Chemosphere 134 (2015) 203–209

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Temporal and spatial variability of trace volatile organic compounds in rainwater

Katherine M. Mullaugh [*], Joanna M. Hamilton, G. Brooks Avery, J. David Felix, Ralph N. Mead, Joan D. Willey, Robert J. Kieber

Department of Chemistry & Biochemistry, University of North Carolina Wilmington, Wilmington, NC, USA

HIGHLIGHTS

- A HS-SPME method optimized for the detection of VOCs in rainwater.
- Rainwater was collected and analyzed for VOCs over a one-year period (111 samples).
- Methylfuran occurred most frequently (detected in 86% of samples).
- Rainwater is not an effective removal mechanism of BTEX at this location (<0.1%).

ARTICLE INFO

Article history:
Received 9 January 2015
Received in revised form 9 April 2015
Accepted 10 April 2015
Available online 15 May 2015

Handling Editor: I. Cousins

Keywords:
VOCs
Rainwater
BTEX
HS-SPME
Methylfuran
Carbon tetrachloride

ABSTRACT

This study presents the first detailed concentration profile of trace VOCs in atmospheric waters. Analytes were detected and quantified in 111 unique rain events in Wilmington, NC, USA over a one-year period. Headspace solid phase microextraction was optimized for detection of these compounds at sub-nanomolar levels. Distinct seasonality in both the occurrence and concentration of compounds was observed with the lowest abundance occurring during low irradiance winter months. In contrast to other rainwater components studied at this location, VOCs did not show any correlation between rainfall amount and concentrations. There was significant spatial variation with regards to air-mass back-trajectory for methyfuran with higher concentrations observed in terrestrial events during the growing season. Air mass back trajectory also impacted CCl_4 concentrations in rainwater with evidence of a possible oceanic input. However there was no significant impact of air-mass back-trajectory on the concentration of BTEX observed in rain indicating that storm origin is not the controlling factor driving concentrations of these analytes in precipitation. Members of the BTEX family did, however, have significant correlations with each other occurring in ratios aligned closely with ratios reported in the literature for gas-phase BTEX. Using available gas-phase data from locations with similar anthropogenic sources and Henry's Law constants, calculated concentrations agreed with VOC levels found in Wilmington rain. Results of this study indicate local gas-phase scavenging is the major source of VOCs in rain and wet deposition is not an efficient removal mechanism (<0.1%) of VOCs from the atmosphere.

1. Introduction

During the last three decades, extensive research has reported the concentrations and atmospheric reactions of volatile organic compounds (VOCs) in the atmosphere (Field et al., 1992; Monod et al., 2001; Williams, 2004). The concentration, variability and atmospheric fate of these compounds is of interest because they pose a direct risk to human health (Kim et al., 2013) while also indirectly impacting air quality by contributing to photochemical smog (Monod et al., 2001) and the formation of secondary organic aerosol (SOA) (Kalberer et al., 2004). Biogenic emissions of VOCs are generally considered more significant than anthropogenic emissions on a global scale (Williams, 2004) however anthropogenic emissions can be the major source of VOCs on a local scale, largely due to the use of fossil fuels (Field et al., 1992; Perez-Rial et al., 2009). VOCs in this study with known potential biogenic sources include carbon tetrachloride (Roy et al., 2011), toluene (Juttner and Henatsch, 1986; White et al., 2009), and methylfuran, a product of isoprene oxidation (Montzka, 1995).

---

[*] Corresponding author at: Department of Chemistry & Biochemistry, College of Charleston, Charleston, SC, USA.

E-mail address: mullaughkm@cofc.edu (K.M. Mullaugh).

http://dx.doi.org/10.1016/j.chemosphere.2015.04.027
0045-6535/© 2015 Elsevier Ltd. All rights reserved.

Although chemical removal of VOCs in the gas phase by reaction with the hydoxyl radical (·OH) has been studied at length, very little attention has been given to removal by precipitation (Field et al., 1992). It is important to understand the efficiency of wet deposition as a removal mechanism for VOCs, if it is a transport mechanism, and if the scavenging process is governed by aerosol concentration or gas-phase concentration. Table 1 summarizes previous studies that have measured VOCs in rainwater. Prior to this study, the most comprehensive analysis of VOCs in rain is an analysis of members of the BTEX family of compounds (benzene, toluene, ethylbenzene and xylene isomers) in 13 rain samples collected in Yokohama, Japan more than a decade ago (Okochi et al., 2004). The authors sampled ambient air and rainwater simultaneously, and found higher concentrations of BTEX in rainwater than would be expected from their gas-phase concentrations and temperature-corrected Henry's Law constants indicating rain might be a more important removal mechanism than previously thought. Therefore, further research is needed to better assess the contribution of rainwater in removing VOCs from the atmosphere.

The purpose of the current study is to generate the first comprehensive profile of the spatial and temporal variability of these compounds in rain by quantifying concentrations in precipitation in Wilmington, NC over a full year. The ongoing long term analysis of rainwater composition at this site (Willey et al., 2006) and its coastal location that allows for a detailed comparison of the influence of both terrestrial and marine air masses (Avery et al., 2006b; Mullaugh et al., 2013) make it an ideal location for this study. We will also describe a head-space solid phase microextraction (HS-SPME) method optimized for this study. Using this data set, ratios and correlations of VOCs are compared to those found in the gas phase, and the saturation concentrations calculated from gas-phase data using temperature-corrected Henry's Law constants are compared with the concentration ranges measured in Wilmington rain to determine if the measured concentrations are similar to the predicted saturation concentrations.

2. Material and methods

2.1. Sample collection and storage

Rain samples were collected on an event basis at the University of North Carolina Wilmington campus (34.32°N and 77.88°W) from August 12th, 2012 to August 26th, 2013. The rain collection site is located in a clearing (~1 ha) in a wooded area comprised of long leaf pine, turkey oak, and wire grass, and is approximately 8.5 km from the Atlantic Ocean. Samples were collected in 4-L Pyrex glass beakers placed inside Aerochem-Metrics (ACM) model 301 Automatic Sensing Wet/Dry collectors. Before use, all glassware used for rain collection, storage and analysis was rinsed extensively with Milli-Q Plus Ultra pure deionized water (resistivity > 18 MΩ) and then muffled at 450 °C for a minimum of 4 h to remove organic contaminants.

All rain samples were unfiltered and stored in the dark with no headspace in a refrigerator that was free from organic solvent vapors at ⩽4 °C. Two different storage containers were used during this study. Initially, samples were stored in 20 mL borosilicate glass vials with a Polypropylene Teflon backed screw cap. Analyte concentrations for samples stored in this manner were stable for up to 40 d, excluding toluene, which was only stable for 5 d, after which the concentration of toluene increased. A second storage method using 60 mL borosilicate glass vials with a rubber stopper and aluminum crimp-top was tested using both Milli-Q Plus Ultra pure deionized water and a rainwater sample. Neither the Milli-Q nor rain stored in this way showed a change in any analyte after being stored for 36 d and 21 d, respectively. The average time between rain collection and analysis was 15 d. A total of 111 rain events were collected from August 12, 2012 to August 26, 2013 and triplicate analyses were performed on 89% of the events. Toluene data were only used for samples that were stored 5 d or less.

Table 1
Summary of the methods used previously to analyze VOCs in rainwater. Benzene (B), toluene (T), ethylbenzene (E), *m* + *p*-xylene (MPX), *o*-xylene (OX), carbon tetrachloride (CCl_4), methylfuran (MF). The number of samples (*n*) is defined as the number of distinct rain events sampled.

Reference	Location	*n*	VOCs	Method
This study	Wilmington	111	B, T, E, MPX, OX, CCl_4, MF	HS-SPME GC–MS
Sato et al. (2010)	Japan	Unknown	B, T, MPX, OX	HS-SPME GC–MS
Okochi et al. (2004)	Japan	13	B, T, MPX, OX	Purge and trap/GC–MS
Jung et al. (1992)	Japan	11	CCl_4	Purge and trap/GC–MS
Czuczwa et al. (1988)	Switzerland	13	E, MPX, OX	CLSA/HRGC/FID
Ligocki et al. (1985)	Oregon	7	T, E, MPX, OX	Solvent extraction/GC–MS
Kawamura and Kaplan (1983)	Los Angeles	4	T, E, MPX	Solvent extraction/GC-FID
Saunders et al. (1974)	Washington D.C.	1	B, T, MPX, OX	Purge and trap/GC–MS

2.2. VOC standards

Stocks and standards were made from neat solutions of benzene (Sigma–Aldrich, St. Louis, MO), toluene (Sigma–Aldrich, St. Louis, MO), ethylbenzene (EM Science, Gibbstown, NJ), m-xylene (TCI America, Portland, OR), p-xylene (Alfa Aesar, Heysham, UK), o-xylene (Sigma–Aldrich, St. Louis, MO), carbon tetrachloride (Acros, NJ) and 2-methylfuran (Acros Organics, NJ). A super-stock was made by diluting 50 μL of each analyte in 10 mL of GC^2 grade methanol (Honeywell B&J, Muskegon, MI). A working solution and standards were made from the super-stock, and all stocks and standards were stored in the dark at ⩽4 °C and used for up to 1 week. Standards and blanks were made using Milli-Q deionized water that had been UV-oxidized for 4–5 d to remove organics. A calibration curve was constructed for each analyte each day rain samples were run. Because low levels of BTEX have been detected in Milli-Q, blanks were analyzed along with standards and samples. Calibration curves were constructed for the response of at least four standards up to a concentration of 0.4 nM. Representative calibration curves can be seen in Fig. S1 in the Supporting information.

2.3. HS-SPME method

The SPME fiber was housed for manual sampling in a syringe-like casing with a barrel, plunger, adjustable depth gauge and septum-piercing needle (Zhang et al., 1994). Four 24-gauge Stableflex fibers (Supelco) designed for manual holders were tested: 50/30-μm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS), 65-μm Polydimethylsiloxane/Divinyl-benzene (PDMS/DVB), and Carboxen/Polydimethylsiloxane (CAR/PDMS) fiber in two thicknesses: 75 μm and 85 μm. The 85-μm CAR/PDMS fiber was chosen because it showed the greatest pre-concentration effect for all analytes. Before a new fiber was used for sampling, it was conditioned in the GC injection port at 300 °C for 1 h according to manufacturer instructions. The fibers were reused for up to 50 extractions after which point sensitivity decreased and fibers were discarded.