounds (Brun et al., 2024). Brodfuehrer et al. (2024) applied a PTR-TOF-MS to monitor water disinfectant degradation kinetics and demonstrated a sensitivity consistent with other analytical methods (Brodfuehrer et al., 2024).

As an online monitoring technique with high time-resolution, PTR-TOF-MS can also be implemented for mobile air or water sampling. PTR-TOF-MS can be installed on a mobile vehicle or a ship to map the spatiotemporal distribution of VOCs in the air (Oladeji et al., 2023) or in surface water (Liang et al., 2023). PTR-TOF-MS has the potential to be applied for rapid screening of volatile chemicals in surface water samples with a headspace sampling system. Such an online technique can be particularly valuable in emergency response to chemical disasters such as the East Palestine train derailment where rapid decisions are critical and can greatly enhance the capability to manage environmental and public safety more effectively.

In this study, we used a high-resolution PTR-TOF-MS to demonstrate its potential to be applied for rapid screening of contaminated surface water samples collected from chemical disaster sites. The objectives of this study are to: (1.) develop a methodology for rapid screening of VOCs in surface water samples collected from a chemical disaster site and (2.) characterize the VOC loadings in surface water samples collected from East Palestine in the weeks after the train derailment and subsequent chemical spill and burn. Surface water samples were collected from waterways near the train derailment site at East Palestine from February 27 to March 25, 2023. A static headspace sampling system was created with a PTR-TOF-MS to characterize VOCs in the surface water samples. This approach can inform future field response efforts at chemical disaster sites.

2. Materials and methods

2.1. Surface water sample collection and storage

A total of 20 surface water samples were collected from 16 sites alongside Sulphur Run, Leslie Run, Bull Creek, North Fork Little Beaver Creek, and Little Beaver Creek near and around the train derailment site at East Palestine, Ohio from February 27 to March 25, 2023, 24 to 51 days after the train derailment. The train derailment occurred approximately 30 m away from Sulphur Run (Fig. 1). Sulphur Run flows into Leslie Run, subsequently merging with Bull Creek. The flow continued into North Fork Little Beaver Creek, which feeds into Little Beaver Creek before ultimately merging into the Ohio River. All surface water samples were collected within the Upper Ohio watershed. Six samples (C1 to C4, C15, and C16) were collected from Sulphur Run inside East Palestine, Ohio, about 0.8 to 2 km downstream of the train derailment site. Five samples (C9 - Upstream, C11 - Upstream to C14 - Upstream) were collected from waterways upstream of the train derailment affected area as reference samples. Other samples were collected from waterways more downstream of the train derailment site outside East Palestine, Ohio. Information about the surface water samples analyzed in this study, including collection date and location, are summarized in Fig. 1 and Table 1. The samples were collected in headspace-free amber glass jars (Thermo Fisher Scientific Inc., Waltham, MA, U.S.) with polytetrafluoroethylene (PTFE)-lined caps precleaned with HNO_3 . After collecting the samples, they were transported back to Purdue University in a cooler and then stored at 4 °C in a climate controlled chamber until being analyzed.

2.2. Preparation of surface water samples for headspace analysis

20 mL high-performance vials and septa (SureSTART Level 3, Thermo Fisher Scientific Inc., Waltham, MA, U.S.) were used to prepare

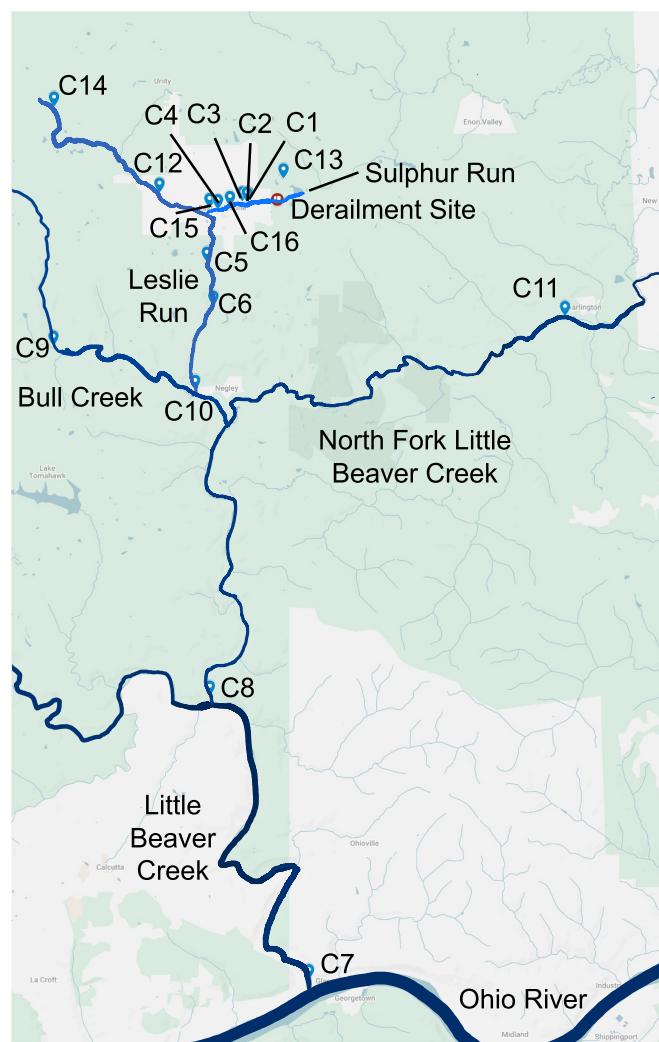


Fig. 1. Locations of the surface water samples collected around East Palestine, Ohio. 20 samples were collected from 16 locations from Sulphur Run, Leslie Run, Bull Creek, North Fork Little Beaver Creek, and Little Beaver Creek. The base map was obtained from Google Maps.

the surface water samples for the headspace analysis. Level 3 vials and septa contain the lowest levels of extractable compounds to ensure consistent and reproducible sensitivity and selectivity. 1 mL of surface water was transferred from the amber jar to the headspace sampling vial using a glass pipette. Details of the quality assurance/quality control are provided in Section 2.6. The jar was shaken well before transferring the water. The headspace sample was then placed in the laboratory for at least 1 h to reach ambient temperature before analysis. The ambient temperature in the laboratory was logged via a handheld humidity and temperature meter (HM70, Vaisala Oyj, Helsinki, Finland), and was kept at $21^\circ\text{C} \pm 1^\circ\text{C}$ during all headspace analysis. Triplicate samples of each surface water sample were prepared and analyzed.

2.3. Real-time headspace sampling of surface water samples with PTR-TOF-MS

Mixing ratios of VOCs in the headspace were measured with a PTR-TOF-MS (PTR-TOF 6000 X2, Ionicon Analytik Ges.m.b.H., Innsbruck, Austria) (Ding et al., 2023b, 2023a; Jiang et al., 2023, 2021b, 2021a; Liu et al., 2024; Rosales et al., 2022). Hydronium (H_3O^+) was used as the reagent ion. In the drift tube, compounds with proton affinities (PA) greater than the PA of water will collide with H_3O^+ and be ionized through a proton transfer reaction (Blake et al., 2009; Lindinger et al.,

Table 1

Locations and dates of surface water sample collection in East Palestine, Ohio.

Sample ID	Location in East Palestine, Ohio	Coordinates	Sample Collection Date
C1-1	Sulphur Run	40.835251°, -80.532075°	02/27/2023
C1-2	Sulphur Run	40.835245°, -80.532074°	03/25/2023
C2-1	Sulphur Run	40.835219°, -80.532463°	02/27/2023
C2-2	Sulphur Run	40.835215°, -80.532457°	03/25/2023
C3	Sulphur Run	40.835294°, -80.533963°	02/27/2023
C4	Sulphur Run	40.833391°, -80.541770°	02/27/2023
C5	Leslie Run	40.820607°, -80.545319°	02/27/2023
C6-1	Leslie Run	40.809916°, -80.543209°	02/27/2023
C6-2	Leslie Run	40.809916°, -80.543209°	03/18/2023
C6-3	Leslie Run	40.809916°, -80.543209°	03/25/2023
C7	Little Beaver Creek	40.6458284°, -80.5126049°	03/03/2023
C8	North Fork Little Beaver Creek	40.71506°, -80.544442°	03/03/2023
C9 - Upstream	Bull Creek	40.8001787°, -80.5944924°	03/03/2023
C10	Leslie Run	40.7894052°, -80.5490397°	03/03/2023
C11 - Upstream	North Fork Little Beaver Creek	40.8073921°, -80.4306232°	03/03/2023
C12 - Upstream	Leslie Run (East Palestine City Lake)	40.8374055°, -80.56051°	03/03/2023
C13 - Upstream	Lake Upstream of Sulphur Run	40.8408854°, -80.5207431°	03/03/2023
C14 - Upstream	Leslie Run	40.856436°, -80.593724°	03/17/2023
C15	Sulphur Run	40.833679°, -80.544470°	03/25/2023
C16	Sulphur Run	40.834160°, -80.537913°	03/25/2023

1998). Then, the ionized molecules are separated and detected by a TOF-MS. During the experiments, mass spectra for mass-to-charge ratios (m/z) from 20 to 450 were recorded at a sampling rate of 1 Hz. Pressure, voltage, and temperature for the drift tube were set at 2.8 mbar, 500 V, and 120 °C respectively, and the ionization field energy (E/N) was kept at 104 Td.

A schematic of the headspace sampling system setup is depicted in Fig. 2. A miniature PTFE solenoid valve (Parker Hannifin Corp., Mayfield Heights, Ohio, U.S.) was installed on the polyether ether ketone (PEEK) purge tubing connected to the vial, and a stainless steel three-way sample valve (McMaster-Carr, Elmhurst, IL, U.S.) was installed on the PEEK sample tubing inserted into the vial (Fig. 2). The inlet line connected to the PTR-TOF-MS was heated to 80 °C to minimize condensation of VOCs on the sample line. The headspace analysis of a water sample consisted of three steps: (1.) purge for 1 min, (2.) equilibrium for 60 min, and (3.) static headspace sampling for 15 s. Based on the equilibrium established in step (2.), the measurement of the static headspace concentration allows for the estimation of the aqueous VOC concentration based on Henry's Law.

To minimize the interference of laboratory air present before sealing the vial on the headspace air composition during sample preparation, ultra-zero air (Indiana Oxygen Company, Indianapolis, IN, U.S.) was used to purge the headspace volume of the vial. After purging the headspace volume for 1 min, the purge valve was shut down, and simultaneously the sample valve was switched to ultra-zero air. In this way, the vial was isolated from the ambient air and was kept in such

status for 60 min to ensure adequate time for the aqueous volatile species to vaporize and re-reach a gas-liquid equilibrium after the headspace air was purged. After the 60 min equilibrium period, the sample valve was switched to the headspace air in the vial for 15 s with the inlet flow rate of the PTR-TOF-MS set to 20 sccm for the static sampling of the headspace air.

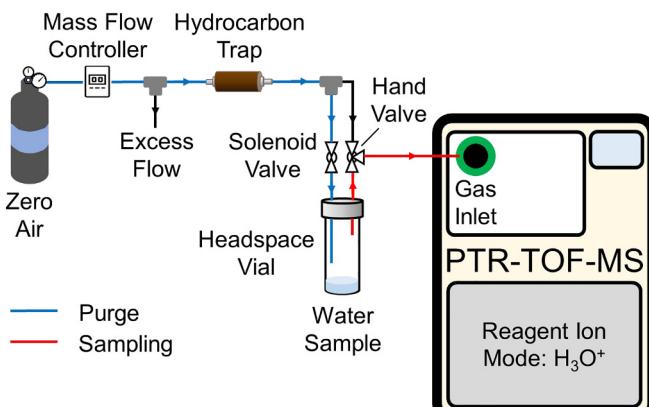
2.4. PTR-TOF-MS data processing

Chemical formulas were identified using Ionicon Data Analyzer (IDA, Ionicon Analytik Ges.m.b.H., Innsbruck, Austria). The mass accuracy limit was set to 30 ppm to determine the chemical formulas based on their m/z values. Details on the calculation of the transmission efficiency of the PTR-TOF-MS (Fig. S1) are provided in the Supporting Information (SI).

The PTR-TOF-MS was calibrated using two VOC gas standard mixtures containing a total of 17 compounds, including vinyl chloride (C_2H_3Cl) and benzene (C_6H_6), which are among the list of chemicals released during the East Palestine train derailment. A full list of compounds and their concentrations in the gas standard mixtures can be found in Table S1. The gas standards were diluted by ultra-zero air to 2 to 40 ppb using a liquid calibration unit (LCU-a, Ionicon Analytik Ges.m.b.H., Innsbruck, Austria) to perform the calibration. Concentrations of VOCs not included in the gas standard mixtures were estimated based on the theory of proton transfer reaction (Ellis and Mayhew, 2013) and analyzed in IDA. Details on the estimation of headspace concentrations based on proton transfer reaction kinetics are provided in the SI.

2.5. Validation of the headspace sampling method with PTR-TOF-MS

Among the VOCs in the gas standard mixtures, acetone (C_3H_6O) was selected to validate the static headspace sampling method with PTR-TOF-MS due to its high volatility and relatively low variations in its Henry's Law solubility constants as reported in the literature (Benkelberg et al., 1995; Sander, 2023; Wang et al., 2017); this reduces uncertainties in estimating its aqueous VOC concentration. An acetone standard (HPLC-grade, Fisher Scientific, Hampton, NH, U.S.) was diluted with HPLC-grade water (Fisher Scientific, Hampton, NH, U.S.) to prepare liquid solutions with different known concentrations to validate that the headspace sampling protocol can successfully detect the aqueous composition of liquid samples. Triplicate acetone solution samples with acetone:water dilution ratios of $1:5 \times 10^6$, $1:10^7$, and $1:2 \times 10^7$ were prepared following the headspace sampling protocol mentioned above.

Fig. 2. Schematic of the headspace sampling setup with the PTR-TOF-MS.

The anticipated headspace acetone concentrations were calculated from the aqueous acetone concentrations based on Henry's Law (Sander, 2023):

$$p = \frac{c_a}{H_s^{\text{cp}}} \quad (1)$$

where c_a is the aqueous acetone molar concentration (mol m^{-3}), H_s^{cp} is the Henry's Law solubility constant ($\text{mol m}^{-3} \text{ Pa}^{-1}$), and p is the partial pressure of acetone in the headspace (Pa). The measured headspace acetone concentrations were then compared with the estimated concentrations based on Eq. (1) to verify the headspace analysis with the PTR-TOF-MS. This experimental validation is for VOCs similar in volatility to acetone and may not be effective for compounds with lower volatility that may be present in the surface water samples.

2.6. Quality assurance and quality control

To minimize background contamination interferences originating from the vials and septa during the headspace sampling, the vials and septa were baked in an oven for 20 min at 80 °C before the water sample preparation to ensure removal of any surface manufacturing residue or surface films. New vials and septa were used for all samples. A new glass pipette was used for each sample preparation. To minimize the interference of any potential emissions from the vials and septa, ten empty vials were analyzed following the protocol described above to determine the background VOC levels. $\mu + 2\sigma$ of the ten empty samples was taken as the background VOC concentration. All the VOC concentrations reported in the following sections were corrected with the background VOC concentrations.

3. Results and discussion

3.1. Calibration and validation of the headspace sampling method with PTR-TOF-MS

The calibration curves of acrolein ($\text{C}_3\text{H}_4\text{O}$, m/z 57.03), vinyl chloride

($\text{C}_2\text{H}_3\text{Cl}$, m/z 62.99), benzene (C_6H_6 , m/z 79.05), p-xylene (C_8H_{10} , m/z 105.07), and trichloroethylene (C_2HCl_3 , m/z 130.92) are shown in Fig. 3. The sensitivities are reported as ncps/ppb, which is the ratio of the normalized counts per second detected by the PTR-TOF-MS to the concentration of the gas standard in ppb. To derive the normalized counts per second, the raw counts were first corrected by the background levels while sampling ultra-zero air, and then normalized by the counts of the hydronium ion and multiplied by 10^6 . The sensitivities of these five compounds are 1447 ncps/ppb, 4.230 ncps/ppb, 2047 ncps/ppb, 1641 ncps/ppb, and 40.21 ncps/ppb, respectively. The R^2 values for all of the calibration curves are >0.9683 (Table S2), indicating good linearity between the measured signals and actual concentrations. The sensitivities for the detection of Cl-containing compounds when using H_3O^+ as the reagent ion are 2–3 orders of magnitude lower than that of hydrocarbons or oxygenated compounds. The PTR-TOF-MS may not be effective in detecting Cl-containing compounds at ultra-low levels with the current configuration. The PTR-TOF-MS can be configured as a CIMS using NH_4^+ , O_2^+ , or NO^+ as the reagent ion, which may enhance its ability in detecting Cl-containing compounds.

The results of the method validation with the acetone solutions are summarized in Table 2. The headspace acetone concentrations of the three acetone solutions measured by PTR-TOF-MS all fall within the ranges derived from gas-liquid partitioning based on the known aqueous concentration of acetone and the range of Henry's Law solubility constants of acetone reported in previous studies. This suggests that the

Table 2
Measured and calculated headspace concentrations of acetone solutions.

Acetone:Water Ratio	Measured Headspace Concentration (ppb)	Calculated Headspace Concentration (ppb)	
		Lower-Bound	Upper-Bound
$1:5 \times 10^6$	68.38	68.97	92.84
$1:10^7$	38.51	34.48	46.42
$1:2 \times 10^7$	23.55	17.24	23.21

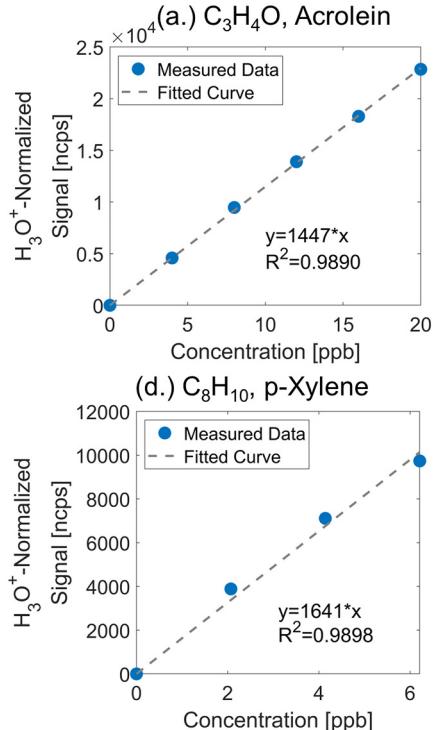


Fig. 3. PTR-TOF-MS calibration curves for: (a.) acrolein, (b.) vinyl chloride, (c.) benzene, (d.) p-xylene, and (e.) trichloroethylene.

static headspace sampling setup with PTR-TOF-MS proposed in this study can effectively detect VOCs released to headspace air due to the gas-liquid partitioning of volatile chemicals in the aqueous solutions. The headspace concentration detected via such an approach can be further applied to back-calculate the aqueous-phase concentrations using Henry's Law for rapid screening of aqueous VOCs at chemical disaster sites. However, this validation may only be limited to volatile compounds.

3.2. Real-time static headspace sampling of surface water samples with PTR-TOF-MS

Fig. S2 demonstrates the high mass resolution of PTR-TOF-MS using m/z 57, m/z 79, and m/z 107 as examples. The high mass resolution of PTR-TOF-MS enables detection and separation of two peaks within m/z 57: $C_3H_4OH^+$ (possibly acrolein) detected at m/z 57.033, and $C_4H_9^+$ (possibly butene) detected at m/z 57.070. Similar separation is achieved for m/z 79 and m/z 107. Fig. 4(a.) presents the time series of the two m/z 57 peaks during the static headspace sampling. The headspace sampling system (Fig. 2) allows detection of stable and constant signals. A plateau of >5 s was reached during the 15 s static headspace sampling period (Fig. 4(a.)). The average of the VOC signals detected during the 5 s plateau was taken for further analysis. Similarly, the PTR-TOF-MS also successfully separated multiple peaks at m/z 79 where benzene ($C_6H_6^+$) was detected (Fig. 4 (b.)) and m/z 107 where xylene ($C_8H_11^+$) was detected (Fig. 4(c.)). This demonstrates that the PTR-TOF-MS is suitable for rapid screening of volatile chemicals in surface water samples, with the capability to characterize the chemical composition of a sample within 15 s. Such a methodology can be utilized to aid emergency response to chemical disasters.

3.3. Mass spectra of selected surface water samples from East Palestine, Ohio

Fig. 5(a.) shows the average mass spectrum of the surface water sample C4 during a 15 s static headspace sampling period as an example. The water sample was collected from Sulphur Run, approximately 1.9 km downstream of the train derailment site. PTR-TOF-MS enables the detection of trace-level VOCs in headspace vapors of water samples. Over 200 ions from m/z 30 to 450 were detected during the static headspace sampling. Among all the detected signals, m/z 115.11 ($C_7H_{15}O^+$), m/z 105.07 ($C_8H_9^+$), m/z 71.08 ($C_5H_{11}^+$), m/z 63.02 ($C_2H_5O_2^+$), m/z 106.08 (isotope of $C_8H_9^+$), and m/z 107.08 ($C_8H_{11}^+$) account for >80 % of the total VOC concentration, with average estimated concentrations at 20.5 ppb, 11.3 ppb, 7.2 ppb, 5.6 ppb, 1.8 ppb, and 1.4 ppb respectively. In the surface water sample C7 collected from Little Beaver Creek right before merging into the Ohio River, the most downstream site among all water samples (Fig. 5(b.)), over 140 ions were detected, with m/z 105.07 ($C_8H_9^+$), m/z 107.08 ($C_8H_{11}^+$), m/z 106.08 (isotope of $C_8H_9^+$), m/z 71.08 ($C_5H_{11}^+$), and m/z 43.01 contributing to 68 % of the total VOC concentration. Surface water sample C15 also presents a complex mixture of VOCs (Fig. 5(d.)), with >190 ions detected, among which m/z 167.06, m/z 225.05, m/z 105.07 ($C_8H_9^+$), m/z 223.06, and m/z 169.04 account for 70 % of the total VOC concentration.

As a contrast with the previous three sampling sites, fewer VOC peaks were detected in the background surface water sample C14 - Upstream (Fig. 5(c.)), which was collected from Leslie Run, approximately 5 km upstream of East Palestine, and thus less likely to be affected by the chemical spill due to the train derailment. Excluding the water cluster ions detected at m/z 37 ($H_2O \bullet H_3O^+$) and m/z 55 ($(H_2O)_2 \bullet H_3O^+$), only 79 ions were detected, and the estimated concentrations of 95 % of the compounds were lower than 1 ppb. m/z 105.07 ($C_8H_9^+$),

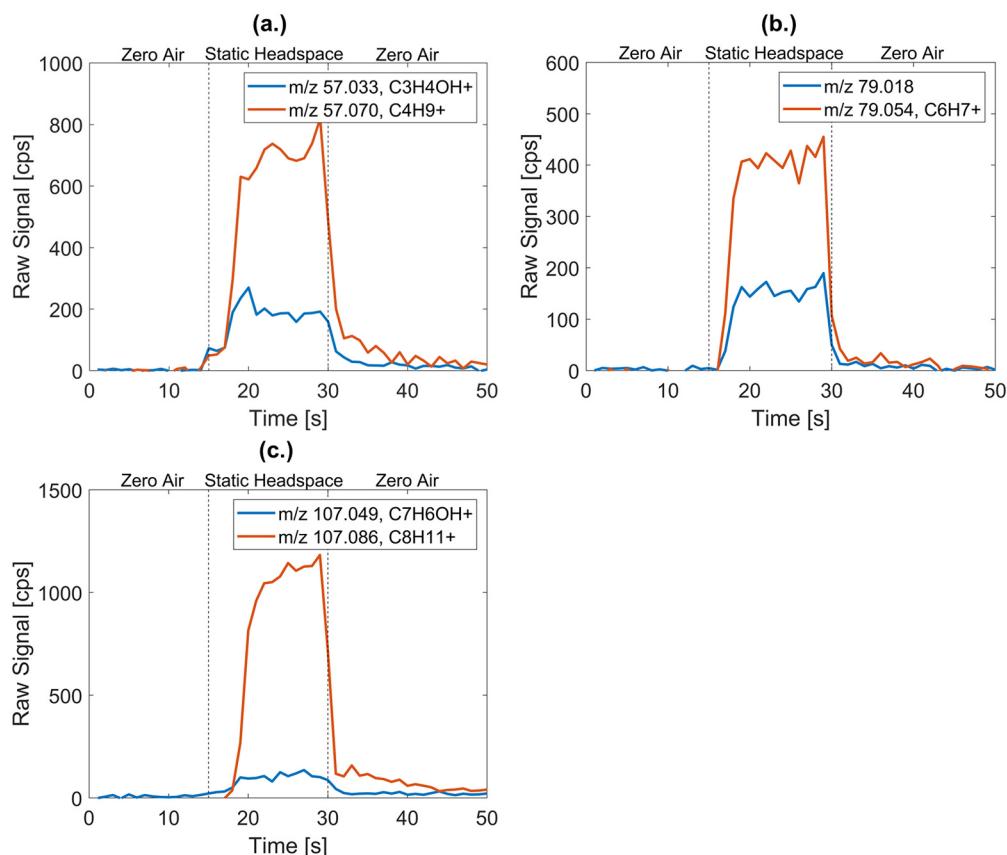


Fig. 4. Time-series analysis during static headspace sampling with the PTR-TOF-MS at: (a.) m/z 57, (b.) m/z 79, and (c.) m/z 107.

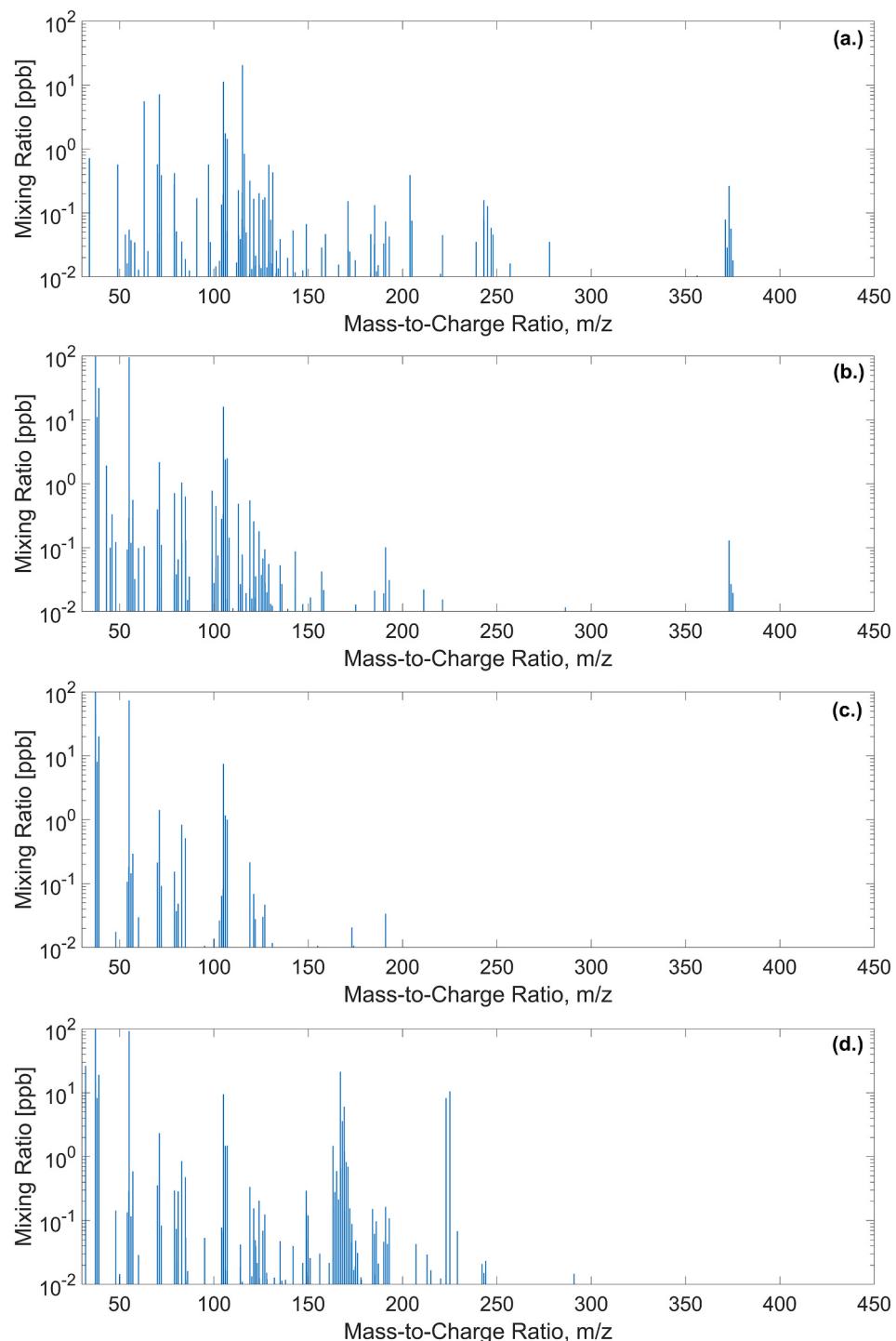


Fig. 5. Background-corrected average mass spectrum of surface water samples as measured with the PTR-TOF-MS: (a.) C4 from Sulphur Run downstream of the train derailment site, (b.) C7 from Little Beaver Creek, (c.) C14 from Leslie Run upstream of the train derailment site, and (d.) C15 from Sulphur Run downstream of the train derailment site.

m/z 71.08 ($C_5H_{11}^+$), m/z 106.08 (isotope of $C_8H_9^+$), and m/z 107.08 ($C_8H_{11}^+$) account for 76 % of the total VOC concentration, with average estimated concentrations at 7.5 ppb, 1.4 ppb, 1.1 ppb, and 1 ppb, respectively. Due to the complexity of the VOCs detected in the surface water samples, the VOCs were categorized into seven categories based on their chemical composition derived from IDA: (1.) hydrocarbons, C_xH_y , (2.) oxygenated compounds, $C_xH_yO_z$, (3.) N-containing, (4.) Cl-containing, (5.) F-containing, (6.) Si-containing, and (7.) unidentified.

3.4. Chemical composition of surface water samples at different locations in East Palestine, Ohio

Spatial variations in the chemical composition of the surface water samples is mapped in Fig. 6. Fig. 6(a.) presents the composition of samples taken within a 3.2-km radius of the train derailment site, and Fig. 6(b.) shows the samples collected outside the 3.2-km radius of the train derailment site. Hydrocarbons dominated the chemical composition of all surface water samples, contributing 50 % to 97 % of the total

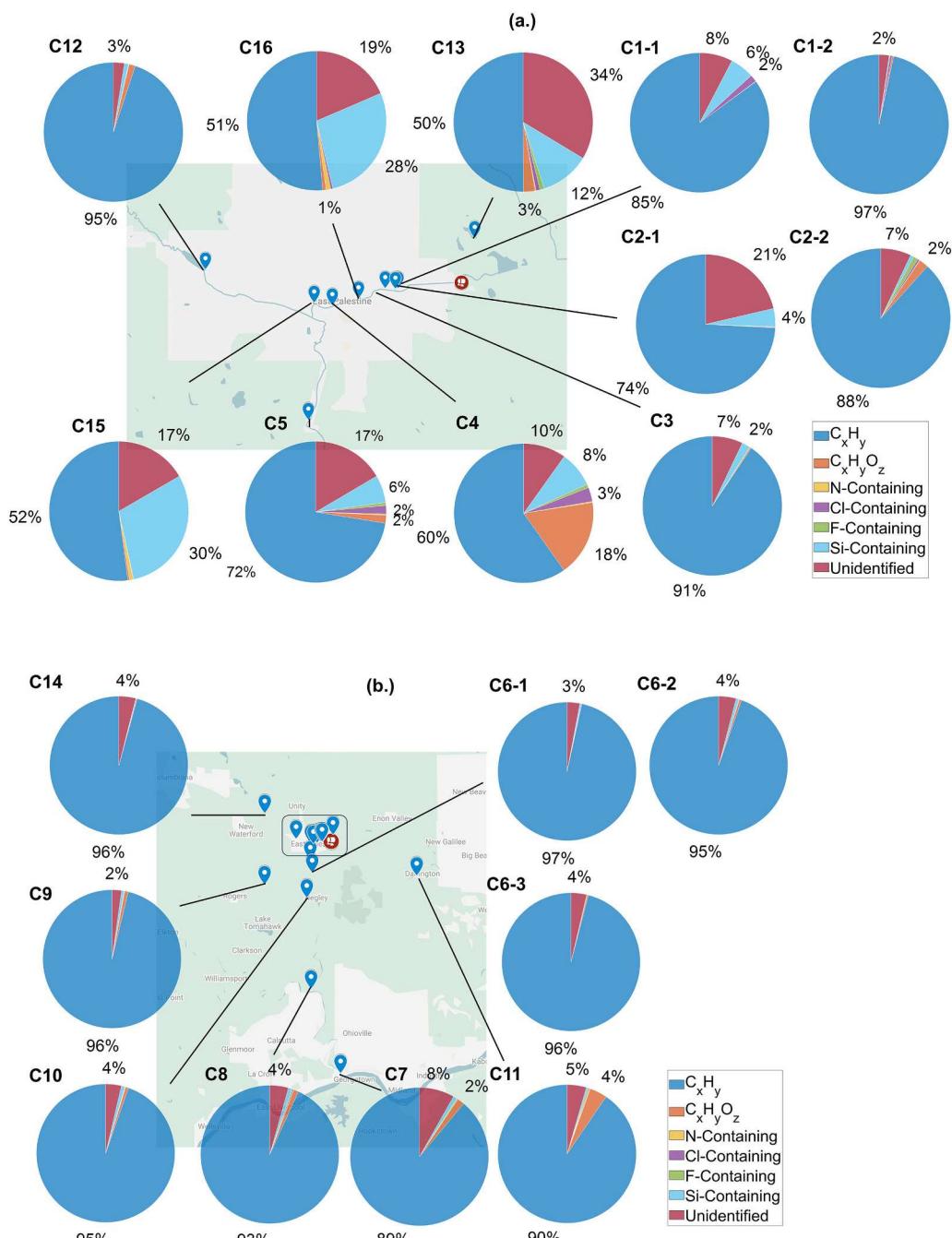


Fig. 6. Chemical composition of surface water samples collected: (a.) within and (b.) outside of a 3.2-km radius of the train derailment site. The mass percentages of chemical groups contributing <1 % were not labeled for better visualization.

VOC mass concentration detected in the headspace air. Spatial variations in the chemical composition of the surface water samples can be observed. Generally, the chemical composition of the surface water samples collected from the sites inside East Palestine are more complex as compared to the samples collected further from East Palestine. The surface water samples (C4, C15, and C16) collected from more downstream sites of Sulphur Run, which is a creek flowing through East Palestine, contain less hydrocarbons, with their mass percentage ranging from 51 % to 60 %. Si-containing compounds were detected in samples collected alongside Sulphur Run, including C1 – C4, C13, C15, and C16, with mass percentages ranging from 2 % to 30 %.

Si-containing compounds contribute more to the total VOC mass

concentration at more downstream sites. For example, among the samples collected on March 25, 2023, C1-2, C2-2, C15, and C16, the mass percentage of Si-containing compounds for sample C15, which is the most downstream site alongside Sulphur Run, is the highest (30 %), followed by C16 which is 0.64 km upstream of C15, accounting for 28 % of the total VOC mass concentration. The mass percentages of Si-containing compounds in C1-2 and C2-2 were much lower, accounting for only 3 % and 1 % of the total VOC mass, respectively. Similar trends were observed for samples collected on February 27, 2023. The mass percentage of Si-containing compounds in the more downstream water sample C4 was higher than that of the more upstream water samples C1-1 and C2-1. Si-containing compounds were also detected in

water sample C5, collected from Leslie Run approximately 0.95 km downstream where Sulphur Run merges into Leslie Run, with a mass percentage at 6 %, slightly lower than that of water sample C4. Such patterns suggest that Si-containing compounds detected in surface water samples are related to emissions from urban human activities. Si-containing compounds, including cyclic and linear volatile methyl siloxanes, have been previously observed in surface water (Companioni-Damas et al., 2012; Sanchís et al., 2013; Yaman et al., 2020; Zhang et al., 2024, 2018).

Comparing the water samples that were collected on the same dates, Cl-containing compounds were detected in most of the samples collected within 3.2 km downstream of the train derailment site on February 27, 2023, including C1-1, C4, and C5, with mass percentages ranging from 2 % to 3 %. However, Cl-containing compounds were not detected in the samples collected on March 25, 2023. No significant temporal variations were observed in the chemical composition of the three surface water samples collected at C6, which is located approximately 2.9 km downstream where Sulphur Run merges into Leslie Run.

3.5. Estimated concentrations of selected VOCs in East Palestine, Ohio surface water samples

Among the VOCs potentially released by the chemical spill and subsequent burn, vinyl chloride, isobutylene, 2-ethylhexyl acrylate, and acrolein were not detected in any of the surface water samples. Butyl acrylate was detected in some of the water samples around the limit of detection. On February 27, the Ohio EPA detected vinyl chloride only at two sampling locations <30.5 m downstream of the derailment site (Ohio EPA, 2023b). Vinyl chloride concentrations were <0.1 % of their highest concentrations, which were detected 5 to 10 days after the train derailment. All of our sampling sites, aside from those labeled as "Upstream," are downstream of these two locations. Vinyl chloride was not detected in the more downstream sites by the Ohio EPA as well. A comparison of VOC concentrations in water samples analyzed in this study and by the Ohio EPA at the same sites and dates is provided in Table S3. The absence of several chemicals from water samples analyzed in the present study could be for several reasons: samples were collected 24 to 51 days after the train derailment, contamination heterogeneity in the waterways, and the dilution and flush of the creeks from rainfall and contractor remediation activities (e.g., aeration, booms, etc.). The burning of released chemicals after the chemical spill may have also removed some of these chemicals.

VOCs that are frequently reported in surface water samples, predominantly aromatics, including benzene (C_6H_6 , detected at m/z 79), styrene (C_8H_8 , detected at m/z 105), and xylene (C_8H_{10} , detected at m/z 107) were observed in most of the East Palestine water samples (all samples except for C16). The estimated headspace concentration of the aromatics - benzene, styrene, and xylene - ranges from 0.06 to 1.54 ppb, 3.59–31.51 ppb, and 0.46–4.54 ppb, respectively. Benzene and xylene were also detected during a mobile air monitoring study conducted around the train derailment site in East Palestine, 18 to 19 days after the train derailment occurred, with benzene concentrations up to 3 ppb and xylene concentrations up to 50 ppb (Oladeji et al., 2023).

The headspace concentrations of individual VOCs can be translated to aqueous concentrations using Henry's Law (Eq. (1)) and their Henry's Law solubility constants reported in the literature (Raventos-Duran et al., 2010; Sander, 2023; Schwardt et al., 2021). The Henry's Law solubility constants, headspace concentrations, and aqueous concentrations are summarized in Table 3. The aqueous benzene, styrene, and xylene concentrations in the water samples were estimated to range from 0.9 to 21.9 ng/L, 94.5–830 ng/L, and 5.9–58.5 ng/L, respectively. The high sensitivity of PTR-TOF-MS enables detection of an ultra-low level of volatile chemicals in water samples. The aqueous xylene concentrations agree well with the concentrations previously reported for surface water samples, while the aqueous benzene concentrations are lower than previously reported values. Furtula et al. (2004) reported

Table 3

Headspace and aqueous concentrations of selected compounds in the East Palestine, Ohio surface water samples.

m/z	79	89	105	107
Chemical Formula	C_6H_7+	$C_5H_{12}OH+$	C_8H_9+	$C_8H_{11}+$
Tentative Identification	Benzene	Methyl <i>tert</i> -Butyl Ether	Styrene	Xylene
Henry's Law Solubility Constant, H_s^P (mol m ⁻³ Pa ⁻¹)				
	0.0018	0.016	0.0025	0.0012
Headspace Concentration (ppb)				
C1-1	0.36	0.56	12.50	1.44
C1-2	0.72	6.20	19.27	2.58
C2-1	1.16	2.50	27.41	3.67
C2-2	1.54	8.93	31.51	4.54
C3	0.54	1.59	13.71	1.71
C4	0.87	9.64	16.19	2.29
C5	0.56	0.92	12.17	1.64
C6-1	0.33	1.19	9.63	1.30
C6-2	0.21	0.99	6.80	1.08
C6-3	0.06	n.d.	3.59	0.46
C7	1.04	4.48	17.33	2.55
C8	0.49	1.58	13.92	2.16
C9 - Upstream	0.50	6.24	7.40	2.72
C10	0.39	1.40	9.44	1.32
C11 - Upstream	0.23	0.97	6.95	1.04
C12 - Upstream	0.30	1.41	8.11	1.11
C13 - Upstream	1.16	4.70	23.16	3.40
C14 - Upstream	0.28	2.91	9.44	1.40
C15	0.36	3.17	12.01	1.85
C16	n.d.	n.d.	n.d.	n.d.
Aqueous Concentration (ng/L)				
C1-1	5.1	79.3	329.4	18.6
C1-2	10.2	884.4	507.7	33.2
C2-1	16.5	356.1	722.0	47.2
C2-2	21.9	1274.3	830.0	58.5
C3	7.7	227.5	361.2	22.0
C4	12.4	1374.7	426.5	29.5
C5	7.9	130.7	320.7	21.2
C6-1	4.6	169.1	253.6	16.7
C6-2	3.0	141.7	179.1	13.9
C6-3	0.9	n.d.	94.5	5.9
C7	14.8	638.7	456.6	32.8
C8	7.0	225.6	366.8	27.9
C9 - Upstream	7.1	890.9	195.0	35.0
C10	5.5	200.0	248.6	17.0
C11 - Upstream	3.3	138.6	183.0	13.4
C12 - Upstream	4.2	200.6	213.6	14.3
C13 - Upstream	16.5	670.7	610.1	43.9
C14 - Upstream	4.1	414.6	248.7	18.1
C15	5.1	452.0	316.4	23.8
C16	n.d.	n.d.	n.d.	n.d.

2165 ng/L of benzene and 968 ng/L of xylene in a lake water sample, respectively (Furtula et al., 2004). Huybrechts et al. reported xylene concentrations ranging from <13 ng/L to 280 ng/L among 47 seawater samples (Huybrechts et al., 2005). The presence of these compounds can be related to industrial sources or chemical spills, posing potential human exposure risks and environmental safety concerns due to their carcinogenic or toxic effects on the human body (Brown et al., 2000; Fishbein, 1985, 1984; Loomis et al., 2017; McMichael, 1988; Niaz et al., 2015; Vodicka et al., 2006; Yu et al., 2022).

Methyl *tert*-butyl ether (MTBE, $C_5H_{12}O$, detected at m/z 89), another commonly detected VOC in surface water samples, was detected in 18 out of 20 East Palestine surface water samples, with estimated headspace concentrations ranging from 0.56 ppb to 9.64 ppb. This translates into estimated aqueous concentrations of 79.3 ng/L to 1374.7 ng/L. Most of these values were also below the detection limit of the Ohio EPA surface water sampling method, suggesting the excellent capability of PTR-TOF-MS in rapidly detecting trace level compounds in water

samples. Similar MTBE ranges were reported for water samples from Lake Zurich during the boating season (10–1400 ng/L) (Schmidt et al., 2004). MTBE is commonly used as a fuel additive in gasoline. The detection of MTBE in water samples may indicate gasoline spills or leakage, raising concerns for human health (Guitart et al., 2004; Gullick and LeChevallier, 2000; Levchuk et al., 2014).

4. Conclusions, study limitations, and future directions

A controlled static headspace sampling system, in conjunction with a high-resolution PTR-TOF-MS, can enable rapid screening of VOCs in surface water samples collected at chemical disaster sites. Spatial variations were observed in the chemical composition of surface water samples collected from the water streams near the chemical spill and train derailment site in East Palestine, Ohio. Hydrocarbons were found to be the most abundant chemical group in all surface water samples, contributing 50 % to 97 % to the total headspace VOC mass. Compounds commonly detected in surface water samples, including benzene, xylene, and MTBE, were also observed in most of the East Palestine surface waters samples, with aqueous concentrations typically at ng/L levels. This study demonstrates the potential of PTR-TOF-MS headspace sampling for rapid screening of volatile chemicals in water samples. However, as the water samples were collected 24 to 51 days after the train derailment, the results reported here may not reflect the water composition right after the chemical spill. As H_3O^+ was used as the reagent ion for the PTR-TOF-MS in this study, specific groups of compounds may not have been effectively detected. The PTR-TOF-MS can most accurately determine VOC concentrations with calibration gas standards. Uncertainties can be introduced when using proton transfer reaction kinetics to estimate VOC concentrations. However, with this methodology, preliminary determination of the existence of VOCs in environmental samples can be achieved. After initial screening and determination of tentative compounds in the samples, analytical methods with higher sensitivity and accuracy can be followed. Such an approach can support fast response to chemical disasters and environmental hazards to protect human health and the natural environment.

Recent studies have implemented PTR-TOF-MS on mobile vehicles to map the spatial distribution of VOC emissions in cities (Coggon et al., 2024; Liang et al., 2020; Richards et al., 2020; Rutherford et al., 2024; Wagner et al., 2021; Zhao et al., 2021). The headspace sampling system can be integrated with a similar setup to monitor the emissions from hazardous chemical incidents. Following the occurrence of a chemical incident, the headspace sampling system with the PTR-TOF-MS can be deployed onto a mobile vehicle to efficiently analyze headspace VOCs of water and soil samples collected at different sites. In addition, the same system can be applied for in-situ or mobile real-time air monitoring in both indoor and outdoor atmospheric environments. This allows for a better understanding of the air, water, and soil contamination released from chemical incidents. Response teams can have access to immediate and reliable data on the presence and concentrations of hazardous chemicals in different environmental media using a single PTR-TOF-MS, significantly improving the speed and effectiveness of emergency response and remediation efforts.

Furthermore, the headspace sampling system with the PTR-TOF-MS can be expanded using different reagent ions to detect a broader spectrum of compounds. In this study, the H_3O^+ ion was used as the reagent ion to identify a wide variety of VOCs. The PTR-TOF-MS can be configured as a CIMS by employing alternative reagent ions, such as NH_4^+ , O_2^+ , or NO^+ , to detect additional categories of VOCs that are not efficiently detected with H_3O^+ . This allows for a more comprehensive analysis of chemical contamination of environmental media in response to hazardous chemical incidents like the East Palestine train derailment.

CRediT authorship contribution statement

Jinglin Jiang: Writing – review & editing, Writing – original draft,

Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. Xiaosu Ding: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis. Paula Coelho: Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Grayson Wittbrod: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Andrew J. Whelton: Writing – review & editing, Resources, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization. Brandon E. Boor: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. Nusrat Jung: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitenv.2024.176056>.

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