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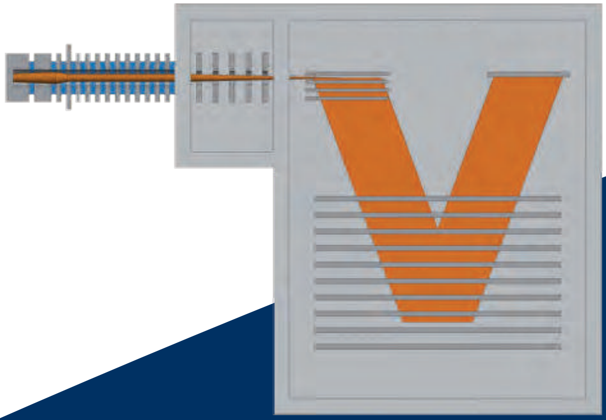

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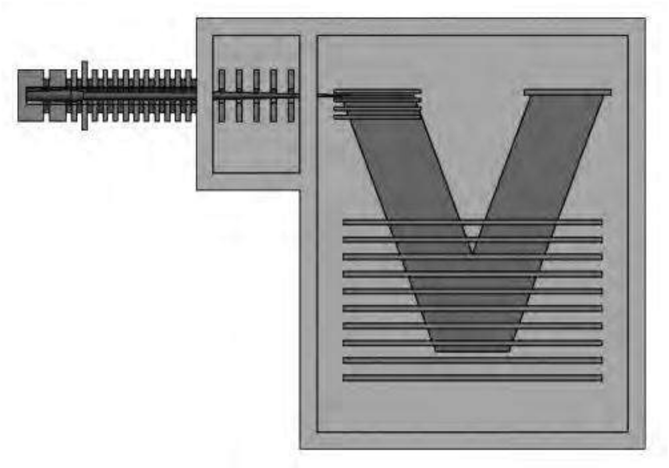

Contributions

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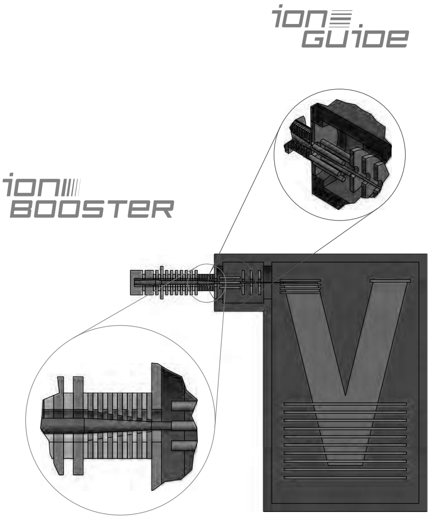

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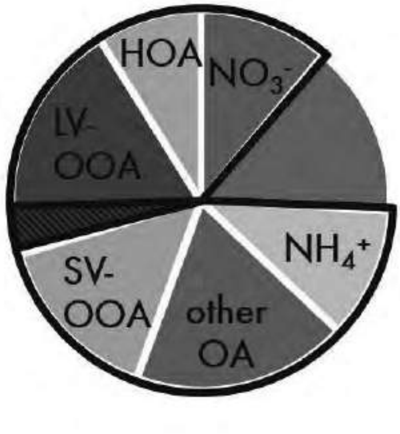
HOA
NO_3^-
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other OA


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Foreword

In the 1990's proton transfer reaction mass spectrometry (PTR-MS) using H_3O^+ reagent ions became a widely used analytical instrument with applications in environmental science, medical applications and food technology due to the large amount of volatile organic compounds (VOC), which can be quantitatively ionized. In 1998 the spin-off company Ionicon Analytik GmbH (www.ionicon.com) was founded to provide PTR-MS instruments to a growing user community and to develop the technology further. Today many research institutions and companies use this technology throughout the world.

The intent in initiating and organizing the 1st International PTR-MS Conference in January 2003 in Igls, Austria was to bring together active scientists and technology experts involved in mass spectrometric measurements of VOC. The 8th PTR-MS conference continues this series to provide a discussion forum for PTR-MS users and scientists from both academia and industry. More than 100 conference participants are expected at this year's conference hosted at the University of Innsbruck celebrating the 350's anniversary in 2019.

The programme will start with a plenary opening talk followed by the first poster session. On the following two days the conference topics PTR-MS in Environmental Science, Health Science and Food Science will be discussed in parallel sessions and the second poster session. On the final day, a plenary session on Instruments / Technology and Future Trends will be followed by Industrial Applications.

I would like to thank the session chairs Thomas Karl (Environmental Science), Franco Biasioli (Food Science) and Jonathan Beauchamp (Health Science) and Jens Herbig (Industrial Applications) for putting together an exciting programme, which exemplifies the growing number of PTR-MS applications in various scientific disciplines.

Special thanks go to Jürgen Dunkl and Sandra Naschberger, who helped organizing this exciting conference. Finally, I would like to thank the UNIVERSITY of INNSBRUCK and IONICON ANALYTIK sponsoring the poster award.

Armin Hansel

Innsbruck, January 2019

PTR-MS

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Abstract

In the 1990's **proton transfer reaction mass spectrometry** (Hansel et al., 1995) using H_3O^+ reagent ions became a widely used analytical instrument with applications in environmental science, medical applications and food technology due to the large amount of volatile organic molecules, which can be quantitatively ionized. H_3O^+ undergoes proton transfer reactions with every molecule having a higher proton affinity than water. In 1998 the company IONICON was founded as a University spin-off. Within the first ten years (1998–2008) IONICON has manufactured more than 100 PTR-MS instruments based on quadrupole mass spectrometry. These **PTR-MS** instruments did not have the capability to distinguish between isobaric species. A mass resolving power of 6000 (FWHM) was achieved introducing **PTR-TOF** [Graus et al. 2010, Jordan et al 2009]. Recently we have developed the **PTR3-TOF** instrument. The reagent $H_3O^+(H_2O)_n$ (n=1,2,3) cluster ion distribution is controlled in the new reaction chamber via a three-phase radio frequency electrode configuration that allows decoupling the ion's axial velocities from the kinetic energies applied to avoid hydration of reagent ions. The instrument uses a corona discharge ion source coupled to a contact free inlet system. [Breitenlechner et al. 2017]. Very recently we modified the PTR3-TOF utilizing NH_4^+-cluster reagent ions. With this new **NH_4^+-CI3-TOF** instrument [Hansel et al. 2018] we can study atmospheric oxidation processes of hydrocarbons forming RO_2 radicals, some of which show fast accretion product formation even competing with NO and HO_2 [Berndt et al. 2018]. Detection of individual RO_2 radicals and highly oxidized accretion products (HOMs) becomes feasibly with NH_4^+-CI3-TOF.

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Applications in Environmental Science

Accretion product formation from RO2 radical self- and cross-reactions

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Abstract

Hydrocarbons are emitted into Earth´s atmosphere in very large quantities by human and biogenic activities. Their atmospheric oxidation processes almost exclusively form RO_2 radicals as reactive intermediates whose atmospheric fate is not fully discovered yet. Here we show that gas-phase reactions of two RO_2 radicals produce accretion products, $RO_2 + R'O_2 \rightarrow ROOR' + O_2$, composed of the carbon backbone of both reactants. This pathway, not considered yet in the modelling of atmospheric processes, can be important for the fate of RO_2 radicals in all areas of the atmosphere. Moreover, the formed accretion products can be featured by remarkably low vapour pressure characterizing them as effective source for secondary organic aerosol.

Introduction

It is generally accepted that the main products of the self- and cross-reaction of RO_2 radicals are either the corresponding oxyl radicals (RO), pathway (1a), or an alcohol (ROH) in conjunction with a carbonyl (R´(-H,=O)), pathway (1b).

$$RO_2 + R'O_2 \rightarrow RO + R'O + O_2 \qquad (1a)$$

$$\rightarrow ROH + R'(-H,=O) + O_2 \qquad (1b)$$

As a result of earlier studies, the formation of dialkyl peroxides has been discussed additionally, pathway (1c). Stated peroxide yields from the self-reaction of the simplest RO_2 radicals, $RO_2 = R'O_2 = CH_3O_2$, $C_2H_5O_2$ or $CH_3C(O)O_2$, were reported to be small.[1-3]

$$RO_2 + R'O_2 \rightarrow ROOR' + O_2 \qquad (1c)$$

The relevance of pathway (1c) has not been investigated yet for RO_2 radicals other than for the small model RO_2 radicals and is currently not considered in atmospheric modelling. However, recent experimental findings, especially from gas-phase ozonolysis of cyclohexene and terpenes, point to accretion product formation that could be at least partly explained by a process according to pathway (1c).

Experimental Methods

The experiments have been performed in a free-jet flow system at T = 297 ± 1 K and a pressure of 1 bar purified air that allows investigations for nearly wall-free conditions.[4] The reaction time was 7.9 s. Ozone premixed with air (5 L min^{-1} STP) is injected through the inner tube into the main gas stream (95 L min^{-1} STP), which contains the second reactant (alkene) and other diluted in air. Ozone was produced by passing 1 - 2 L min^{-1} (STP) air through an ozone generator (UVP OG-2) and blended with additional air to a total flow of 5 L min^{-1} (STP) taken as the feed for the inner tube. The outer gas stream, 95 L min^{-1} (STP), contained the other reactants premixed in a flask from a gas-metering unit. Ozone concentrations were measured at the outflow of the reactor by a gas monitor (Thermo Environmental Instruments 49C). A proton transfer reaction - mass spectrometer (PTR-MS; HS PTR-QMS 500, Ionicon) served as an on-line monitor for organic compounds. In the case of isopropyl nitrite photolysis for OH radical generation the flow system was surrounded by 8 NARVA 36W Blacklight Blue lamps, emitting in the range 350 - 400 nm for homogeneous illumination of the whole reaction zone. Product analysis has been conducted using the NH_4^+-CI3-TOF (chemical ionization-time-of-flight) mass spectrometer based on the proton transfer (PTR3-TOF) mass spectrometer from the University of Innsbruck as well as a CI-APi-TOF (chemical ionization - atmospheric pressure interface - time-of-flight) mass spectrometer (Airmodus, Tofwerk) running either in the CH_3COO^- mode or the $C_3H_7NH_3^+$ mode.

Results

First, product formation from the OH radical initiated oxidation of 1,3,5-trimethylbenzene has been investigated using ozonolysis of tetramethylethylene (TME) as OH radical source. 1,3,5-trimethylbenzene represents an example of aromatic compounds, which are important emissions in urban areas. Measured concentrations of the main RO_2 radicals, i.e. $CH_3C(O)CH_2O_2$ from TME ozonolysis and $HO\text{-}C_9H_{12}(O_2)_xO_2$ with x = 1 - 3 from the aromatic, increased almost linearly with rising ozone and subsequently rising OH radical concentrations. Besides the RO_2 radicals, also the signals of the accretion products according to pathway (1c) from self- and cross-reactions of the RO_2 radicals in the system were detected. Strongest signals appeared for the products $C_{12}H_{18}O_6$, $C_{18}H_{26}O_8$ and $C_6H_{10}O_4$ formed from the possible combinations of the two most abundant RO_2 radicals, i.e. from $CH_3C(O)CH_2O_2$ and $HO\text{-}C_9H_{12}(O_2)O_2$. Additional experiments confirmed that unwanted processes did not influence the product formation during the ionization in the mass spectrometer.

The general validity of product formation via pathway (1c) is demonstrated from a measurement series using 1-butene, isoprene, n-hexane or methane instead of 1,3,5-trimethylbenzene in the experiments with OH radical formation from TME ozonolysis. In each case, the corresponding accretion products from the self- and cross-reactions of OH-reaction derived RO_2 radicals, i.e. $HO\text{-}C_4H_8O_2$, $HO\text{-}C_5H_8O_2$, $C_6H_{13}O_2$ or CH_3O_2, respectively, and $CH_3C(O)CH_2O_2$ were identified. It is to be noted that also small signals appeared for CH_3OOCH_3 from the CH_3O_2 radical self-reaction in line with earlier observations.[1-3] Reliable data analysis in this case, however, was impossible.

Figure 1 shows the experimental findings from the OH + 1-butene reaction using TME ozonolysis for OH radical generation.

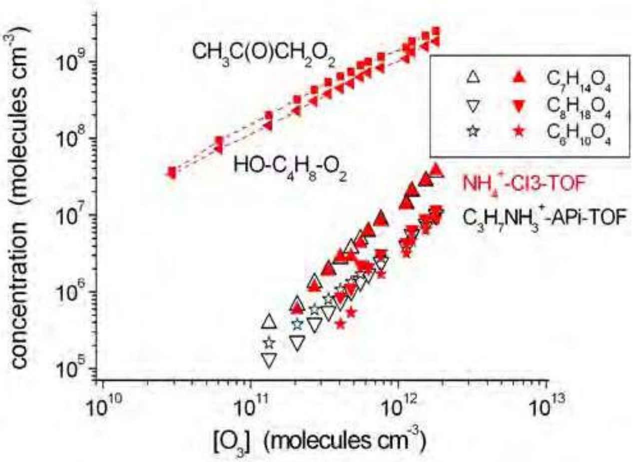

Figure 1: RO_2 radical and accretion product formation from the OH+1-butene reaction with OH radical formation via TME ozonolysis. Measurements have been performed by NH_4^+-CI3-TOF (full symbols) and by $C_3H_7NH_3^+$-APi-TOF (open symbols). Reactant concentrations: [1-butene] = 2.0×10^{12} and [TME] = 2.0×10^{11} molecules cm^{-3}.

Discussion

Accretion product formation according to pathway (1c) has been observed for all possible RO_2 radical self- and cross-reactions in the different reaction systems investigated. Therefore, a complex spectrum of accretion products can be expected in the atmosphere. Rate coefficients of accretion product formation from the self- and cross-reactions of RO_2 radicals, as measured in this work, span a range of more than three orders of magnitude. The different RO_2 reactivity in pathway (1c) is most likely connected to the RO_2 functionalization. Attractive forces from donor-acceptor relationships between functional groups of the two reacting RO_2 radicals are probably a necessary driving force for the rapid accretion product formation via pathway (1c). It can be speculated at this point that based on hydrogen bonds, carbonyl or endo-peroxide groups as acceptor and hydroxyl or carboxylic groups as donor, a more stable thus longer living reactive complex is generated that finally forms the covalently bound accretion product after O_2 elimination.

Finally, the formed accretion products ROOR′ can be treated as a source for secondary organic aerosol (SOA) due to their expected low vapour pressure in the case of functionalized ROOR′. Consequently, this process of accretion product formation can help to explain missing SOA sources in the atmosphere.

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Variability of OH reactivity in a rapeseed field: Results from the COV3ER experiment in April 2017

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Abstract

The hydroxyl radical plays a central role in the daytime troposphere, since it initiates the oxidation of most trace gases leading to the formation of harmful secondary products such as ozone and secondary organic aerosols. Total OH reactivity is defined as total loss rate of OH radicals and can be measured directly or indirectly by several methods. Among these techniques, the comparative reactivity method (CRM) coupled to a PTR-MS, which relies on monitoring competitive OH reactions between a reference molecule and reactive compounds in ambient air, has been widely deployed over an extensive range of applications. In the present study, measurements were conducted in a rapeseed field, west of Paris during the 2017 COV3ER experiment (Biogenic volatile organic compounds (BVOC) emissions by managed ecosystems: new references over French crops and forest and management effects). BVOCs emission measurements by the PTR-Qi-TOF-MS as well as total OH reactivity measurements by CRM/PTRMS were assessed from a dynamic chamber, set up on a non-flowered plant, in order to follow their variabilities during the blooming season. PTR-Qi-TOF-MS measurements were used to calculate the OH reactivity, which was compared to the measured one, showing a difference of 5.4 s^{-1} on average, representing 60% of the measured OH reactivity. The measured total OH reactivity in the rapeseed crop chamber was found in the lower range compared to other ecosystems.

Introduction

Among its different sources, vegetation represents the major source of reactive carbon introduced into the atmosphere, mainly as volatile organic compounds (VOCs). Although forests are globally, the dominant source of Biogenic VOCs (BVOCs), an increased interest in these compounds from agriculture was observed over the past few years mainly after the discovery of significant amounts of oxygenated VOC (OVOC) emissions from crops [1].

On one hand, VOCs are characterized by a wide range of chemical species and their emissions are dependent on several biotic and abiotic factors (e.g. temperature, light, …). In this regard, many techniques have been deployed to measure VOCs in the atmosphere, among which PTR-MS has emerged as a useful tool for long period/ real-time measurements of BVOCs in air with a high sensitivity and a fast response time [2].

On the other hand, once emitted in the atmosphere, VOCs are subject to photochemical processes which are dominated, during daytime, by photo-oxidation with OH, leading to the formation of secondary pollutants in both, the gas and particulate phase, that have serious impacts on the environment and on human health. OH reactivity is defined as the total loss frequency of the hydroxyl radical in the atmosphere due to the reaction with ambient reactive molecules.

Measurement of OH reactivity over an agricultural site represents the main objective of the presented study, which took place during the blooming season of a rapeseed (*Brassica napus)* field located in an agricultural region about 40 km to the west of Paris (FR-Gri ICOS site) [3]. Rapeseed represents one of the main oil and protein producing plants grown in Europe: in 2015, the French agricultural area dedicated to oil-producing crops went up to 2.2 million hectares, of which two-thirds were rapeseed.

Experimental Methods

Atmospheric mixing ratios of VOCs were measured using a time of flight- quadrupole injection-proton-transfer-reaction-mass spectrometer (PTR-Qi-TOF-MS) (national instrument within the ANAEE-France framework) and total OH reactivity was measured based on the comparative reactivity method (CRM) coupled to a PTR-QuadMS used as the detector [4]. Measurements were done in a 60 L PTFE dynamic chamber enclosing an entire rapeseed stem initially non-flowered. Ambient air was dynamically injected (12 L.min^{-1}) so that it was renewed every 5 min. The photosynthetic active radiation (PAR), the temperature (T) and the relative humidity inside the chamber were monitored continuously as well as the CO_2 and H_2O exchanges in order to follow the physiology of the studied biomass.

Results

Total OH reactivity measured from the dynamic chamber between the 20th and the 24th April, 2017 is presented together with ambient air temperature. OH reactivity exhibited a diurnal cycle with a maximum during day-time and a minimum during night-time in agreement with the temperature and the light circadian cycles (Fig. 1). In addition, a first list of 10 compounds measured with the PTR-Qi-TOF-MS (Gonzaga Gomez et al., submitted) were selected to calculate the "theoretical" OH reactivity. These included isoprene, monoterpenes and oxygenated VOCs (methanol, acetone, acetaldehyde, …). We note that some compounds which had relatively high concentration like methanol (which was the main emission measured from *Brassica napus*), had a low contribution to OH reactivity (1.6% on average for the period from the 19th to the 24th, April), whereas other compounds like isoprene and monoterpenes, which had lower concentrations had a more significant contribution to the calculated OH reactivity.

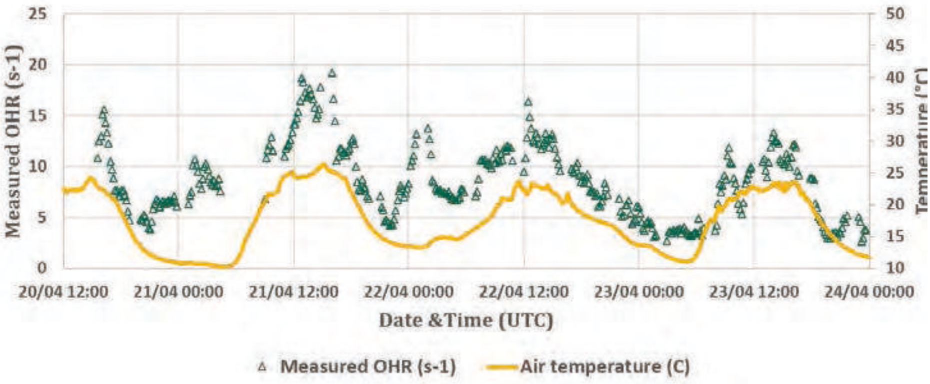

Figure 1: Variability of total OH reactivity measured in the dynamic chamber with temperature.

These observations demonstrate that the measured OH reactivity was driven by primary biogenic species emitted by rapeseed (monoterpenes, acetaldehyde). In addition, the comparison between the measured and the calculated OH reactivity highlights a mean difference of 60%; however, only the 10 compounds described above were used so far for these preliminary calculations. Further work is thus required in order to (i) evaluate if an overall difference between calculated and measured OH reactivity emerges from our measurement, and (ii) identify the possible unmeasured or unknown reactive compounds among the wide range of masses measured with the PTR-Qi-TOF-MS (~600). The next challenge will consist in finding their rate coefficients of their reaction with OH, in order to better understand the overall impacts of rapeseed BVOCs emissions on the oxidative capacity of atmosphere.

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Eddy-Covariance Measurements in NO+ mode

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Introduction

Urban environments are characterized by high population density and human activities that result in the emission of numerous organic compounds as well as inorganic pollutants into the air. Recently cooking, traffic, use of solvents and personal hygiene products as well as biogenic emission where classified as source factors of volatile organic compounds (VOC) in an urban flux study [1]. Combustion processes (traffic, heating and warm water) provide an abundance of NOx, sustaining the oxidation capacity of the atmosphere and oxidizing primarily emitted VOC to various oxygenated VOCs. These can serve as precursors in the course of tropospheric ozone and secondary organic matter production. Consequently, the urban atmosphere is a very complex mixture of organic trace gases and pollutants [2].

Proton Transfer Reaction Mass Spectrometry (PTR-MS) has been demonstrated to be an excellent method for the fast quantification of VOCs in the atmosphere [3-5]. Complementing this ionization technique with high resolution time-of-flight (TOF) mass spectrometry [6, 7] greatly increases the identification capability of such instruments [8] and outperforms comparable quadrupole mass analyzer instrument also with regards of limit of detection (LOD) [9]. Further enhancements in sensitivities by transferring the ions from the drift tube to the mass spectrometer [10] or even replacing the static drift field with radio frequency (RF) fields [11, 12] and improvements in mass resolving power are pushing the boundaries towards lower LOD and more unambiguous ion identification.

Proton transfer by H3O+ ions is a great choice for the detection of many VOC because for broad compound classes the occurrence of protonation and the resulting parent ion mass are easily predictable. Even reaction rate coefficients of uncalibrated VOC can be estimated with relatively small error margins [13]. In many cases this allows for the quantification of full mass spectra with acceptable uncertainty by applying sensitivities to the bulk of uncalibrated VOC signals that are estimated from the calibration of a manageable number of calibrated compounds. Fragmentation of parent ions, however, adds uncertainty to quantification and identification, and with that ambiguity to metrics such as carbon number, O/C ratio, C/H ratio. Fragmentation can result in the generation of a few common and unspecific fragment ions loosing most of the chemical information of the parent ion. The advantage of relatively unspecific protonation of many VOC by H3O+ turns into a disadvantage if one is interested in the identification of isomeric species that might have very different properties with regards to atmospheric chemistry.

In contrast to the straight forward protonation by H3O+, ionization by NO+ may proceed along four different pathways

$$R>+>NO^{+}>\rightarrow>R^{+}>+>NO> \qquad (1)>$$

$$RH>+>NO^{+}>\rightarrow>R^{+}>+>HNO> \qquad (2)>$$

>

$$\mathrm{ROH + NO^+ \rightarrow R^+ + HNO_2} \qquad (3)$$

>

$$\mathrm{R + NO^+ + M \rightarrow R.NO^+ + M} \qquad (4)$$

>

where (1) is charge transfer, (2) hydride abstraction, (3) hydroxide abstraction and (4) three body association reaction [14]. An extensive body of knowledge on ion-molecule-reaction pathways in selected ion flow tube experiments has been produced by Patrik Spanel and David Smith and co-workers [15-23]. Whether and by which pathway(s) NO+ ionizes a given molecule is governed by the reaction enthalpies; Koss et al. provide a comprehensive overview (see [24] and references therein). VOC that – in H3O+ mode operation – react to isomeric or otherwise indistinguishable species may be ionized by different paths in NO+ mode depending on their respective compound class and thus become separable. Hollow-cathode ion sources of PTR-MS instruments can be used to produce NO+ at high intensity and low impurity, and several applications have been demonstrated [25, 26, 14, 24].

Experimental Methods

A SRI-Qi-TOFMS system (Ionicon Analytik) was operated in NO+ mode. Calibrations were performed periodically throughout the study period by quantitatively mixing of a calibration gas standard containing several VOC into catalytically scrubbed, ambient air in order to provide mixing ratios in the order of 10 ppbv. In addition, organic compounds not present in the gas standard were analyzed in one suite of calibration experiments using a liquid calibration unit (LCU, Ionicon Analytik), which allowed for the determination of an effective reaction rate coefficient for these compounds.

Ambient air sampling took place at the Innsbruck Atmospheric Observatory (IAO). IAO offers 70 m2 lab-space and a 9.6 m high sampling tower on top a nine floor high university building (Bruno-Sander-Haus) in Innsbruck, Austria. Sonic anemometers (CSAT3, Campbell Scientific) measure turbulence at three different elevations. Co-located with the top-level anemometer (47.2640351561°N, 11.3857068°E, 617 m above sea level, ca 40 m above the surrounding terrain) is the sampling inlet of a pressure and temperature controlled manifold (PFA, 3/8” outer diameter, ¼” inner diameter, ca 13 m long) that provides ambient air to instruments set up in the laboratory below the tower. Air was co-sampled by SRI-Qi-TOFMS and co-added spectra were recorded at a rate of 10 Hz. Post-processing includes mass scale calibration, peak integration, background correction based on periodic zero calibrations, and fitting of transmission curves based on periodic gas phase calibrations. Turbulent fluxes of VOC are calculated from the covariance of 10 Hz VOC time series and vertical wind speed using our InnFLUX scripts programmed in Matlab (MathWorks).>

Results and Discussion

We will present results of calibration measurements for selected VOC, and use these to interpret common ions observed in urban air based on NO+ ionization. Table 1 shows a list of ions that dominated the NO+ spectrum in Innsbruck. In addition we investigate whether these species exhibit vertical exchange by analyzing their turbulent vertical fluxes. The identification potential of SRI-Qi-TOFMS in NO+ mode will be discussed for an urban air matrix.

m/z>	formula>	>	m/z>	formula>	>	m/z>	formula>
41.0386>	C3H5+>	>	71.0855>	C5H11+>	>	93.0699>	C7H9+>
43.0179>	C2H3O+>	>	75.0441>	C3H7O2+>	>	97.1012>	C7H13+>
43.0542>	C3H7+>	>	77.0597>	C3H9O2+>	>	99.0441>	C5H7O2+>
45.0335>	C2H5O+>	>	78.0464>	C6H6+>	>	99.0804>	C6H11O+>
57.0335>	C3H5O+>	>	81.0699>	C6H9+>	>	100.0393>	C4H6O.NO+>
57.0699>	C4H9+>	>	82.0413>	C5H6O+>	>	102.0550>	C4H8O.NO+>
59.0491>	C3H7O+>	>	82.0777>	C6H10+>	>	104.0621>	C8H8+>
61.0284>	C2H5O2+>	>	83.0491>	C5H7O+>	>	105.0335>	C7H5O+>
63.0441>	C2H7O2+>	>	83.0855>	C6H11+>	>	106.0777>	C8H10+>
68.0257>	C4H4O+>	>	85.0284>	C4H5O2+>	>	108.0444>	C6H6NO+>
68.0621>	C5H8+>	>	85.0648>	C5H9O+>	>	120.0934>	C9H12+>
69.0335>	C4H5O+>	>	85.1012>	C6H13+>	>	134.1090>	C10H14+>
69.0699>	C5H9+>	>	88.0393>	C3H6O.NO+>	>	136.1247>	C10H16+>
70.0777>	C5H10+>	>	90.0186>	C2H4O2.NO+>	>	>	>
71.0491>	C4H7O+>	>	92.0621>	C7H8+>	>	>	>

Table>1:>mass>peaks>and>identification>of>sum>formula>

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Effect of agricultural practices on volatile organic compound (VOC) emissions from winter wheat

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Abstract

Despite the important land cover of crops, biogenic volatile organic compounds (BVOCs) emissions from agricultural areas remain poorly characterized, especially from field experiments. There is even less knowledge about the effect of agricultural practices (fertilization, pesticide spreading, etc.) on these emissions. The global aim of the present study is to reinforce our knowledge on BVOC emissions from agricultural crops. A field campaign was carried out at a measurement station located at Grignon ICOS site (France), 40 km southwest from Paris. The goal of the study was i) to quantify BVOC fluxes over a wheat stand and ii) to evaluate the effect of agricultural practices (manure and pesticide spreading) on these emissions. The experimental set-up consisted in measuring eddy covariance fluxes of momentum, latent and sensible heat, CO2 and BVOCs (with a PTR-Qi-TOF-MS - national instrument within the ANAEE-France framework). Results show that methanol was the most emitted BVOC, in agreement with few reported studies about wheat. Immediately after manure spreading, an increase of emissions of several compounds was observed. Especially, m/z 109.06 (C7H8O), which was previously characterized as strongly emitted by liquid manure, was observed in the field. We also report the first online measurement of pesticide with a PTR-Qi-TOF-MS. The spread fungicide Chlorothalonil was surprisingly still detected in the gas phase 21 days after spreading. Our results provide new insights in BVOC emissions from crops and the effect of pesticide and manure spreading on these emissions.

Introduction

Vegetative ecosystems emit large amounts of biogenic volatile organic compounds (BVOCs), estimated to reach around 760 Tg C each year, which largely exceed those from anthropogenic origin[1]. Most BVOCs reacts with atmospheric oxidants (mainly OH, O_3, NO_3), promoting the formation of secondary pollutants such as O_3 or secondary organic aerosols (SOAs). According to the Food and Agriculture Organization of the United Nations (FAO), agricultural areas cover around 35% of the Earth land surface. Like all vegetative ecosystems, agricultural crops emit significant amounts of BVOCs. However, despite their important land cover, studies regarding BVOC emissions from agricultural ecosystems remain very sparse. Karl et al. (2009) [2] pointed out that agricultural crops could be a major source of BVOCs, contributing up to 27% of total BVOC emission in Europe. However, another study estimated that BVOC emissions from agricultural stands could be overestimated [3]. The understanding of BVOC emissions thus remains highly uncertain, and needs new investigations.

The global aim of the present study was to reinforce our knowledge on BVOC emissions from agricultural crops. Among all the crops, wheat is the most cultivated one at the global scale (in area harvested, according to the FAO). However, wheat BVOC emissions remain poorly characterized, especially from field experiments. Moreover, there is no study dealing with the effects of the different agricultural practices (e.g. the use- of organic fertilizer or pesticides) on VOC emissions from the ecosystem and the applied substance.

Therefore the goal of the study was i) to quantify BVOC fluxes over a wheat stand and ii) to evaluate the effect of agricultural practices (pesticide and manure spreading) on VOC emissions in terms of composition and magnitude.

Experimental Methods

Site description

The measurement campaign was conducted at the FR-GRI site (integrated to the ICOS -Integrated Carbon Observation System- European network), located a Grignon, 40 km west from Paris. The field site consisted in a 19 ha agricultural stand of winter wheat (*Triticulum aestivum* L., variety boregar), over a silt loam soil. A more complete description of the experimental site can be found elsewhere [4, 5]. The field campaign lasted from 03-28-2018 to 09-05-2018. Manure spreading occurred on the evening of the 03-29-2018, and pesticide spreading on the morning of the 17-04-2018.

Experimental set up

The experimental set-up consisted in measuring eddy covariance fluxes of momentum, latent and sensible heat, CO_2 and BVOCs (with a PTR-Qi-TOF-MS - national instrument within the ANAEE-France framework). All the measurements were performed at 2 m above ground level, over a mast located around 25 m inside the wheat stand but with a fetch larger than 200 m in the main wind direction. The principle of the eddy covariance methodology is to evaluate the covariance between the vertical wind speed and the fluctuations of a scalar, and is fully described in previous studies [6, 7]. In our study, wind speed components were measured with a 3-D sonic anemometer (R3-50, Gill Instruments). Water vapor and CO_2 were measured using an open path infra-red gas analyzer (LI-7500, LICOR Biosciences). VOC concentrations were recorded with a PTR-Qi-TOF-MS (Ionicon), through a 50°C heated, 30 m Teflon tubing (1/2 inches inner diameter) with a flow rate of 50 L/min. Blank and calibrations (using gas standards) of the PTR-Qi-TOF-MS were frequently performed all along the campaign. Nitrogen oxides (NOx) and O_3 concentrations were routinely monitored on the site, as well as meteorological parameters (air temperature, relative humidity, solar radiation, wind speed and direction).

PTR-Qi-TOF-MS characterisation

Prior to the field experiment, we characterised the mass spectra on the PTR-Qi-TOF-MS of one of the fungicide applied during the campaign (Chlorothalonil) and of liquid manure coming from the same farm as the one applied. Using a small atmospheric chamber, we established that m/z 109.06, corresponding to C_7H_8O (frequently identified as cresols), was one of the most emitted compound by the liquid manure. We thus will use this compound as a tracer for liquid manure emissions in the field study. Regarding the fungicide, we analysed the headspace of a vial containing chlorothalonil, to catch the footprint of the Chlorothalonil ($C_8Cl_4N_2$) on the mass spectra. The Chlorothalonil footprint on the PTR-Qi-TOF-MS contained more than ten ions. That high number of ions is due to *i*) the natural abundance of the isotope of chlorine atoms and *ii*) the high clustering behaviour of chlorothalonil. We finally retained six masses that represented more than 90% of the total chlorothalonil signal.

Results and discussion

As the field study is recent, we should stress that the results presented and discussed below are only preliminary and not exhaustive. Results first highlight that CO_2 was deposited during daytime on the wheat stand, as a result of a photosynthesis flux larger than the respiration flux. The increase of CO_2 deposition during the campaign indicates that the field campaign took place during wheat growing season. We clearly identified that the most emitted compound was methanol (m/z 33.03), in agreement with previous studies over crops [3, 8]. Emissions of isoprene were also detected at our site, although these emissions were very low (one order of magnitude below methanol fluxes), and only significant during the second part of the campaign. Liquid manure spreading induced new VOC emissions. Immediately after spreading, emissions of cresols (C_7H_8O, detected at m/z 109.06) were recorded, whereas there was no clear flux before spreading. The emission of cresols on the site was attributed to emissions from liquid manure, as confirmed by laboratory measurements performed prior to the experiment. Cresols fluxes bring decreased quickly to near-zero within four days following spreading. The few rainfalls that occurred the days following manure spreading may explain this behavior. Other emission fluxes of oxygenated compounds such as propanoic acid, acetic acid or C_2H_2O for example, were also observed just after the liquid manure spreading. The time profile of these oxygenated compounds is close to that of cresols, even though propanoic acid emissions were still present 5 days after spreading. Such direct OVOCs (?) emissions from liquid manure on a wheat stand are reported for the first time.

Chlorothalonil was measured after spreading on the winter wheat stand. Unfortunately, no significant Eddy-covariance fluxes of Chlorothalonil were measured, probably due to a detection limit too high. However, the PTR-Qi-TOF-MS was able to measure a clear increase of Chlorothalonil concentrations in the gas phase following spreading. Chlorothalonil concentrations presented a clear diurnal cycle, following the diurnal cycle of temperature by reaching highest levels around 13h TU. This diurnal cycle was clearly observed during more than 20 days after chlorothalonil spreading over the wheat stand, which might also reflect spreading in surrounding fields.

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Aromatic Compounds in the Urban Atmosphere: Analysis of total carbon and gas and particle phase oxidation products

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Abstract

Aromatic hydrocarbons, primarily from anthropogenic sources, are an important fraction of volatile organic compounds in the urban atmosphere and play an important role in the formation of urban secondary organic aerosol (SOA). However, the multi-generational, gas-phase oxidation mechanism of aromatic compounds is currently not well understood. We investigate the multigenerational oxidation of three aromatic hydrocarbons by the OH radical: toluene, 1,2,4-trimethylbenzene (1,2,4-TMB) and 1,3,5-trimethylbenzene (1,3,5-TMB). OH radicals are known to react with aromatic hydrocarbons to form peroxy radicals which can isomerize by intramolecular hydrogen abstraction and lead to the formation of highly oxygenated molecules (HOMs). In this work, we report the elemental composition of HOMs in gas and particle phases. We show that under urban conditions, in the presence of nitric oxide (NO), the reaction of peroxy radicals with NO competes with the auto-oxidation pathway and leads to the formation of highly oxygenated species both with and without nitrate groups, which we detect in the gas and condensed phases.

Methods

Oxidation products were characterized - for the first time - in both the particle and the gas phase by two PTR3 [1] instruments, equipped with novel switchable reagent ion sources (SRI-PTR3). The instruments were run in standard proton transfer reaction mode using hydronium primary ions, as well as in ammonium mode utilizing $NH_4^+ \cdot H_2O$ clusters as primary ions [2]. In the latter mode, ionization mostly proceeds via ligand switching reactions. As shown in another presentation in this conference series [4], a voltage scan method can be utilized to predict sensitivities in this ion mode without direct calibration. For the particle phase, a SRI-PTR3 was equipped with a gas phase denuder followed by a thermal desorption unit [2, 3], as shown in Figure 1:

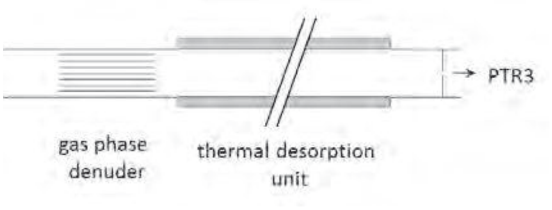

Figure 1: Inlet system for particle phase measurement: a multichannel gas phase charcoal denuder followed by a thermal desorption unit (TDU). The TDU consists of a ¾" glass tube, typically heated to a temperature of 180 °C, with a residence time of approx. 3 seconds.

Results

The unique suite of instruments employed during this study allows simultaneous quantitative measurements of the gas and particle phase. In the gas phase, we determine the kinetics of the formation of the main oxidation products of toluene and TMB and compare them with the calculated values from the Master Chemical Mechanism (MCM version 3.3.1). In the particle phase, we demonstrate good quantitative agreement between a state-of-the-art aerosol mass spectrometer (AMS) and the particle phase SRI-PTR3 (Figure 2a). Information on the molecular level provided by the particle phase SRI-PTR3 also reveals insights into the range of volatilities and oxidation states of the compounds making up the condensed phase (Figures 2).

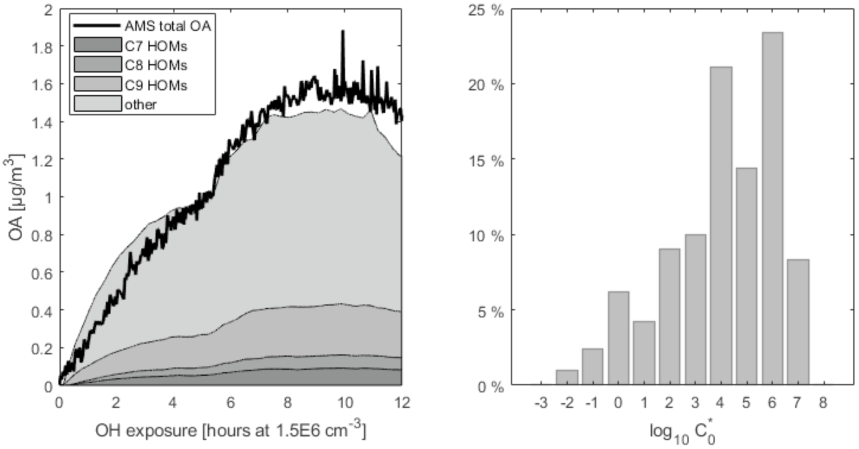

Figure 2: a) SOA produced during photo-oxidation of 1,2,4-TMB in a laboratory experiment. The total organic mass is measured by the AMS and compared to OA measured with the particle phase SRI-PTR3. b) Volatility distribution of detected OA.

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Vertical Divergence of Reactive Trace Gases – Comparisons for three different photochemical environments

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Abstract

We will present integrated data analysis of ground and airborne observed trace gas datasets from three recent community field campaigns – SOAS in the Southeastern U.S., GOAmazon in Amazonas Brazil, and KORUS-AQ in Seoul South Korea. These three very distinctive photochemical environments have a wide range of anthropogenic influences – a critical element in determining oxidation capacity of the lower troposphere. The analysis will particularly examine vertical divergence of reactive volatile organic compounds both anthropogenic and biogenic origins utilizing ground and airborne observational datasets. Specifically, the direct comparison between ground observed and airborne overpass datasets is expected to provide quantitative snapshots of the vertical divergence of various VOCs so that we can observationally constrain how fast trace gases are getting oxidized in the very low part of the boundary layer. As this process is crucial in model simulation but unable to be constrained by satellite observations, the discussion will be integral for the improvements of a model simulation capability and satellite retrieval activities

Understanding abiotic stress effects on carbon partitioning between plant primary and secondary metabolism by combined PTR-TOF-MS, IRIS and GC-MS-C-IRMS measurements

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Abstract

The coordination of the numerous processes controlling carbon partitioning into plant primary and secondary metabolisms, such as photosynthetic CO_2 uptake, respiratory CO_2 release and Biogenic Volatile Organic Compound (BVOC) biosynthesis, remains widely unclear. In addition, photosynthetic carbon isotope discrimination and ^{13}C-fractionation during respiratory CO_2 emission cause an isotopic imprint to plant-atmosphere CO_2 exchange [1]. Plant CO_2 release is closely connected to carbon partitioning at metabolic branching points of plant primary and secondary metabolisms. Pyruvate is a key metabolite which is formed in primary metabolism and acting as substrate in numerous secondary pathways forming many BVOCs, such as isoprene, volatile terpenoids, oxygenated compounds (acetaldehyde, acetic acid), benzenoids and fatty acid oxidation products (several wound VOCs), which can be emitted by plants [2]. Within the ERC project VOCO, we established an innovative analytical setup enabling us to simultaneously measure stable carbon isotope composition of leaf exchanged CO_2 (Infrared Isotope spectroscopy; IRIS) together with BVOC release (PTR-TOF-MS). In addition, compound specific isotopic signatures could be determined (GC-MS-C-IRMS). Position specific ^{13}C-labeled pyruvate was applied in feeding experiments to elucidate carbon partitioning at metabolic branching points into BVOCs *vs.* CO_2 in heat and drought stressed plants.

Studying plant species of contrasting habitats, we observed species-specific patterns of BVOC emission including isoprene, volatile terpenoids, oxygenated BVOCs, green leaf volatiles, aromatics, sulfides, and nitrogen containing volatile compounds. Tracing ^{13}C, we elucidated if compounds were *de novo* synthesized from ^{13}C-labeled pyruvate. Position-specific labeling with [1-^{13}C]-pyruvate and [2-^{13}C]-pyruvate suggested that most BVOCs were synthesized from the C2-C3 moiety of pyruvate whereas the C1 position was decarboxylated resulting in $^{13}CO_2$ release during night (dark respiration) but also – though to a smaller extent - in the light. We observed abiotic stress related shifts in $^{13}CO_2$ release and BVOC emissions. Our observations suggest that BVOC emissions are associated with significant pyruvate C1 decarboxylation which is released to the atmosphere. This novel approach contributes to a better understanding of the metabolic links of processes of primary and secondary plant metabolisms which is relevant for the vegetation-atmosphere exchange of CO_2 and BVOCs.

Introduction

Climate models forecast globally increased air temperatures of up to 5ºC together with dramatic changes of precipitation patterns by 2100, depending on the scenario applied. The frequency of heat waves and drought periods already increased in recent decades and will become even more frequent and severe in the future. Model simulations predict that some regions such as tropical areas and the Mediterranean will particularly be affected by such weather extremes.

Plants are sessile organisms which - due their lifestyle – had to evolve a plethora of mechanisms to cope with the prevailing environmental constraints of their natural habitats. However, the forecasted weather extremes will bring plants to the limits of their capability to deal with the expected levels of stress with cascading effects on ecosystem functioning [3]. In order to cope with oxidative stress which can be caused by heat or drought, plants activate pathways mediating scavenging of reactive oxygen species (ROS) and biosynthesis of antioxidants, as well as many processes at the molecular level. Biosynthesis of isoprene and volatile terpenoids also seem to be part of the plants arsenal to cope with oxidative stress [4]. Consequently, many plant species enhance the release of isoprene and monoterpenes under heat exposure. Products of such stress responses, e.g. many BVOCs, are secondary plant metabolites and their production happens at the expense of plant primary intermediates which are needed, for example, for plant growth. Thus, in response to stress, plant metabolism might activate the production of numerous plant secondary compounds.

For the present work, we selected plant species from very contrasting habitats such as the tropics, the Mediterranean as well as from temperate/boreal climates. The aim of our study is to investigate how these contrasting plant species, strongly differing in BVOC emission and activity of plant secondary metabolism, cope with different abiotic stressors. We tested the hypotheses that under prolonged periods of stress, plants invest more carbon into stress defense compounds which are mainly products of plant secondary metabolism at the expense of intermediates of plant primary metabolism. By feeding ^{13}C-position labeled pyruvate and following the ^{13}C tracer into individual volatile compounds ($^{13}CO_2$, BVOC), we were able to better understand the carbon partitioning between plant primary and secondary metabolisms and the effects of abiotic stress on this partitioning.

Experimental Methods

Branches of the experimental plants were placed into cuvettes. After characterization of BVOC emissions from intact plants, the branches were cut and the cut ends placed in deionized water. For feeding branches with ^{13}C-labeled pyruvate, the deionized water was replaced by 10 mM 99% ^{13}C-labeled pyruvate; pyruvate was labeled either at the [1-C]- or the [2,3-C]-position. The emission of BVOCs together with their ^{13}C-labeled isotopologues was followed for 60 min with a 4000ultra proton-transfer-reaction-time-of-flight-mass spectrometer (PTR-TOF-MS) (Ionicon Analytic, Innsbruck, Austria) [2]. Humidity dependent calibration was done with a multicomponent calibration gas standard (1000 ppb ± 5%, Ionicon Analytic, Innsbruck, Austria) using the Liquid Calibration Unit (LCU, Ionicon Analytic, Innsbruck, Austria).

The flux of $^{13}CO_2$ was calculated by accounting for the difference in $^{13}CO_2$ isotopic composition and concentration between empty and plant-containing cuvette as analyzed by a Delta Ray Isotope Ratio Infrared Spectrometer (IRIS, Thermo Fisher Scientific, Bremen, Germany).

In addition, carbon isotope signatures of individual BVOC were determined by GC-MS-C-IRMS with a system consisting of a gas chromatograph (model 7890N, Agilent, Waldbronn, Germany) equipped with a thermodesorption unit (Gerstel, Mülheim, Germany), a cold injection system (CIS, Gerstel, Mülheim, Germany). Analytes were channeled into a mass spectrometer (MSD 5975C, Agilant, Waldbronn, Germany) and a combustion oven (GC5, Elementar, Hanau, Germany) to convert organic compounds into CO_2. The CO_2 was further channeled into an isotope ratio mass spectrometer (IRMS, Elementar, Hanau, Germany) to determine carbon isotope signatures, which allowed us to follow the ^{13}C tracer of pyruvate.

Photosynthetic gas exchange was determined with a differential infrared gas analyzer (LI-7000; LI-COR, Lincoln, USA). Rates of net CO_2 assimilation and transpiration rate, as well as stomatal conductance to water vapor (G_{H2O}) were calculated as described earlier [2].

Results and Discussion

We demonstrate that in a great variety of plants from contrasting habitats the ^{13}C-atom from the C1-position of pyruvate is mainly decarboxylated and released from leaves in substantial amounts as $^{13}CO_2$. Interestingly, $^{13}CO_2$ release occurred not only during night but also in the light period [5,6]. The differences in $^{13}CO_2$ emission rates between [1-^{13}C]-pyruvate and [2-^{13}C]-pyruvate feeding strongly suggested that mitochondrial respiration was not the main process responsible for CO_2 release during day, which is in line with the view of inhibited TCA cycle during day. Thus, CO_2 must have been produced from decarboxylation of pyruvate in other pathways such as biosynthesis of fatty acids and other compounds. In contrast to the C-atom from the C1 –position of pyruvate, the ^{13}C from the C2-C3 moiety of pyruvate is preferentially emitted as BVOCs. Most of the plant species emitted isoprene and volatile terpenoids. However, we also detected ^{13}C-labeled benzenoids as well as short-chained oxygenated compounds such as acetaldehyde, acetic acid and methyl acetate. Emission of the latter compounds closely correlated, suggesting biosynthesis in common pathways. Among non-labeled compounds were semi-volatiles such as diterpenes [7]. Abiotic stress strongly affected the emission of BVOC. For example, heat exposure stimulated the emission of isoprene and several other volatiles supporting the view that isoprenoids mediate plant thermotolerance via membrane stabilization and protection of the photosynthetic apparatus.

Our work provides first evidence that the isotopic signature of respired CO_2 is closely linked to carbon partitioning between pathways of the primary and secondary metabolisms of plants and indicates strategies of carbon investment into secondary compound synthesis in response to abiotic stress.

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Estimation of wood burning and traffic contributions to VOC in Paris region

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Abstract

Among the diverse sources contributing to deleterious pollutants in the urban environment, wood burning and traffic are of particular importance. This work is based on a winter (December 2017 – March 2018) PTR-QMS campaign which took place at the SIRTA-ACTRIS station (20 km from Paris); additional data, as collocated black carbon measurements are used. This study showed that some VOC are highly correlated with wood burning (e.g. methanol), with traffic (e.g. C8-aromatic) or with both sources (e.g. benzene). The diurnal cycle is another powerful tool to attribute the main source to each VOC (e.g. wood burning: acetic acid, methylfuran; traffic: toluene, C9 aromatic). A source contribution estimation was calculated using PMF: about 40 % of the measured VOC are attributed to wood burning and 20 % to traffic. At last, some VOC identified as important SOA precursors were measured (as benzene diol) which give interesting input for a better understanding and modelling of SOA formation.

Introduction

Today atmospheric pollution is a well-identified threat both for human health and for the environment. The cities experienced pollution levels exceeding regulatory thresholds. In Paris, particulate matter, nitrogen dioxide and benzene are still an issue. Among the numerous anthropic sources, traffic and wood burning are particularly important.

Baudic *et al.*, (2016) [2] showed that in Paris, in wintertime, wood burning would be responsible for almost half of the measured VOC. This source is also occasionally a major source of particulate matter as demonstrated by Favez & Amodeo (2017) [5] for the pollution episode of December 2016.

In the meantime, the secondary organic aerosol formation is not totally understood [1], even though wood burning is an important emitter of VOC which are SOA precursors [3, 4].

This study hence aims at quantifying the contributions of traffic and wood burning in Paris region towards an estimation of contribution of each source to SOA formation. A particular interest is given to the VOC recently identified by Bruns *et al.* as SOA precursors.

Experimental Methods

This study is based on an intensive PTR-QMS campaign conducted from November 2017 to March 2018. These measurements took place at the SIRTA station, 20 km south-West from Paris. This station belongs to the ACTRIS infrastructure and it is worth noting that the PTR-MS used in this work has successfully participated to the ACTRIS PTR-MS comparison performed in Cabauw, Netherlands, in September 2017. For the present study, compounds masses were scanned from the 21 to the 151 with a measurement time resolution of 15 min.

For a comprehensive study of traffic and wood burning influences, additional datasets have been used, including other compounds measured at the SIRTA station: PM (mass and chemical composition), NO_x, ozone, black carbon, etc. Furthermore, to study the representativeness of our measurements, additional datasets were used for comparisons: VOC and black carbon from several locations in Paris (Airparif data) and VOC measurements from another PTR-MS located at the LISA, in Créteil (10 km south-east of Paris).

An important data processing has been conducted on the measurements. This includes PMF runs as well as other analyses (mostly powered by R and OpenAir as wind roses for instance).

Results

Correlations between BC and VOC

From black carbon (BC) data, we estimated two fractions: BC_{ff} and BC_{wb}, respectively standing for fossil fuel and wood burning. These two fractions were used as tracers and correlations between them and each VOC were calculated. Some VOC were mostly related to wood burning as methanol and m/z 69 (r^2 of 0.78 and 0.68 respectively), while other were mainly correlated with BC_{ff} as toluene and C8 aromatics (r^2 of 0.78 and 0.71). Finally, some VOC as benzene or acetaldehyde were associated with both BC fractions (r^2 benzene-BC_{wb} = 0.73, r^2 benzene-BC_{ff} = 0.74, r^2 acetaldehyde-BC_{wb} = 0.79 and r^2 acetaldehyde-BC_{ff} = 0.74).

Diurnal cycle

The two portions of BC showed a distinct diurnal cycle: BC_{ff} experienced a peak in the morning (9:00 local time) and another one in the evening (19:00 local time) while BC_{wb} showed only one distinctive wider peak in the evening (20:00-22:00 local time), slightly later than the BC_{ff} peak.

The diurnal cycles have been calculated for all the measured VOC and the results can be split into two groups: the wood burning-like pattern (only one peak in the late evening) and the traffic-like pattern (one peak in the morning and one in the early evening).

Contribution estimation

A Positive matrix factorization (PMF) was then applied to this dataset. A solution with three factors was retained (Fig. 1).

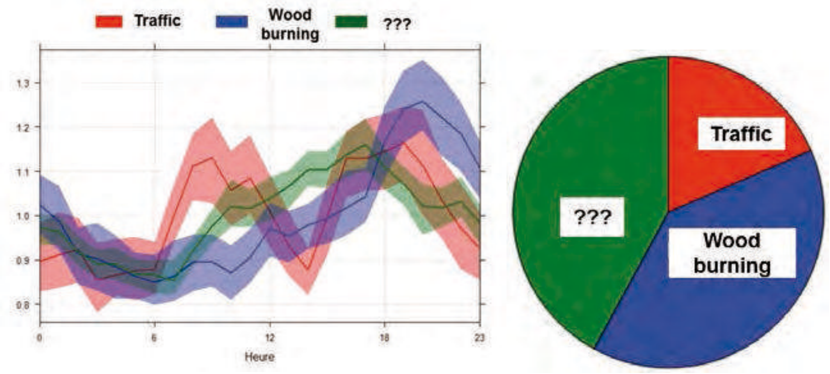

Figure 1: PMF results: diurnal cycle of the three factors (left) and pie chart of the factors contributions (right).

Two factors could be identified as “traffic” and “wood burning” using both their fingerprint (compared with the correlation calculated in the related section) and their diurnal cycle. Although being totally independent, BC fractions diurnal cycle match the factors diurnal cycle, which strengthens the identifications of these two factors. The third one has been preliminary identified as related to solvent use based on comparison with former work on source apportionment in the region [2].

Discussion

Some VOC identified by Bruns *et al.* were also measured in the present study (benzenediol, dimethylfuran, acetic acid) but others were not as phenol and naphthalene. This discrepancy may be due to the loss of VOC into the inlet line.

The PMF gave a contribution of 40 % to wood burning, which is in general agreement with the study of Baudic *et al.* 2016 [2] (≈ 50 %). It is worth noting that different VOC were considered in this study.

Based on this contribution quantification, a further work would be to estimate the SOA attributed to wood burning and traffic.

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Oxidation of volatile organic compounds as the major source of formic acid in a mixed forest canopy

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Abstract

Formic acid (HCOOH) is the most abundant carboxylic acid in the atmosphere but its budget is poorly understood. We present eddy flux, vertical gradient, and soil chamber measurements from a mixed forest canopy by PTR-QiTOF, and apply the data to better constrain HCOOH source/sink pathways. While the cumulative above-canopy flux was downward, HCOOH exchange was bidirectional, with extended periods of net upward and downward flux. Net above-canopy fluxes were mostly upward during warmer/drier periods. The implied gross canopy HCOOH source corresponds to 3% and 38% of observed isoprene and monoterpene carbon emissions, and is 15´underestimated in a state-of-science atmospheric model (GEOS-Chem). Gradient and chamber measurements identify the canopy layer as the controlling source of HCOOH and its precursors to the forest environment; soil and other below-canopy sources were minor. A correlation analysis using an ensemble of marker VOCs implicates secondary formation, not direct emission, as the major source driving ambient HCOOH.

The detection of organic peroxy radicals and study of their autoxidation by proton-transfer ionization

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Abstract

Mass spectrometry with proton transfer ionization at high pressure was used to study the autoxidation of a series of RO_2 (1-butyl, 1-pentyl, 1-hexyl, 1-ethylhexyl, and dimethylhexylO_2) at room temperature in a flow reactor: $RO_2 \rightarrow QOOH\ (k_{iso}) \rightarrow O_2QOOH$ or "QO_2".

Each individual RO_2 was produced photochemically in a flow reactor and both RO_2 and QO_2 were detected. k_{iso} (s^{-1}) was determined from their ratio and from the absolute concentration of RO_2 in the reactor, the later being determined by titration with NO. The results, including the RO_2 signal calibration, and potential effects of relative humidity, will be discussed.

Introduction

Organic peroxy radicals ("RO_2", with R organic) are key intermediates in the oxidation of organic compounds in many chemical systems. In the Earth atmosphere, thousands of different RO_2 are present but, for decades, the lack of detection technique distinguishing between different RO_2 ("speciated" detection) has limited the understanding of their reactivity. Since then, different mass spectrometric techniques have been developed to detect RO_2 and solve this challenge. In particular, proton transfer ionization at high pressure (10 - 600 torr) was shown to be efficient for the detection of RO_2 [1] and used to study their cross-reactions [2]. In the present work, this technique was used to study the autoxidation of RO_2:

$$RO_2 \rightarrow QOOH,\ k_{iso}\ \text{(rate-limiting)}$$

$$QOOH + O_2 \rightarrow O_2QOOH \text{ or "}QO_2\text{" (fast).}$$

These reactions were recently suggested to be significant in the atmosphere, but studied either indirectly, i.e. from stable products formed several reaction steps away, or in complex reaction systems, such as the ozonolysis of alkenes and terpenes. In this work, a series of RO_2 were produced individually in a flow reactor and was monitored directly, together with their corresponding QO_2, which allowed to determine the autoxidation rate, k_{iso} (s^{-1}).

Experimental Methods

The peroxy radicals were produced by the photolysis of organic precursors in a flow reactor. The RO_2 and QO_2 were detected by the CIMS by sampling 30-40 cm below the irradiation zone (Fig. 1). A photoluminescent NOx analyzer (Thermo 42i) was also connected to measure the NO concentration added to the reactor for the calibration of the RO_2 signal (Fig. 1).

k_{iso} (s^{-1}) was determined experimentally from the ratios QO2/RO2, the concentration of RO_2, and the other reaction rates in the systems, according to an expression obtained by solving the kinetic equations:

$$k_{iso} = \frac{[RO_2]}{10^{13}} \times \left[\left(\frac{[QO_2]}{[RO_2]} + \pm 0.8 \right)^2 - 0.64 \right] .$$

Results and Discussion

The results, including the ratios QO_2/RO_2 obtained for each radical, the radicals detection sensitivities, and potential effects of relative humidity will be discussed.

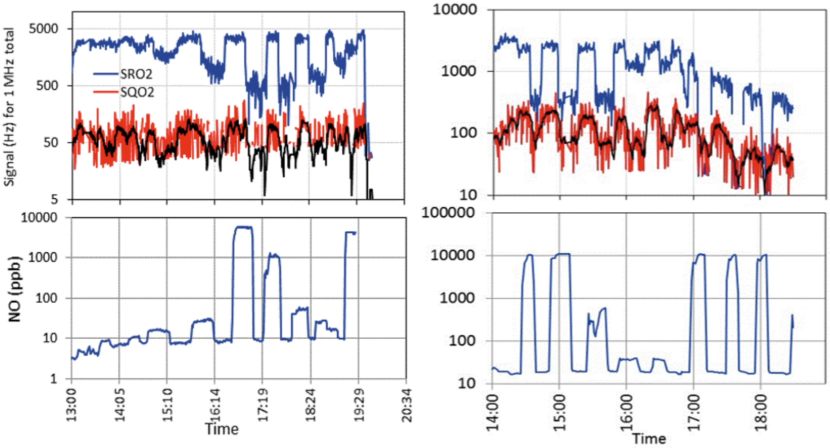

Figure 1: Evolution of RO_2 (blue) and QO_2 (red) in the reactor detected by proton transfer CIMS, (top graphs) and corresponding concentration of NO (bottom graphs) for 1-pentylO_2 (left) and 1-hexylO_2 (right).

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Total OH reactivity changes above the Amazon rainforest during an El Niño event

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Abstract

In the Amazon basin, unprecedented drought and warming occurred during the 2015/16 El Niño event. How tropical forests react to such extreme conditions in terms of volatile organic compound (VOC) emissions is of interest as the frequency of these events is predicted to increase through climate change. The diverse VOCs emitted in response to drought stress can be significant for both the plant-internal and global carbon budgets, they can influence ozone and particle production, and through their reactivity impact OH concentrations. Total OH reactivity is a directly measureable quantity that gives the reaction frequency of OH radicals with all reactive species in the atmosphere in s^{-1}. Here we present a comparison of the OH reactivity diel cycle from November 2015, i.e. extreme drought and elevated temperatures associated with strong El Niño conditions, with November 2012, a “normal” El Niño Southern Oscillation (ENSO)-neutral period. Interestingly, the diel maximum of OH reactivity during the El Niño event occurred at sunset instead of, under normal conditions, early afternoon. The absolute total diel OH reactivity, however, did not change significantly. Daytime OH reactivity averages were 24.3 ± 14.5 s^{-1} in 2012 and 24.6 ± 11.9 s^{-1} in 2015, respectively. Our findings suggest that a combination of stronger turbulent transport above the canopy with stress-related monoterpene and, possibly, other drought specific biogenic volatile organic compound (BVOC) emissions were responsible for the increased reactivity at sunset.

Ecosystem-scale BVOC flux measurements at a poplar bioenergy plantation in Lochristi (Belgium)

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Abstract

The fluxes of 46 ions corresponding to 36 biogenic volatile organic compounds (BVOCs) were continuously monitored with a PTR-TOF-MS (proton-transfer reaction time-of-flight mass spectrometer) along with the exchanges of mass (carbon dioxide and water vapour) and energy (sensible and latent heat) during an entire year in a poplar (Populus) short-rotation crop (SRC), using the eddy covariance methodology. Total net BVOC emissions were 19.20 kg C ha−1 yr−1, which represented 0.63% of the net ecosystem exchange (NEE), resulting from 23.59 Mg C ha−1 yr−1 fixed as CO2 and 20.55 Mg C ha−1 yr−1 respired as CO2 from the ecosystem.

The ecosystem-scale BVOC flux measurements were also used to characterize the BVOC flux dynamics associated to leaf senescence during autumn, loss of canopy greenness and leaf area index. A decrease of isoprene and methanol emissions was observed during late summer as a result of the decline of photosynthetic activity and leaf growth, respectively. At the time of the onset of leaf senescence a peak of BVOCs related to catabolism was observed. The results highlight the importance of canopy-scale BVOC measurements as they are a crucial scale in the leaf-canopy-ecosystem continuum for the future modelling of annual BVOC emission budgets across ecosystem types.

A volatile Arctic: Studies on BVOC release from tundra ecosystems

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Abstract

Arctic ecosystems are characterized by low-statured sparse vegetation, high soil organic matter content and cold temperatures. As the emissions of biogenic volatile organic compounds (BVOCs) are mainly driven by plant biomass and temperature, models predict negligible BVOC emissions for the Arctic. We have challenged this prediction and conducted field campaigns in various vegetation types from the Subarctic to the High Arctic. Many locations lack line power, and therefore the ecosystem plots consisting of a plant community and the soil beneath have been sampled for volatiles using sorbent cartridges and offline analysis by gas chromatography-mass spectrometry. We have shown that the ongoing climatic warming is likely to increase BVOC emissions from arctic tundra several fold higher that at present [1-2]. Also the vegetation changes following warming drive increases in emissions from tundra [3].

In this presentation, we give an overview of our recent and ongoing work on Arctic volatiles using proton transfer reaction-time of flight-mass spectrometry (PTR-TOF-MS). Studies include controlled laboratory experiments on BVOC release from soil and decomposing leaf litter, field studies in climate change experiments as well as ecosystem-scale flux measurements on the tundra with eddy covariance technique.

In laboratory, we have shown that permanently frozen soil (permafrost), that was thawed under real-time monitoring by PTR-TOF-MS, released a large quantity of BVOCs, especially ethanol and methanol [4]. As permafrost is currently thawing in large areas of the Arctic, this could be a new significant source of BVOCs to the Arctic atmosphere. However, our work has also shown that microbial communities in the surface soil efficiently take up BVOCs converting them to CO_2 [5]. Therefore, the net release to the atmosphere depends on the balance between the production at the permafrost thaw front deeper down and the uptake of the compounds in the soil above.

In the field, we have used the PTR-TOF-MS at a mesic tundra heath to assess effects of long-term experimental warming and leaf litter addition on BVOC fluxes in the ecosystem. The preliminary results suggest strong responses to the moderate warming by both terpenoids and lighter hydrocarbons.

Our ongoing work combines eddy covariance measurements of BVOC fluxes to remote sensing of vegetation phenology and surface temperatures on a Subarctic wetland. We have hooked up a PTR-TOF-MS instrument to two eddy masts, one at a dry permafrost palsa area and another at a shoreline between a lake and a sedge-dominated wet fen. Our goal is to assess variations in

surface temperature and plant phenology, and couple these to fluxes of BVOCs between the permafrost-affected ecosystem and the atmosphere.

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VOCs from soil-born fungi and plant-fungi interactions

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Abstract

Fungi release broad and complex spectra of VOCs (Müller et al. 2013, Weikl et al. 2016) which belong to several chemical groups with different biochemical origins such as monoterpenes, sesquiterpenes, alcohols, aldehydes, aromatic compounds, esters, furans, hydrocarbons, ketones, as well as nitrogen- and sulfur-containing compounds. So far, however, most of the studies on fungal VOCs focused on the emissions from single species, and the odor profiles of different fungal or microbial species were rarely compared. To gain information regarding the global VOC emission patterns, we investigated the entire volatilome by GC-MS and online PTR-ToF-MS of 47 different fungal species from different functional guilds (mycorrhiza, saprophytes, pathogens, antagonists) selected from about 350 sequenced fungal species currently available using PTR-ToF-MS analysis and in combination with stir bar sorptive extraction (SBSE) followed by GC-MS analysis. Results show that fungal VOCs expressed phylum- and eco function-based patterns. In addition, PTR-ToF-MS analysis showed advantages in smaller (<C5) compounds detection compared to GC-MS, but remain lacking ability for isomers separation.

Introduction

Volatile organic compounds (VOCs) can mediate biotic interactions between plants, fungi and bacteria. Fungi release broad and complex spectra of VOCs (Müller et al. 2013, Weikl et al. 2016). The ecological significance of these volatiles has rarely been explored (Peñuelas et al. 2014). There is evidence that mycorrhizal fungi prime plant´s defenses, thereby, increasing plant stress tolerance. However, the mechanisms are unclear. Recently, we discovered that Laccaria bicolor, an ectomycorrhizal fungus that forms mutualistic interactions with various tree species, promotes lateral root formation when roots are in aerial contact to fungal-derived sesquiterpenes (Ditengou et al. 2015). Another mycorrhizal fungus (Cenococcum geophilum) lacks sesquiterpene emission and does not induce lateral root formation. The different volatile profiles of the fungi potentially indicate adjustment to different ecological niches. In a previous study (Müller et al. 2013) we characterized and compared the odor profiles of 8 fungal species including 9 strains (four EM, three pathogens and two saprophytes) using SBSE coupled with gas chromatography - mass spectrometry (GC-MS). This study revealed that the fungal species differ in their odor profiles, particularly in the pattern of sesquiterpenes. The functional groups and species could be classified by using their specific emission patterns. Moreover, the different ecological groups could be statistically predicted with probabilities of 90 to 99%, whereas for the individual species the probabilities varied between 55 and 83% (Müller et al. 2013). This study strongly supports the concept that the VOC phenotyping can be used for non-invasive identification of different functional fungal groups.

The current study investigated the VOCs emission from 47 phylogenetically and eco-functionally different fungi using PTR-TOF-MS followed by GC-MS measurement to further confirm the molecular structures of the detected masses and possible separation of isomeric compounds like monoterpenes and sesquitеprenes. Aim of the project was to characterize the overall VOC emission patterns (analysis of all measurable VOCs) of the fungi, and to use these patterns to differentiate them according to their functional group or specie. Data mining provided information whether fungal guilds or phylogenetically related fungal species can be distinguished by typical VOC profiles. Another aim consisted in "chemotyping" the fungal groups and species by using the most relevant volatile compounds as biomarkers for characterization. In follow-up experiments, fungal species from functional groups having strongly contrasting VOC profiles, will eventually be used as "senders" to challenge two exemplary "receiver" plant species, i.e., Arabidopsis and poplar. In these bioassays (head space co-cultivation) we will analyze plant fitness parameters (growth, root surface, biotic and abiotic stress tolerance) and molecular responses.

Experimental Methods

Forty-seven different fungal species from different functional guilds (mycorrhizas, saprophytes, pathogens, antagonists) were selected from about 350 sequenced fungal species currently available for VOCs investigation. In the initial step we developed and tested an on-line microbial VOC screening platform (mVOC-SCREEN) for microbes and fungi. The fast screening of fungal VOCs is performed by PTR-ToF-MS analysis and in combination with SBSE followed by GC-MS analysis.

Results

In this presentation we will give an overview firstly on the setup and proof-of-principle experiments with the mVOC-SCREEN platform and secondly on the chemical diversity of fungal derived VOCs and their use to chemotype species and ecological functions. By PTR-TOF-MS, 65 masses could be detected from the 47 fungi; however, the GC-MS analysis revealed the emission of 205 compounds. Of the 65 masses detected by PTR-ToF-MS, the structural identity of 13 masses could be confirmed by GC-MS. Based on the PTR-TOF-MS data, fungi VOCs expressed phylum- and eco function-based patterns. Finally, in the talk, we will present initial data on fungi-fungi and plant-fungi interactions mediated by fungal VOCs.

Discussion

Fungi are known to emit a large spectrum of volatile compounds. However, so far, fungal VOCs are usually studied in single species for various purposes and rarely compared phylogenetically and functionally. In the current study, we performed a global investigation and comparison of VOCs from 47 fungi belonging to different phylum and functional guilds (mycorrhizas, saprophytes, pathogens, antagonists). Multivariate analysis showed that fungi VOCs express phylum- and eco function-based patterns. In previous studies of fungal VOCs, headspace-solid phase microextraction (SPME) GC-MS has been used as a routine technology for fungal VOCs detection due to its powerful separation and highly sensitive detection capabilities (Matysik et al., 2009). However, due to the limitations of SPME trapping technology, polar and/or smaller compounds (<C5) will be skipped, outputting incomplete VOCs profiles of fungi. Consequently, PTR-ToF-MS in conjunction with GC-MS provide an optimized methodological tool to gain the almost entire volatilome of the different fungal species.

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Source characterization of volatile organic compounds measured by PTR-ToF-MS in Delhi, India

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Abstract

Highly time-resolved volatile organic compounds (VOCs) measurements were performed using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) in winter 2018 in Delhi, India. During the measurement periods, very high concentrations of VOCs were observed, with very high concentrations of anthropogenic VOCs at night and secondary VOCs during daytime. Source apportionment analysis indicate that traffic related emissions were the dominant source at IITD and various solid fuel combustions contributed significantly at night as well. During daytime, oxygenated VOCs are mainly explained by secondary factors suggesting tropospheric transformations of primary VOCs.

Introduction

Volatile organic compounds (VOCs) are important precursors in the production of ozone (O_3) and secondary organic aerosol (SOA) (de Gouw et al., 2005) and thus have an impact on regional air quality and climate (IPCC, 2013). In urban areas, anthropogenic VOCs can be dominant (Borbon et al., 2013), which originate from solvent use, evaporation, industrial processes and especially a variety of combustion processes, including vehicle emissions, biomass burning, coal burning, etc. Previous studies indicate that vehicle emissions could be the dominant source of VOCs in urban areas, while biomass burning and coal combustion could be the major sources of winter time pollution (Müller et al., 2012).

Delhi, the capital city of India, with a population of 18.98 million (2012) people, has been suffering from the most severe air pollution problems in the world. The critical air quality problems have left India with the highest death rate from respiratory disease and asthma. Despite the fact that air quality in Delhi was ranked as the worst of any major city in the world among 1600 cities (WHO, 2015), the pollution levels of VOCs in Delhi are scarcely known. With the fast urbanization, increasing vehicle numbers and various solid fuel combustions, there is a great need to understand VOC emissions and sources in Delhi.

Experimental Methods

In this study, we employed PTR-ToF-MS 8000 to understand the VOC composition in Delhi, and applied positive matrix factorization (PMF) to understand various contributions from primary sources, and their oxidation and further transformation in the urban atmosphere. An intensive campaign was conducted from mid-January to mid-March, 2018 to capture the winter combustion events and change of seasons. The measurement site was on the top floor of an educational building on the campus of the Indian Institute of Technology Delhi (IITD).

Results

The measured VOCs were classified into 7 families, namely aromatics, other hydrocarbons, molecules with one, two, or three oxygen atoms (O_1, O_2 and O_3 containing molecules, respectively), nitrogen-containing, and nitrogen and oxygen-containing. As shown in Figure 1, aromatics and O_1 and O_2-containing molecules were the dominant families, indicating significant emissions of primary sources as well as the formation of secondary VOCs and their potential contribution to high aerosol mass loadings.

Substantial contributions from anthropogenic emissions were identified at night, including traffic related emissions and solid fuel combustions. Traffic related emissions contribute most and are dominated by aromatics. Meanwhile, the solid fuel combustion factors are explained by high loadings of aromatics as well, but are featured with high contributions to phenols and furans, which were observed in emissions from various biomass burning and coal combustion. These combustion factors are prevailing during the whole measuring periods and explained most of the nocturnal VOC concentrations. In the daytime, however, higher levels of secondary compounds were identified than at night. Two secondary VOCs factors are identified by high mass contributions to several O_2 and O_3 containing compounds, which likely originated from a variety of oxidation processes of primary emitted VOCs.

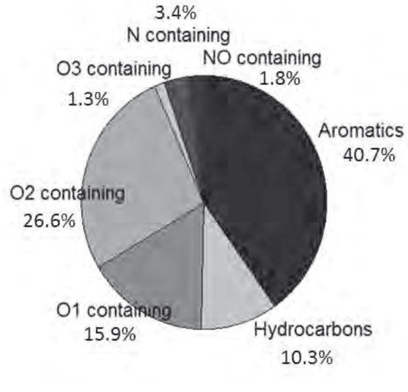

Figure 1: Contributions (percentage of ppb) of seven families of VOCs during the measurement.

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Significant emissions of volatile chemical products in New York City

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Abstract

During winter, significant enhancements of D5-siloxanes and monoterpenes were observed in New York City relative to less populated areas of New Jersey and Long Island. These enhancements clearly correlated with the population density and were not located in the area of biogenic emissions. In summer, biogenic emissions were orders of magnitude larger than in winter, but anthropogenic monoterpene emissions were still dominant in the most densely populated areas. Other tracers for consumer product emissions, such as D5 siloxane, showed little seasonal dependencies. Using CO inventories, we evaluate the emission strength of fragrances and other consumer product emissions and compare these estimates to mobile sources and biogenic fluxes in New York City area.

Introduction

Nitrogen oxides (NOx) and volatile organic compounds (VOCs) emitted into the urban atmosphere have the potential to impact air quality by ozone and aerosol formation. For decades, fossil fuel usage has been considered to be the primary source of urban VOCs in megacities around the world, such as Los Angeles [1]. However, tighter emission regulations in the US and Europe have led to sharp reductions in transportation VOCs such that new sources of pollution have emerged as potentially important precursors to ozone and aerosol formation [2, 3]. McDonald et al. [4] have shown that volatile chemical products (VCPs) are a major, under-studied source of urban VOCs that potentially play a significant role in urban air quality and human health. In industrialized cities, VCPs may make up as much as 50% of the total petrochemical VOC emissions and, consequently, could be responsible for as much as 50% of the mass associated with fossil-derived ozone and secondary organic aerosol (SOA) formation. Unlike emissions from vehicles and energy production, VCPs are emitted from a wide range of human activities over large areas. Quantifying the chemical fingerprint and emission strength is challenging. For instance, a significant fraction of VCPs originate from use in residential or commercial buildings, and emitted via building exhaust. These “indoor” VCPs, which include cleaning and personal care products, constitute approximately 50% of VCP emissions and are composed of oxygenated molecules that could form SOA efficiently and fragrances such as monoterpenes that are very efficient ozone precursors [4].

Experimental Methods

The NOAA CSD proton transfer reaction-time of flight-mass spectrometer (PTR-ToF-MS) [5] and integrated whole air sampler (iWAS) [6] systems were deployed in NYC, and are state-of-the-art instruments that are designed to measure the chemical fingerprint of emissions from a wide spectrum of industries. The measured VOCs include several hundred different VOCs many of which are not routinely measured by state or federal agencies. In addition, methane was measured with a Picarro analyser and CO with a Los Gatos Research analyser. Using these instruments, we have the ability to identify specific VOC markers indicative of various human activities, such as energy usage (e.g. mobile emissions, home heating), solvent application (e.g. painting, application of personal care products), and cooking.

Results

VOCs emitted from anthropogenic and natural sources often contain chemicals that are unique to the specific emission source. These chemical markers are useful in identifying pollution sources and constraining emissions from different sectors. The fingerprints for traditionally-studied urban sources are well-known (e.g. small aromatics like benzene and toluene for tailpipe emissions, cyclic alkanes for oil and natural gas), but fingerprints for non-combustion sources such as consumer products and cooking have not been well-established. Primary oxygenated compounds, which likely result from VCPs or cooking emissions, have been observed in urban air [7]. Presently, several VOCs linked to emissions from personal care products, adhesives, dry cleaning, and coating applications have been identified in the NYC dataset (Figure 1).

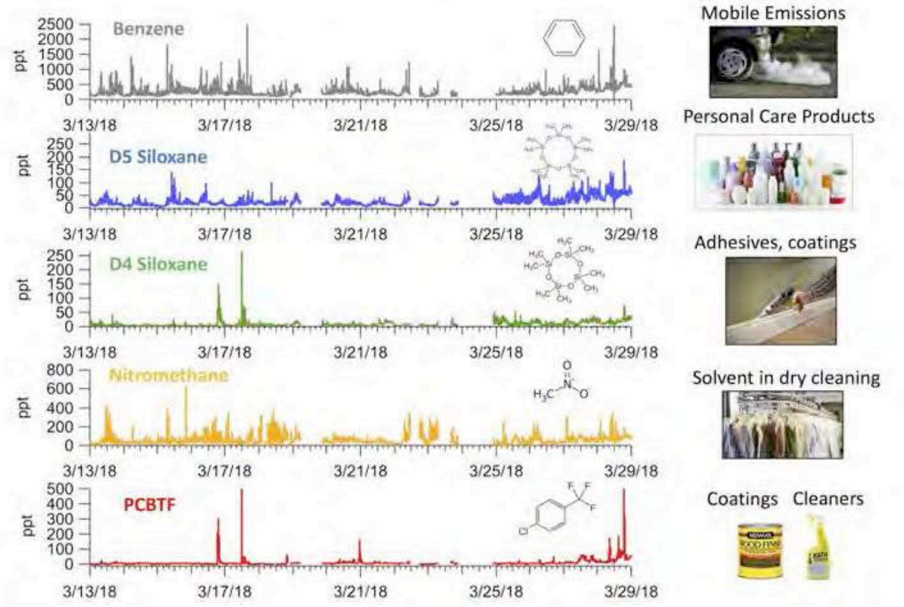

Figure 1: Temporal profile of select VOCs from NYC in March 2018. To the right are likely emission sources.

Mobile measurements can be used to map out the spatial distribution of VOC emission sources. During winter, significant enhancements of monoterpenes were observed in New York City relative to less populated areas of New Jersey and Long Island. These enhancements clearly correlated with the population density and were not located in the area of modeled vegetative emissions. In Manhattan, the monoterpene distribution was dominated by limonene, which is the most commonly used fragrance, whereas alpha- and beta-pinene dominated in wooded areas, which are the dominant biogenic monoterpenes. In summer, biogenic emissions were orders of magnitude larger than in winter, but anthropogenic monoterpene emissions were still dominant in the most densely populated areas. Monoterpenes are very reactive and can strongly contribute to ozone and PM2.5 formation, especially limonene, which is the most commonly used monoterpene in consumer products. Other tracers for consumer product emissions, such as D5 siloxane, showed little seasonal dependencies. Using CO inventories, we evaluate the emission strength of fragrances and other consumer product emissions and compare these estimates to mobile sources and biogenic fluxes in New York City area.

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Comparison of different VOC measurement techniques in Shenzhen, China

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Abstract

In this study, four independent instruments were deployed to monitor ambient VOCs during autumn 2018 at an urban site in southern China, where is characterized by high concentrations of ozone (O3). A novel Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS 6000X2) and a Proton Transfer Reaction Quadrupole Mass Spectrometer (PTR-QMS) were employed during this campaign. Besides, two Online Gas-Chromatograph coupled to a Mass Spectrometer (Online GC/MS; one is Agilent, the other is from SHIMADZU) were simultaneously applied for measurement.

The higher mass resolution of PTR-TOF-MS 6000X2 could distinguish the nominal m/z 69 which measured by PTR-QMS. We found that a stronger correlation between the sum (m/z 69.0699 and m/z 69.0335) and nominal m/z 69 was better than that with m/z 69.0699 (isoprene). Toluene has been identified as a higher activity compound which was dominated by vehicular emission, solvent usage and industrial activities. The mixing ratio of toluene measured by PTR-QMS was higher than PTR-TOF-MS 6000X2 and Online GC/MS, especially during heavy pollution period. Contrarily, the sum of monoterpenes measured by PTR-TOF-MS 6000X2 was 15 % higher than that measured by PTR-QMS. Greater correlations (R>0.94) were found in the species which measured by the two PTR instruments than that by GC-MS, which was mainly due to the discrepancy in the resolutions and measurement methods.

Experimental Methods

The novel instrument PTR-TOF-MS 6000X2 was applied in this study, the single spec time was 5 seconds, and the expected mass range was 225.6 amu.

The PTR-QMS could determine 17 compounds at the same time, and the time resolution was 30 seconds.

Two online GC/MS were used during this campaign. One was based on 7820A/5977E, Agilent. The other was based on GC-QP2010, SHIMADZU. The time resolution was 1 h, and could quantify 113 compounds simultaneously.

The sampling site was on the campus of Peking University Shenzhen Graduate School (23.5925°N, 113.9711°E; 20 m a.s.l.) located in the western urban area of Shenzhen, and there were no anthropogenic pollution sources nearby except a local road approx. 100 m far away. The sampling inlets for ambient air were setup approximately 15 m above the ground level.

Results

The mixing ratio of isoprene (m/z 69.0699) were between 10 and 1500 pptv during the measurement campaign. Figure 1 demonstrates the time series of m/z 69.0699 ($C_5H_8H^+$, isoprene), m/z 69.0335 ($C_4H_4OH^+$, furan) that detected by PTR-TOF-MS 6000X2 and the nominal m/z 69 which measured by PTR-QMS. The correlation between m/z 69 measured by QMS and the sum (m/z 69.0699 and m/z 69.0335) was better than that only with m/z 69.0699 (isoprene), which suggest that isoprene measured by QMS may be overestimated.

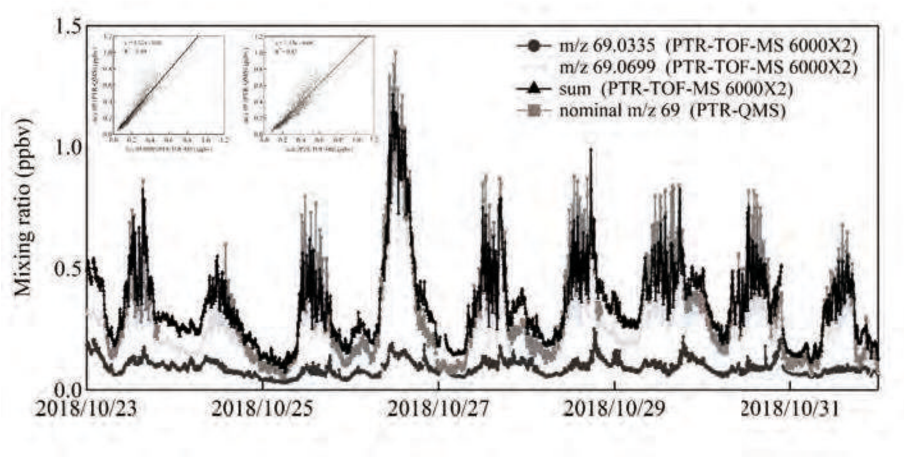

Figure 1: Comparison between isoprene measurements from PTR-MS at the nominal m/z 69 and the sum of the two relevant peaks found at the m/z 69.0995 ($C4H4OH^+$) and m/z 69.0699 ($C5H8H^+$) by PTR-TOF-MS 6000X2.

Figure 2 shows the comparison of toluene measured by four instruments during this campaign. Toluene is an activity compounds which has many sources like traffic and industrial activities. PTR-QMS has higher mixing ratio than PTR-TOF-MS 6000X2 and Online GC/MS, especially during the heavy pollution period, indicating that there may exist some other compounds nearly m/z 93.

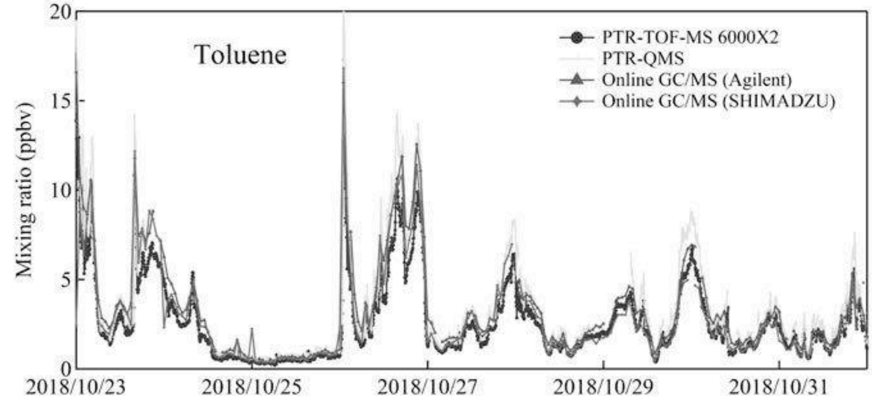

Figure 2: Time series of toluene of the PTR-TOF-MS 6000X2, PTR-QMS, Online GC/MS (Agilent) and Online GC/MS (SHIMADZU).

Figure 3 depicts the time series of monoterpenes measured by PTR-TOF-MS 6000X2 and PTR-QMS. For monoterpenes, no standard gas was used to help quantify its mixing ratio by PTR-TOF-MS, while the standard gas of monoterpenes was used by PTR-QMS. We found that the trends of the diurnal variations were remarkably identical, and the correlation was good (R^2=0.89).

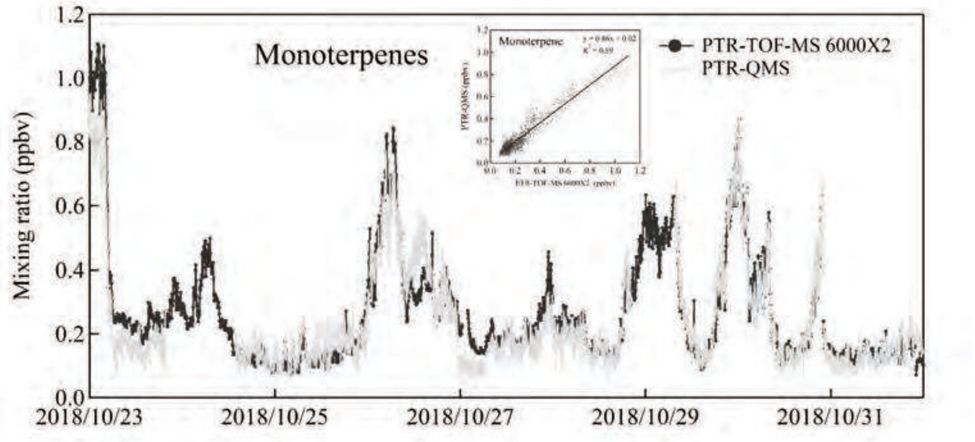

Figure 3: Time series of the PTR-TOF-MS 6000X2 and PTR-QMS monoterpene.

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Applications in Food Science

Dynamic headspace analysis of sunlight flavor during the photochemical oxidation of methionine-riboflavin

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Abstract

Methionine and riboflavin are key reactants in the development of light-induced off-flavors. However, the formation of these volatiles during the early stages of light exposure is still unclear. To provide new insights into the light-induced oxidation of milk, methionine and riboflavin model solutions were exposed to fluorescent light for up to 6 h and the volatiles generated were monitored in real-time by proton transfer reaction mass spectrometry (PTR-MS). Upon light exposure, methionine underwent a series of reactions, including the rapid formation of methanethiol. The formation of methanethiol appeared to occur through two simultaneous paths, which were oxidative degradation of methional and directly from methionine. The occurrence of the latter path was supported by the formation of methanethiol even when the formation of methional was blocked by reduction amination and the absence of other expected degradation products that should have been produced simultaneously with methanethiol. Tannic acid was the most effective antioxidant to limit the formation of methanethiol. Overall, such findings will extend the understanding of the light-induced off-flavor development in milk.

Introduction

The degradation of sulfur containing amino acids, such as methionine, have been identified as responsible for the initial flavor defects in light-exposed milk. In the presence of riboflavin and light, methionine is transformed to methional, which, in turn, lead to a cascade of further volatile organic compounds, such as methanethiol, dimethyl disulfide (DMDS), dimethyl sulfide (DMS) and hydrogen sulfide[1,2]. The oxidative degradation of methionine to methional and then to methanethiol is relatively well accepted. However, methional has not always been detected in milk exposed to light1[3,4]. This has raised questions about its relative role in the formation of methanethiol. Overall, the mechanisms of volatile organic compound (VOC) evolution during the early stages of light exposure remains unclear[1].

To gain an improved understanding of the VOCs formed during the early stages (0 to 6 h) of light exposure, PTR-MS was used to monitor VOC release from a methionine-riboflavin model solution during light exposure.

Experimental Methods

Methionine model solution consisting of methionine (75 mg.L^{-1}) and riboflavin (1.7 mg.L^{-1}) in 100 mL deionized water or in TRIS buffer (0.1 M, pH 8.0) was prepared. For the aldehyde blocking experiment, sodium cyanoborohydride (5.0 M in 1.0 M NaOH) was added (10 µL.ml^{-1}) to methionine model solution in TRIS buffer. Finally, both model solution and milk samples (150 mL) were transferred into 250 ml glass and exposed to fluorescent light (irradiance intensity 14.12 Wm^{-2}). Control samples were kept foil-wrapped for the measurement duration.

Dynamic headspace analysis was performed using a high-sensitivity PTR-MS (Ionicon, Analytik GmbH, Austria). PTR-MS operating conditions as described by Beauchamp et al[5] except the drift temperature was 70°C resulting, E/N ratio of 136 Td and mass scan range was m/z 21-170. The signal intensities were normalized primary ion signal (H_3O^+), water cluster $H_2O.H_3O^+$), m/z specific transmission efficiency and drift tube pressure. Response of methional was corrected based upon the fragmentation of a methional standard.

Results and discussion

Methionine model solution under light and dark:

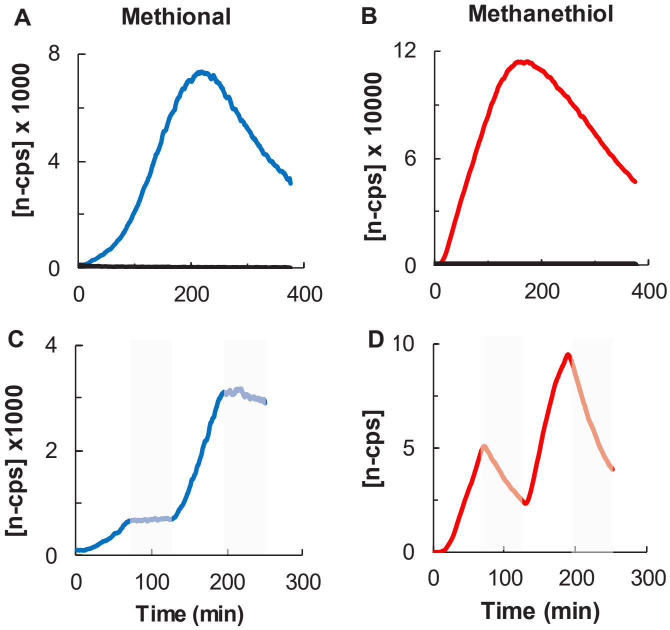

Figure 1: Release profiles of methional (Blue) and methanethiol (red) from methionine model solution, either exposed to light (A and B) or held in dark (black line) up to 6 h and light alternatively turned on and off (1 h each, grey shaded) along 4 h (C and D).

The dynamic release of selected VOC were measured from methionine and riboflavin solutions (pH 8.0) exposed to continuous light, no light or intermittent light and dark periods (Figure 1). In the absence of light the the signal intensity of methional (m/z 61) and methanethiol (m/z 49) were negligible (Figure 1A and 1B). During intermittent light and dark periods (1 h each) for 4 h methional and methanethiol evolution increased in the presence of light and ceased in the dark (Figure 1C and 1D), demonstrating that their formation was entirely ascribed to the photooxidative break down of methionine[5,6]. Upon exposure of methionine to light, the signal intensity of methanethiol increased within 2.5 min reached its highest signal intensity (peak max. 121018 ± 6000 n-cps) at 170 min. Whereas, methional not detected until after methanethiol (about

5.3 min), initially increased slowly (up to 100 min) then evolved quickly to peak max (8269±800 n-cps) at 215 min. The dynamic release profile data together with the formation kinetics of other degradation products suggests the possible existence of simultaneous routes of methanethiol formation during the initial stage (<100 min) of light exposure.

Blocking methional functionality by reductive amination:

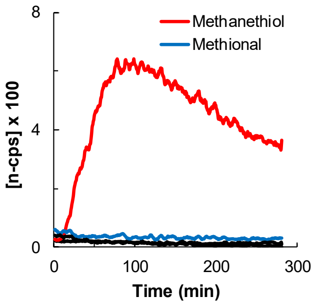

Figure 2: Signal intensity of methional (Blue) and methanethiol (red) from methionine model solution in TRIS buffer (reductive amination) either exposed to light or held in dark (black line)

To further investigate the formation of methanethiol the methional functionality was blocked by mixing the methionine model solution with sodium cyanoborohydride in TRIS buffer (pH 8.0, 0.1 M)[7] and exposing the solution to light. **Figure 2** shows the signal intensity evolution of methional and methanethiol up to 4.5 h of light exposure. Upon exposure to light signal intensity of methanethiol increased rapidly as observed in **Figure 1.** However, no commitment increase in the signal intensity of methional (m/z 61) was observed. This supports the findings that during the early state of light exposure, the photochemical oxidation of methionine result in the direct formation of methanethiol without the presence of intermediate compound "methional".

Natural antioxidant to control the photooxidation of methionine:

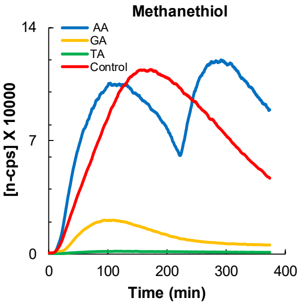

Figure 3: Release profiles of methanethiol from methionine model solution with different antioxidant (0.5mM) exposed to light up to 6 h. Where, TA= tannic acid, GA= gallic acid and AA= ascorbic acid

To reduce the photooxidative degradation of methionine in model solution, the effect of three antioxidants (tannic acid, gallic acid and ascorbic acid) were studied. Figure 3 showed the evolution of methanethiol signal in presence corresponding antioxidants (0.5 mM). Tannic acid, was most effective in decreasing the amount of methanethiol released followed by gallic acid and ascorbic acid was least effective. Though ineffective at preventing an increase in methanethiol release during photooxidation of methionine ascorbic acid resulted in an unusual methanethiol release pattern whereby two maxima were observed.

Conclusion

In a model system of methionine and riboflavin light-induced oxidation led to the formation of methanethiol through two simultaneous paths which appeared to be oxidative degradation of methional and directly from methionine. The occurrence of the latter path was supported by the formation of methanethiol even when the formation of methional was blocked by reduction amination and the absence of other expected degradation products that should have been produced simultaneously with methanethiol. Tannic acid was the most effective antioxidant to limit the formation of methanethiol. The present study demonstrates the utility of PTR-MS in characterising fast oxidation reaction and off flavour development during early stage of light exposure.

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Beyond calibration: misappropriation of the LCU to quantify liquid-phase concentrations of volatiles in aqueous samples

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Abstract

After finding footing in food-flavour research over two decades ago, it is no great revelation now to assert the strengths of PTR-MS in its ability to characterise fast flavour release processes, an obvious example being nosespace analysis of aroma release during food mastication. The Achilles heel of PTR-MS in this applied research field, however, is its limitation to analyse only in the gas-phase, thereby occluding an area of equal importance, namely the qualitative and quantitative determination of aroma compounds present in the (solid or liquid) food matrix itself. To address this issue, we used a liquid calibration unit (LCU) to volatilise aroma compounds present in liquid foods to enable their direct detection and quantitation in the gas-phase by PTR-TOF-MS and subsequently calculate the liquid-phase concentrations of targeted aroma compounds in the original matrix based on the LCU operating parameters. A proof-of-concept is reported herein based on the example of quantifying phenol in a selection of Scotch whiskies from the western isle of Islay, which are characterised by their smoky, peaty aroma that is associated with the presence of phenol and related compounds. The results yielded phenol concentrations in the range of 2.6-6.1 ng/µL, which were comparable to literature reports of the analysis of similar whiskies by conventional gas-chromatography (GC). To summarise in one word: Sláinte.

Introduction

Broadly speaking, food scientists investigating aroma are interested either in the (degree of) aroma compounds bound within the matrix of a food, or wish to characterise the release of flavour compounds from the food under specific conditions (e.g., during processing or preparation, storage, spoilage, consumption, etc.). For the past two decades, PTR-MS has been an attractive alternative or complement to conventional headspace analysis by gas chromatography (GC) owing to its high time resolution that gives access to observations of fast processes. One particular weakness of PTR-MS in this field, however, is that any attempts to determine aroma compound quantities in the food matrix itself based on their gas-phase concentrations in the food headspace is a complex and highly challenging if not impossible endeavour, depending on the food in question.

The established method to quantify individual aroma compounds within the matrix of foods is a lengthy process requiring laborious sample preparation and extraction followed by chromatographic separation and subsequent detection. In addition, accurate quantitation requires the use of isotopically-labelled standards for each of the target aromas, which are added to the sample at defined quantities at the outset in order to compensate for losses during sample workup; this is the premise of stable-isotope dilution analysis (SIDA).

In recent years, the development of peripheral interfaces such as the LCU and fastGC has extended the power of PTR-MS by broadening the range of accurately quantifiable target compounds and offering the possibility to separate certain isomeric compounds [1]. Focussing on the LCU, this dynamic calibration system obviates the need for gas standards by generating accurate, stable and variable levels of individual target compounds in the gas-phase via the use of bespoke aqueous solutions [2]. In brief, two micro-pumps differentially pump the aqueous solution (containing the target compound(s)) and pure water at user-defined rates – but constant total flow – through a nebuliser into an evaporation chamber that is heated to 100 °C to promote and maintain the gaseous state of volatiles from the solution. By changing the flow rates through the pumps the quantity of target compounds being volatilised in the chamber can be varied.

Experimental Methods

Equipment, chemicals and samples

A LCU (advanced model) and PTR-TOF 8000 (both IONICON Analytik, Innsbruck, Austria) were used for the present trials. The PTR-TOF-MS was operated with reaction chamber conditions of 600 V (extraction, 35 V), 2.2 mbar, and 60 °C, Phenol (99 % purity; Fluka, Steinheim, Germany) was used for calibration purposes. Whiskies investigated (with attributed sample code in brackets and % alcohol by volume (ABV) in parentheses) were: Laphroaig Quarter Cask Islay Single Malt Scotch Whisky [LAPH QC] (48 % ABV), Laphroaig PX Cask Islay Single Malt Scotch Whisky [LAPH PX] (48 % ABV), Bunnahabhain Single Malt Scotch Whisky Aged 8 Years [BUNN] (43 % ABV), Lagavulin Islay Single Malt Scotch Whisky Aged 16 Years [LAG] (43 % ABV), The Arran Malt Single Malt Scotch Whisky Aged 10 Years [ARRAN] (46 % ABV), and Nikka Coffee Grain Whisky [NIKKA] (45 % ABV); the latter two samples were not Islay whiskies and were analysed for comparison. Samples were diluted to ~5 % v/v in distilled water to reduce the amount of ethanol being vaporised by the LCU and limit or avoid primary ion sequestration.

Calibration of phenol

The PTR-TOF-MS instrument was connected to the LCU in the usual configuration, i.e., by inserting the inlet capillary (1/16” OD, 0.04” ID PEEK) into the evaporation chamber of the LCU, with the inlet heating hose (80 °C) connected to the housing of the LCU to avoid cold spots along the transfer line. The instrument was initially calibrated for phenol, whereby the MH^+ signal at *m/z* 95.051 was observed to be the predominant product ion and was used to represent phenol for all subsequent analyses. The calibration run and resulting calibration curve are plotted in figure 1.

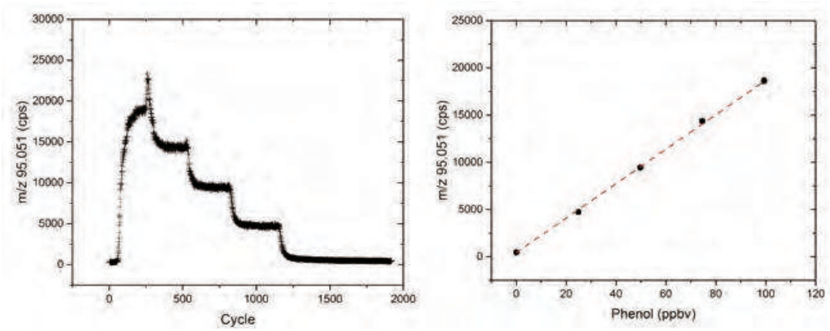

Figure 1: Calibration of phenol (detected at m/z 95.051) using the LCU, with four concentration steps (left) and the corresponding calibration curve (right).

A dram of Scotch

The analyses of whisky samples proceeded similarly to the calibration, albeit with the calibration solution replaced with the individual whisky samples, diluted in 5 % v/v water. The pump flow rate for a whisky sample was initially high and successively reduced over several steps in order to find a compromise between the phenol signal intensity and the primary ion signal stability, as depicted in figure 2. After a low initial background the signal of phenol increased rapidly upon activating the pump to purge the whisky solution via the nebuliser into the evaporation chamber of the LCU (at around cycle 120). After quickly reaching stability, the sample flow rate was reduced in two successive steps. At a pump flow rate of 10 µL/min the primary ion signal had recovered sufficiently – despite the continual presence of high levels of ethanol – and phenol elicited a stable signal. The data from this section of the analysis (annotated in figure 2) were used to calculate the phenol content of the individual samples.

Calculation of phenol concentrations in the samples was made as follows. The gas-phase concentration of phenol from the selected period of whisky analysis during LCU operation was calculated from the raw signal intensities using the sensitivity value for phenol, as determined in a prior calibration (cf. figure 1). The calculation tool provided with the LCU (by IONICON) to determine the required aqueous-phase concentration of a target compound in order to generate a desired gas-phase concentration in the LCU was used in reverse: the gas-phase concentration detected via the LCU together with knowledge of pumping rates and the physicochemical properties of phenol allowed for calculation of the amount initially present in the liquid-phase. Taking into account the dilution of the whisky in water, the actual concentration of phenol in the whisky could be thus calculated.

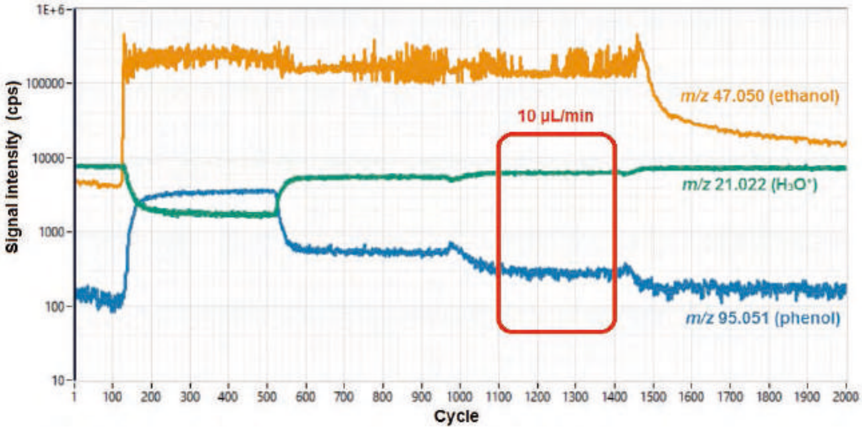

Figure 2: Raw signals of H_3O^+ (detected via its isotopologue at m/z 21.022), ethanol (m/z 47.050) and phenol (m/z 95.051) during the volatilisation of 5 % v/v aqueous solution of Islay Scotch whisky. After analysing an initial background the sample was injected into the evaporation chamber of the LCU at successively reduced pumping rates, as is observable by the decreasing signal intensity of phenol (and successive recovery of the primary ion signal).

Results

The concentrations of phenol in the whisky samples were as follows: LAPH QC; 4.3 ng/µL, LAPH PX; 6.1 ng/µL, BUNN; 4.7 ng/µL, and LAG; 2.6 ng/µL. Phenol was not detected in the samples ARRAN and NIKKA, which was expected as these were not Islay whiskies and do not exhibit the peaty aroma that is characteristic of those whiskies. A comparison with the literature revealed that these concentrations are within the range found for phenol in peaty whiskies. An application note on the use of stir-bar sorptive extraction (SBSE) with GC-MS analysis, for example, quantified phenol in two peaty whiskies (of unspecified origin) as 3.7 and 4.8 ng/µL [3].

Discussion

This proof-of-concept trial shows how use of the LCU gives access to determining the liquid-phase concentrations of targeted compounds within a liquid matrix, such as alcoholic beverages, as demonstrated in the present study. The work involved is less laborious by far than in conventional quantitative methods using GC-MS in that sample preparation is quick and easy (a simple dilution of the beverage in distilled water) and the analysis equally so, with screening of a single sample achievable within a matter of minutes rather than hours.

It should be noted that the mass spectra of the whisky samples are very rich in features, thus other compounds could be similar quantified in this manner. Specifically in relation to the Islay whiskies, for example, further compounds are associated with the peaty, smoky aroma, namely cresol (*m/z* 109.065), 4-ethyl phenol (*m/z* 123.080), guaiacol (*m/z* 125.060), and 4-ethyl guaiacol (*m/z* 153.091), all of which were detectable in the present samples but were not (yet) further quantified. One caveat of this approach is that *a priori* knowledge of the sample constituents is beneficial – if not essential – in order to ensure certainty in the detection of the specific target compounds of interest, as well as to enable prior (or subsequent) calibration of the PTR-MS system for those compounds. The additional implementation of the fastGC would further broaden the spectrum of analysis by allowing the discrimination of isomeric compounds in many cases.

Acknowledgement

The idea to (mis)use the LCU to quantify volatile constituents of aqueous samples came about in discussions between myself, a colleague Mohamed Mahmoud, and Franco Biasioli – the authority on PTR-MS applications in flavour science – on a 'road trip' from Bologna to San Michele, Italy, after attending the 5th MS Food Day in October of 2017. Franco's suggestion to analyse off-flavoured water samples in this manner soon transmuted into targeting a different kind of water – *uisce beatha* – the water of life, or whisky in today's vernacular.

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Does the tapping dispenser system influence the aroma of beer?

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Abstract

Beer is one of the most consumed alcoholic beverage in the world. The fresh aroma is one of the main characteristics for consumers and it is strongly affected by microorganisms growing in the dispensing system. A patent for a new tapping dispenser system has been recently filed. Here, the results of the headspace analysis of lager beer taken from barrel and dispensed through traditional and the new dispenser system are reported.

Introduction

The term "beer" refers to very wide range of fermented beverages produced from different malts, brewing water, varieties of hops and two species of yeast top- and bottom-fermenting (*Saccharomyces cerevisiae* and *Saccharomyces pastorianus*, respectively) [1].

The most appreciated sensory characteristics by consumers is fresh flavor [2], therefore flavor stability is an important quality feature and a concern for the brewing industry [3, 4, 5].

The tapping dispenser system and thus, the cleaning of the dispense tap, has a major impact on the aroma perception of beer [6, 7].

Quaglia and collaborators of SQC Systems S.r.l. filed in 2017 an Italian patent application and in 2018 an international one on a new tapping dispenser system with a related procedure for the treatment of the tapping tubes [8, 9]. The patented dispenser system, Titazero, consists of a sensor, which informs the control unit that the beer barrel is finished. Then, the central unit starts the cleaning process, using water only, avoiding any kind of chemical or mechanical cleaning agent. The automatic cleaning process is followed by the manual substitution of the new beer barrel.

PTR-MS has been largely used in the monitoring of food processes involving aroma release in beverages, such as wine and vodka [10], but very little has been published on beer.

Here, the headspace of lager beer samples from beer barrels and dispensed through traditional and the new, Titazero, dispensing systems are analyzed by PTR-QMS.

Experimental Methods

PTR-QMS Headspace Analysis

Lager beer samples from beer barrels and dispensed through traditional and Titazero dispensing systems were provided by SQC Systems S.r.l.. Samples were labeled with "F" (beer barrel), "N" (traditional dispensing system) and "T" (Titazero dispensing system). A number was added after the letter N or T, indicating the number of months passed since the last mandatory sanitation by Italian law. Samples were kept at -20 °C until the analysis.

The headspace of beer samples was measured by PTR-QMS (Ionicon Analytik GmbH, Innsbruck, Austria). To avoid saturation of the mass spectrometer and the consequent depletion of the primary ion, 100 µL of beer samples were placed to equilibrate in 40-mL glass vials at 25 °C for 15 min. The instrumental conditions were the following: drift voltage 600 V, drift temperature 70 ^{o}C, inlet temperature 70 ^{o}C and drift pressure 2.20 mbar, affording an E/N value of 141 Townsend (1 Td = 10^{-17}cm^{2} V^{-1} s^{-1}).

Five replicates for each samples were analyzed. The measurement order was randomized to avoid possible memory effect. Four empty vials were analyzed and considered as blanks. The signal intensities were corrected and normalized as previously described [11], with the following equation:

$$\text{ncps}\left(\text{RH}^{+}\right)= \frac{\text{cps}\left(\text{RH}^{+}\right)\cdot 10^{7}\cdot \text{trasmission rate}}{500\cdot \text{cps}\left(\text{H}_{3}{}^{18}\text{O}^{+}\right)\pm\pm\text{cps}\left(\text{H}_{2}\text{O}\cdot\text{H}_{3}\text{O}^{+}\right)} \quad (1)$$

Where ncps(RH^{+}) is the normalized count rate for each ion intensity, cps(RH^{+}) is the counts per second of each ionized molecule, cps $\left(\text{H}_{3}{}^{18}\text{O}^{+}\right)$ is related to the primary ion (m/z 21) and cps $\left(\text{H}_{2}\text{O}\cdot\text{H}_{3}\text{O}^{+}\right)$ to water cluster (m/z 37).

Statistical Analysis

Fingerprints obtained by the five replicates were averaged. Afterwards, one way - Analysis of Variance (ANOVA) was performed on PTR-QMS dataset. The differences among samples were visualized performing a Principal Component Analysis (PCA) of the masses selected by ANOVA. All the statistical analysis were performed using XLSTAT 2017: Data Analysis and Statistical Solution for Microsoft Excel (Addinsoft, Paris, France, 2017).

Results and Discussion

Figure 1 shows the results of the PCA performed on the masses selected by the ANOVA ($p < 0.05$). Beer sample from barrel (F) is characterized by high negative values for both PCs. Samples dispensed by the traditional dispensing system (N0, N1 and N2) are on the opposite site of the graphic; on the contrary, samples dispensed by the Titazero system (T0, T1 and T2) can be found near the sample F. It is possible to detect a clear separation among the samples N and T. Moreover, a trend due to timing is observable in both groups. Samples dispensed just after the sanitation mandatory by law (T0 and N0) are the one closer to the barrel sample. After 1 and 2 months, the samples are characterized by less negative values for PC1. Thus, PC1 is probably related to time, while PC2 to differences due to the dispensing system.

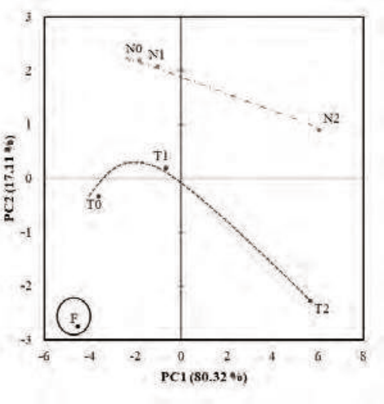

Figure 1: PC2 vs. PC1 plot of the masses selected by the ANOVA.

Figure 2 shows the counts per second of some of the ion fragments selected by the ANOVA. All ion fragments, with the exception of m/z 45 and 61 (tentatively identified as acetaldehyde and acetic acid, respectively) show the same trend: low counts in the barrel sample and increasing counts during time in both the N and the T samples. It is interesting to point out that the amount found in the T1 samples is often lower that the one found in the N0 samples. This trend suggests that the beer dispensed through the Titazero system undergoes the spoiling process at a lower rate, compared with the beer dispensed through the traditional system.

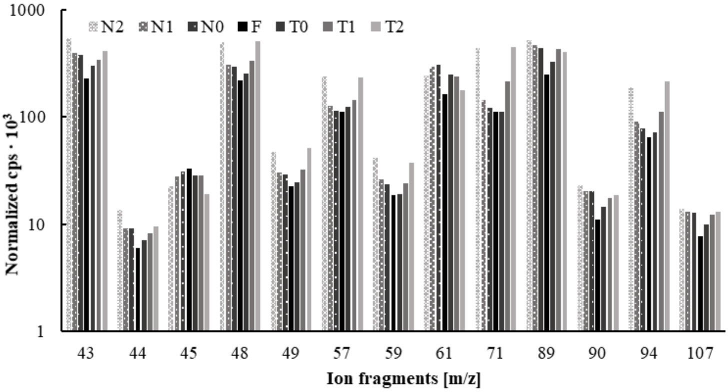

Figure 2: Normalized cps (· 10^3) of some ion fragments selected by ANOVA

Most of the selected masses (m/z 43, 44, 57, 61, 71 and 89) are related to acids [12] produced by the metabolism of microorganisms typically found in the dispenser systems (*Lactobacillus*, enterobacteria, *Pectinatus*, *Megasphaera*) [7]. M/z 90 (tentatively identified as ethyl carbamate) is a group 2A carcinogen; it has been detected in yeast-fermented beverage as a result of the reaction of ethanol with urea, a product of the metabolism of yeast [13]. Acetaldehyde (m/z 45) is the precursor of ethanol during fermentation. Afterwards, bacterial metabolism and oxidation can reduce acetaldehyde to acetic acid [14]. Benzaldehyde (m/z 107) is a typical off-flavor found in beer due to oxidation and aging processes. Samples dispensed through the Titazero system show a slower spoiling process compared to the beer samples dispensed though traditional the tapping system.

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High performing VOC phenomics to improve fruit quality

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Abstract

Fruit quality can be defined by the achievement of four key factors: appearance, flavor, texture and nutritional properties. Among them, flavor directly impacts the consumers' appreciation, therefore the fruit marketability. Although the importance of these factors can hardly be underestimated, breeding efforts have historically been oriented to improve mostly fruit appearance and storability. However, often, selection for yield, fruit size, color, and shelf life properties had unintended negative consequences on other fruit quality traits, such as taste and aroma [1]. Defining and quantifying these quality components, in relation with distinct segments of the production chain, needs comprehensive investigations and a tight synergy of analytical approaches, with a particular focus on rapid and non-invasive methods. Understanding the stability of each quality trait during different storage and growing conditions may allow a better definition of future breeding strategies aimed, for example, at the selection of accessions suitable to improve distinct markets.

The monitoring of volatile organic compounds (VOCs) produced by fruits and vegetables needs analytical techniques that are capable of dealing with challenging issues: i) the need of separating and quantifying VOCs in complex gas mixtures, ii) the need to detect concentrations that may span a large range, from trace levels to parts per million and iii) the need to track concentrations that rapidly change over time. Because of these experimental constraints, the ideal methodology for VOC monitoring should be highly selective, with high sensitivity and dynamic range, and with high time resolution [2].

Non-chromatographic techniques, based on direct injection mass spectrometric (DIMS) VOC assessment, are receiving great interest mainly i) because of their capacity to carry out rapid, high-throughput measurement of large sample sets without affecting samples and without interfering with the VOC production process and ii) because the possibility of rapid process monitoring. Besides its technological performances (e.g., sensitivity and selectivity), advanced DIMS is also increasingly being used because of its stability since the mass/charge ratio does not vary with the experimental conditions. However, the greatest difficulty arising in DIMS, due to the lack of chromatographic separation, is the need to identify hundreds of compounds produced by fruits.

The fruit breeding research activity at the Foundation E. Mach, based on genomics, sensory and conventional characterization tools, has been recently complemented with advanced DIMS phenotyping tools, such as PTR-ToF-MS, and with tailored pre- and post-harvest studies aimed to simulate the entire fruit production chain. This synergism of novel analytical approaches is fully applied into the breeding activities of blueberry, raspberry, strawberry, and apple in order to develop new cultivars characterized by both prolonged storability and high perceived quality.

comprehension of the genetic and physiological aspects controlling fruit quality. These studies, for instance, allowed to determine the possible interaction between genetic variability and fruit ripening stages on the aroma development of different fruit species during cold conservation at different atmospheric condition, to develop several genetic and molecular markers [3-6]. This knowledge would enable, in a close future, for a more precise selection of the most favorable new accessions distinguished by superior fruit quality.

In this presentation we will report several experimental trials about the four analytical approaches, based on PTR-MS technology, suitable to fully investigate the complexity of fruit and vegetable aroma: i) non destructive VOC assessment; ii) automated analysis of frozen tissue; iii) dynamic destructive analysis; iv) monitoring of processes. In our opinion these proposed methodologies can be applied, with slight modification, on every kind of fruit or vegetable.

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Dark chocolates organoleptic differences: a PTR-ToF-MS success story

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Abstract

Aroma of dark chocolate depends on process and cocoa origin and variety. Repeated sensory analyses of standardized chocolates produced from various cocoa beans batches using a standard fabrication process allowed classifying them into four sensory categories. These categories were confirmed in a PTR-ToF-MS analysis of the volatilome of 206 chocolate samples through supervised multivariate data analyses (PLS-DA). Variable selection using dedicated methods pinpointed some volatile compounds important for the discrimination of the chocolates. Moreover, the nosespace of a subset of chocolates was measured by twelve assessors using PTR-ToF-MS with simultaneous determination of their sensory temporal profile (Temporal Dominance of Sensations methodology, TDS) to better explain the sensory categorization at a perception level. The two sets of data were analysed conjointly by defining an index of abundance of each detected aroma compound while a given attribute was dominant: the Abundance While Dominance (AWD) index. Through correspondence analyses (CA) of these AWD indices some relationships between certain aroma compounds and the sensory attributes expected to be related to them were found.

Introduction

Based on a quantitative descriptive analysis (QDA) conducted by an internal trained panel rating 36 flavour attributes, it has been possible to categorize into four distinct sensory poles dark chocolates of diverse cocoa origins and cultivars, but manufactured using the same standard process at pilot level at an industrial plant. This categorization of 'standard' dark chocolates into the four sensory poles is the basis of a quality control procedure for defining the ultimate use of dried fermented cocoa beans batches upon reception at the factory. Therefore, the main objective of this study was to investigate the potentiality of PTR-MS to predict these aroma-based sensory categories. For this, the headspace of 206 dark chocolate samples representative of the four sensory poles was analysed using a PTR-ToF-MS in direct introduction mode and the resulting

VOCs MS-based fingerprints submitted to multivariate data analyses. Moreover, a subset of 8 representative chocolates was submitted to a nosespace analysis using the PTR-ToF-MS instrument with simultaneous sensory temporal profiles determination using TDS in the aim to better explain the chocolates sensory categorization at a molecular and perception level.

Experimental Methods

All the experiments were conducted with a PTR-ToF-MS instrument (PTR-ToF 8000, Ionicon Analytik GmbH, Innsbruck, Austria) with H_3O^+ as reagent ion. The drift-tube parameters were fixed as follows: P_{drift} 2.3 mbar, T_{drift} 80°C, U_{drift} 480 V resulting in an E/N value of 111 Td (1 Td = 10^{-17} $V.cm^2$). Mass spectra were acquired at a scan speed of 0.5 s (headspace) or 0.1 s (nosespace) for the mass range *m/z* 0-250.

Chocolates samples

Chocolate samples (n = 206), produced in an industrial pilot plant using the same 'standard' transformation process with the same mass of cocoa from different origins and varieties, of sugar, of soy lecithin and of vanillin were retained for this study as being representative of four sensory categories, named 'sensory poles', previously determined on a QDA basis systematically conducted on 'standard' chocolates. For the headspace study 52 chocolates were evaluated to belong to the sensory pole 1, 47 to pole 2, 55 to pole 3, and 52 to the pole 4. For nosespace, 8 samples were selected from the 206 (2 representative ones per sensory pole).

Data collection and analysis

The chocolates volatilomes (in triplicates) were collected at 36.2°C using an experimental setup that allowed analysing sequentially the background zero air, the sample and the mass calibrant according to [1]. The data converted into concentration (ppbV) were expressed in areas under the curve (AUCs) calculated for an analysis window of 120 s starting from the moment when the sample headspace entered the instrument. After background subtraction and elimination of source ions, water clusters, compounds isotopologues and peaks below their LOQ, the final data matrix contained 143 ions and it was used for supervised (PLS-DA) multivariate data analyses (MATLAB packages) [1].

For each of the selected 8 samples, simultaneous nosespace and TDS data were recorded in triplicates by 12 assessors using a nosepiece device according to [2]. The two sets of data were analysed conjointly by defining an index of abundance of each detected aroma compound (35 were measured with a significant S/N ratio) while a given attribute was dominant: the Abundance While Dominance (AWD) index [2]. The resulting AWD contingency tables were used for correspondence analyses (CA) conducted for each chocolate sample (Statistica software).

Results and discussion

In order to evaluate the possibility to predict the chocolate sensory poles on the basis of the PTR-ToF-MS data, a supervised classification model (PLS-DA) was employed. Specifically, the retained method consisted of i) regressing the categorical response Y (the 4 poles to be predicted) on X (206 samples, 143 ions) by using PLS, ii) applying a discrimination approach (LDA) on PLS-predicted scores and iii) classifying new samples (test samples) using the previously chosen discrimination model [1]. The first two dimensions of the PLS-DA score plot evidenced a good discrimination between the four sensory poles (Figure 1). Along the discriminant axis 1, the poles

1 and 2 were well discriminated from each other, as well as from poles 3 and 4 whose scores presented a partial but moderate overlap. However, samples from poles 3 and 4 were well separated along the discriminant axis 3 (not shown). Moreover, in each pole the calibration and the test sets were very close with test scores found in good accordance with calibration scores (no bias, no spreading) showing a good performance of the prediction model. Furthermore, the confusion matrix of the test set generated by the LDA (Table 1) confirmed the quality of the prediction model since nearly 97 % of the test samples were correctly assigned in the sensory poles.

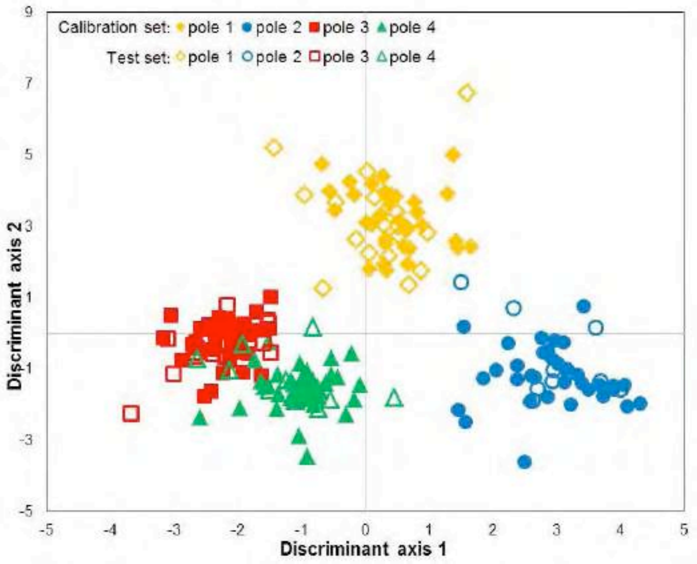

Figure 1: Score plot (discriminant axes 1 vs 2) of the PLS-DA conducted on the matrices X (206 samples, 143 ions) and Y (the 4 poles to be predicted). The calibration set included 146 samples and the test set 62 samples.

Only two samples were not correctly predicted: one belonging to pole 2 was predicted in pole 1 and one sample belonging to pole 3 was assigned to pole 4 (Table 1).

Table 1: Confusion matrix on the test set generated by the PLS-DA.

		Real classes			
		1	2	3	4
Predicted classes	1	**18**	**1**	**0**	**0**
	2	**0**	**11**	**0**	**0**
	3	**0**	**0**	**18**	**0**
	4	**0**	**0**	**1**	**13**

To better explain the sensory categorization at a perception level, a combined nosespace-sensory evaluation study was undertaken. The dynamics of perception have been considered only scarcely in comparison to nosespace measured simultaneously by on-line mass spectrometry. TDS is able to dynamically capture multidimensionality of perception. The obtained TDS curves clearly differentiated the chocolates that were regrouped by sensory categories as revealed by a principal component analysis (PCA). Computation of the AWD indices at individual level allowed to statistically assess the differences between the products over subjects and replicates and assessed statistically the relationships between the two sets of data. Through correspondence analyses (CA) some relationships between certain aroma compounds and the sensory attributes expected to be related to them were found (see Figure 2 for an example). For instance, the *Roasted_Nuts* and *Cocoa* descriptors were found in good correspondence with the ions *m/z* 137.106 and *m/z* 123.089 attributed to substituted pyrazines (Figure 2).

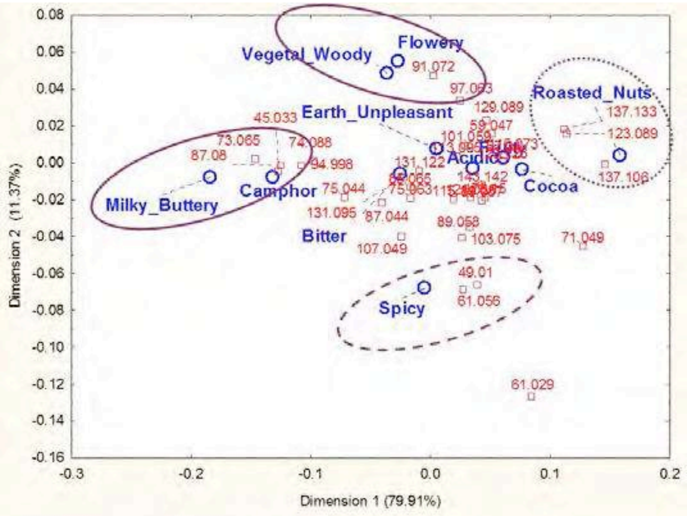

Figure 2: Correspondence analysis of AWD scores of one chocolate sample (35 ions, 11 descriptors). χ2 = 6736, df = 340, p < 0.0001

Conclusion

PTR-ToF-MS analyses of the volatilome of dark chocolates have been used successfully for classification of samples that were previously assessed by sensory evaluation in four distinct categories. A classification model has been constructed that presented excellent prediction capability, and discriminant ions have been characterized through dedicated selection methods. Pairing nosespace with Temporal Dominance of Sensations evaluation of dark chocolates categorized in four sensory groups provided meaningful data that could be analysed at individual level thanks to the AWD indices. Descriptive multivariate analyses of these AWD indices gave interesting clues on the relationships between the aroma compounds released in mouth and their expected perceived sensory attributes.

PTRMSomics: a new pipeline for untargeted analysis of PTRMS data based on peak picking methods from a food industry perspective

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Abstract

Given the global trends in the food and flavour industry, i.e. naturality, organic food, authenticity, transparency as well as ‘clean label’, it has become essential to revisit the way flavour is imparted in foods and beverages, as well as the way it is measured with fast reproducible methods, close to the overall consumer experience. In the last decade, there has been an increase in flavour analytical methods allowing on-line, in-vitro & in-vivo, real time measurements. PTR-(TOF)MS is a real time technique used for online monitoring of volatile organic compounds (VOCs). A technique becoming increasingly popular in the food science community. The application purpose of this technique includes a variety of projects from origin and history assessment of food and raw products, to food quality monitoring, to flavour release and/or generation profiles as function of product composition, to sensory related studies. However, the limitation of these high-throughput techniques remains with the considerable amount of data generated in a single analysis, in a complex data structure, and the required prior number of steps to a robust analysis of the acquired information. Hence, the need to develop alternative data treatment concepts, capable to extract relevant information, supporting the usage of fast real time measurements, close to the overall consumer experience. The present talk will elaborate on a few of these current issues and on how the food industry is transforming challenges into opportunities, with the development of a pipeline, for real time measurements, consisting on: data importation, peak apex’s extraction to reduce the number of variables and integrating several statistic tools for data comparison and visualisation.

PTR-MS opens new avenues for quality control of dairy raw materials in agroindustry

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Abstract

Among the many factors which drives food acceptance, sensory properties, flavor in particular, play a fundamental role [1]. Therefore, industrial food products are manufactured to deliver certain sensory characteristics to consumers, [2] and it is essential to monitor their quality not only for safety but also in relation to perceived quality. Product reliability in sensory experience has been recognized as an important feature which must be warranted to support consumer confidence for brands or products [3]. For this reason, food industries are constantly looking for flexible, fast, and reliable methodologies to monitor the quality of their product by focusing on flavor and aroma [4]. In this context instrumental methods that analyze volatile organic compounds (VOCs) seem a promising option since they are involved in sensory perception and they are constantly released by food products allowing for non-invasive analysis of foods [5].

A promising analytical approach of VOCs detection in food science and technology is direct injection mass spectrometry (DIMS) which has been implemented by different experimental strategies [5]. At the Volatile Compound Facility at Fondazione Edmund Mach (FEM), we explored the performance of Proton Transfer Reaction Mass Spectrometry (PTR-MS) a fast and non-invasive reliable tool for quality control of different raw and processed dairy products with emphasis on the link with sensory analysis [6]. In particular anhydrous milk fat, skimmed milk powder, and semi-finished products were analyzed.

Anhydrous milk fat (AMF)

In particular, a PTR-MS instrument equipped with a Time of Flight (ToF) detector was used to monitor the accelerated shelf life of anhydrous milk fat (AMF) and to verify the performance of two different type of packaging – Bag-in-Box (BIB) and cardboard packages (CT) - on the volatile profile during refrigerated storage. The technique was able to discriminate the two type of packaging based on the volatile emissions through all the storage (120, 180 and 240 days).

Moreover, different trends of key aroma volatile organic compounds were highlighted in both accelerated shelf life at 50°C (for 11 days) and during the 4 months shelf life [7].

PTR-MS VOCs fingerprinting was used to classify a set of industrial AMFs from different European producers evaluated through sensory evaluation and subjected to a thermal treatment. In this case also Selective Reactive Ion (SRI) mode was applied by measuring the samples not only with H_3O^+ as precursor ion but also NO^+ and O_2^+. Both unsupervised (Principal Component Analysis) and supervised (Partial Least Square Discriminant Analysis) multivariate statistical analysis showed promising results for the differentiation and the classification of the samples. In particular, data fusion of spectra obtained by different precursors ions allows for an improvement of classification efficiency..

Skimmed milk powder (SMP)

PTR-ToF-MS measurements were conducted also on different sample sets of skimmed milk powders (SMPs). In this case, due to the low emissions of VOCs from the food matrix, the introduction of an ion funnel (RF) after the drift tube increased the sensitivity up to 10 times. The increase in sensibility allowed a good discrimination of the samples. In particular, the samples that were classified as optimal by the industrial partner (sensory score ≈ 9) presented lower VOCs emissions while the one classified with a lower sensory score (≈8) had higher emissions indicating the existence of sensory defects and off-flavours (e.g. rancid, cardboard, metallic).

Semifinished products

Finally, the technique was applied on semi-finished products manufactured with both AMF and SMP with different sensory quality. As well, in this case, a good discrimination of the samples based on both fingerprints and specific mass peaks was observed.

In this contribution we present an overview of recent innovative applications of PTR-MS technique at FEM for the quality control of industrial dairy raw material. The analytical approach, combined with sensory analysis and chemometrics has showed promising results in addressing quality control issues related to sensory quality, processing, shelf life and packaging.

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Use of proton transfer reaction time of flight mass spectrometry to improve understanding of flavor generation in beer

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Abstract

As the brewing industry looks to create beers with greater flavor diversity, harnessing yeast biotransformations may provide a pathway to achieve this goal. Unfortunately, these pathways for some compounds are still poorly understood. Proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS) coupled to an autosampler to provide online measurements during fermentation may provide a pathway to help unlock these pathways. PTR-ToF-MS was used in two studies to help our understanding of how beer flavour is generated and in particular how yeast modulates hop aroma compounds. Using PTR-ToF-MS coupled to an autosampler allowed insights into the release kinetics of volatiles important in beer flavor and allowed multiple variables to be simultaneously examined and replicated. It was found that the magnitude and kinetics of biotransformations are heavily yeast-strain dependent and to adequately describe the formation of these compounds yeast strain variability needs to be considered in experimental designs.

Introduction

Beer drinkers and brewers are increasingly looking for bolder flavours and greater diversity in beer. To achieve these bolder flavours brewers are increasingly interested in how these can be achieved by leveraging yeast driven biotransformations. Yeast are responsible for the generation of higher alcohols and esters that form the main flavour profile of beer, and also the less desirable vicinal diketones e.g., diacetyl [1]. The role of yeast in modulating the compounds contributing to hop flavour is also gaining widespread attention in industry and academia. However, the understanding is incomplete for both ester and hop-derived biotransformations. In ester synthesis the pathways are well described but knowledge on time of generation during fermentation is relatively poor. In contrast, the transformations of terpene compounds from hops in fermenting wort are unclear and the time of generation during fermentation is even less understood.

Due to sample preparation and analysis time, gas chromatography techniques are not well suited to monitoring changes in rapidly fermenting systems especially when needing to compare multiple variables simultaneously. PTR-ToF-MS coupled to an autosampler allows rapid, direct, non-invasive sampling with a low detection limit [2]. The use of the autosampler as a microfermentation incubator allows fermentation to occur under defined conditions and the automated analysis improves analytical precision and sampling [3].

Using PTR-ToF-MS to understand the time of generation for these compounds will improve our understanding of flavour generation in beer and unlock opportunities for brewers to leverage biotransformations to create new beers and provide some control over the sensory properties.

Experimental Methods

Experimental design

Two studies were carried out. Study 1 used 2 yeast strains (Scottish ale and California Ale) x 2 hop varieties (Motueka and Nelson Sauvin). Study 2 involved 6 yeast strains (Fermentis WB-06, US-05, S-33, S-189, S-23, and W-34/70) x 1 hop variety (Motueka).

Wort preparation

Malt extract (120 g/L) was dissolved in filtered tap water, brought to a boil, Waimea bittering hops (0.24 g/L; ~20 International bitterness units, IBU) were added and boiled for 30 min. The wort was cooled to 90 ± 1 °C, aroma hops (5.0 g/L) added and held for 5 min at 90 °C. The bitter wort was cooled to 20 °C, filtered and its gravity standardized to 10.0 °P by the addition of sterilized water. The bitter wort was aerated for 10 min with filtered air using a peristaltic pump and an aeration stone (pore size: 0.5µm).

The wort was inoculated at 20 °C with the propagated yeast to achieve a pitching rate of about $1.0\text{x}10^7$ yeast cells/mL. Six aliquots (3 mL) of each of the treatments were transferred into separate headspace vials (20 mL) which were capped and placed into the PTR-ToF-MS auto sampler (Gerstel, Mulheim am Main, Germany). The fermentation was carried out in the vial in the auto sampler at 15, 20 or 25 °C. During fermentation, the headspace of each vial was sampled every six hours for four days with the first set of measurements conducted within 2 hours of inoculation.

PTR-ToF-MS

The sample headspace was measured using a PTR-ToF-MS 8000 (Ionicon Analytik GmbH, Innsbruck, Austria; drift voltage and temperature of 520 V and 110 °C, respectively; E/N of ~130 Td; coupled with an autosampler especially adapted for PTR-MS analyses (1). Headspace sampling was carried out for 1 min at a flow of 120 mL/min with a 3 min break between samples. The headspace in the vial was replaced with N2 gas during the sampling. To minimize measurement problems due to high ethanol concentrations, argon was directly injected into the drift tube at a flowrate of 1.2 mL/min to dilute the samples (1:2) prior to measurement (Campbell-Sills et al., 2016) [4]. Data was extracted and pre-processed (including dead time correction, calibration, peak detection and peak extraction) [5], converted to ppbv (parts per billion by volume) [6] and the mean of 20 spectra for each measurement were calculated.

Results and discussion

Headspace sampling under dynamic conditions allowed the time of volatile generation to be observed during fermentation. Ethanol and carbon dioxide release provided a valuable estimation of fermentation vigor and time to completion. Time to maximum CO_2 release was dependent upon yeast strain, yeast inoculation and fermentation temperature.

PTR-ToF-MS measurements allowed ester generation to be matched to CO_2 release. It was observed that the highest rate of ethyl hexanoate production was up to 12 h after the maximum rate of CO_2 release. This is interesting as the time of ester generation during fermentation has been associated with the period of most vigorous yeast growth [1]. Temperature influenced ester generation in a yeast strain specific manner, where time to maximum ester concentration decreased as temperature increased, although the yeast strain effect seemed more complex that simply related to differences in fermentation vigor.

Generally, the contribution to volatile composition from hops was greatest at the start of fermentation indicating that a large number of volatiles from hops directly contribute to the volatile composition. However, not all changes in the release rates of the hop derived compounds that were observed could be related to stripping through the sampling regime. For example, citronellol showed a standard stripping profile with an exponential decay in concentration, suggesting the only contribution was directly from the hops and biotransformation did not make a meaningful contribution to citronellol concentration. In contrast citronellol acetate demonstrated an initial decrease in concentration and then started increasing in concentration. The rate of increase did not match the rate of decrease of citronellol, so could not be solely attributed to esterification of citronellol. The use of fast GC coupled to the PTR-ToF-MS may help provide more detailed information by aiding deconvolution of concentration changes in isomeric compounds, e.g. terpene alcohols and terpene esters.

PTR-ToF-MS allowed insight into the generation and release kinetics of volatiles important in beer flavor. The use of the autosampler allowed multiple variables to be simultaneously examined and replicated to provide robust results. The results demonstrate that biotransformations are heavily yeast-strain dependent. To ensure that biotransformation pathways are adequately described, these results suggest yeast strain variability needs to be considered in experimental designs exploring hop biotransformations.

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PTR-MS Sampling Techniques for On-line Coffee Analysis

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Abstract

Analysis using PTR-MS has added value in the area of coffee aroma research by allowing us to monitor aroma formation, release and degradation. The high sensitivity as well as temporal resolution complements traditional techniques such as GC/MS analysis while enhancing our understanding of the dynamic processes occurring within coffee. Analysis using PTR-MS is highly reproducible and the methodology is well established; nevertheless, sampling remains one of the main challenges in developing a robust and successful on-line setup.

We present three cases of on-line sampling of coffee aroma and coupling to PTR-MS. Each case studied involves processes occurring on different time scales and at varying conditions, therefore diverse sampling techniques were developed for successful coupling. First process is the analysis of roaster exhaust gas, where a gas stream at high temperature and high VOC concentration is sampled. Second, highly reproducible and automatized dynamic headspace analysis of roasted and ground coffee is performed by coupling an autosampler to the PTR-MS instrument. Third, the reconstitution of soluble coffee (instant coffee) and subsequent release of aroma from the beverage was studied by a highly reproducible simulated beverage preparation.

The important parameters that need to be considered for developing sampling setups for on-line coupling to PTR-MS are: VOC intensity in sampled gas, volatility of analytes, humidity of sampled gas, time response of the system and heating of the transfer lines. Due to the diversity of conditions encountered during on-line coffee aroma analysis only customized sampling interfaces can assure required robustness of the sampling setup and quality of data.

Exploring volatile profile of apple cultivars by PTR-MS and link with sensory and other instrumental analyses

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Abstract

The feasibility to differentiate cultivars using solely instrumental techniques was explored. Comparison between instrumentally-measured properties and those gained from descriptive sensory analyses were made. Sensory odour/ flavour descriptors were compared to VOC profiles obtained from PTR-ToF-MS, while textural descriptors were compared to mechanical and acoustic textural parameters. Cultivar characterisation using both techniques proved to be very similar, highlighting the value of solely instrumental techniques in separating apple cultivars based on their VOC profiles and textural properties.

Introduction

The aroma and texture of apples are known to influence the overall perception of flavour. The volatile organic compounds (VOCs) released from the apple before (orthonasal) and during consumption (retronasal) are perceived by consumers as aroma. One factor that can influence VOC release is texture. Cultivar-specific texture, microstructure, and mechanical breakdown the apple flesh during mastication can have a profound impact upon the overall profile. Although the importance of VOC release and textural breakdown in shaping flavour perception have been reported in the literature, the interplay between the two factors during apple consumption have not been clearly defined. In addition, it was not known whether cultivar characteristics measured instrumentally can be linked to descriptors reported by panellists. This study [1] discovered cultivar-specific differences of apple texture, microstructure and VOC release in relation to their role in the overall flavour perception. Furthermore, the correlations between sensory derived attributes and instrumental-derived parameters were also explored.

Experimental Methods

To delineate the relationship between texture and volatile organic compound (VOC) emission, *in vitro* (orthonasal) and *in vivo* (retronasal) measurements of VOC release from 21 different apple cultivars were performed using a proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS). The *in vivo* and *in vitro* headspace VOCs data were then combined with texture, physico-chemical and swallowing parameters, and processed using Multi Factor Analyses (MFA) to identify any possible correlations.

Results & Discussions

The first three dimensions of the MFA explained 51.7% of the total variance (Figure 1). There was a separation on Dim1 based on *in vivo* nosespace parameters, textural and physico-chemical properties. The main variables that separated cultivars on positive Dim1 were physico-chemical, texture parameters and a majority of the I_{max} and Area Under the Curve (AUC) variables associated with ester related compounds. These variables were associated with firm cultivars such as Braeburn, FEM7 and FEM4 that contained high amounts of VOCs; or cultivars that were firm with low amounts of ester related VOCs (Dalinette, Pilot, Gold Rush). Negative Dim1 was associated with force ratio, difference in force, acidity, most T_{max} variables and hexanal (m/z 101), butanoate/acetate esters (m/z 71.05), methyl butanal (m/z 87.082) and methyl butanoate (m/z 103) I_{max} and AUC variables. These variables were strongly associated with soft cultivars such as Renetta Grigia, Renetta Bianca and Topaz. Dim 2, separated cultivars based on their VOC composition and abundance. Positive Dim 2 was explained by a majority of the in vitro VOCs whereas negative Dim 2 was only associated with aldehydes, ethylene and terpene/sesquiterpene related compounds.

Time of consumption, T_{con} was longer for firmer cultivars indicating panellists took a longer time to finish an entire sample when given a firm sample to consume. This was based on the association of T_{con} with textural properties (Figure 1). T_{con} was positively correlated to force peaks ($r = 0.627$) in which a higher number of force peaks indicated firmer and crunchier cultivars. N_{swals} was found in the same quadrant and was positively related to T_{con} ($r = 0.538$). This could be interpreted as panellists taking longer and having more swallows when consuming firmer samples.

The relative abundance of VOCs in the in vivo nosespace profiles of each cultivar is dependent on the available in vitro VOC concentration. However, the release of flavour depicted by T_{max} is observed to be dependent on the behaviour of texture breakdown. In the current study apple cultivars on Dim 2 were separated by their differences in VOC abundance and composition whereas Dim 3 separated cultivars based on texture and nosespace parameters. Firm cultivars (Braeburn, FEM7 and FEM4) that emitted high intensities of ester related VOCs for both in vitro and in vivo measurements were associated with T_{con}, N_{swals} and the accompanying I_{max} and AUC variables on negative Dim 3. A negative association to T_{max} indicated that a shorter time was needed to reach I_{max} despite the cultivars firm texture. This was contradictory to previous research which reported a shorter T_{max} was associated to soft gel matrices due to the ease of gel breakdown during mastication causing a faster increase in surface area.

In the current study, the shorter T_{max} could be driven by a shorter T_{swal} for Braeburn, FEM7 and FEM4 cultivars. The short T_{swal} times for these cultivars could be due to juice expressed during mastication causing a greater need to swallow. This resulted in faster swallows and expiration of retronasal air which other studies did not involve due to their gel system. Therefore, apart from texture and VOC composition, other factors such as juiciness may influence T_{swal}, T_{max} and I_{max}. Additionally, T_{swal} could also be related to ease of swallow which has been observed to be dependent on sample juiciness or the time needed during mastication to reduce the sample size to form a bolus.

In general, firm-juicy cultivars had a shorter time to first swallow (Tswal) and a higher number of swallows (Nswal), while softer-mealy cultivars had a longer Tswal and a lower Nswal. Firm-juicy cultivars containing high VOC concentrations had a short time to maximum intensity (Tmax) owing to a shorter Tswal and a higher Nswal as juice was released during mastication. Swallowing increased VOC flow through the nasal cavity. These results differ from previous flavour release studies with gel/gel-like model systems as juiciness/release of fluids is not a factor in such matrices.

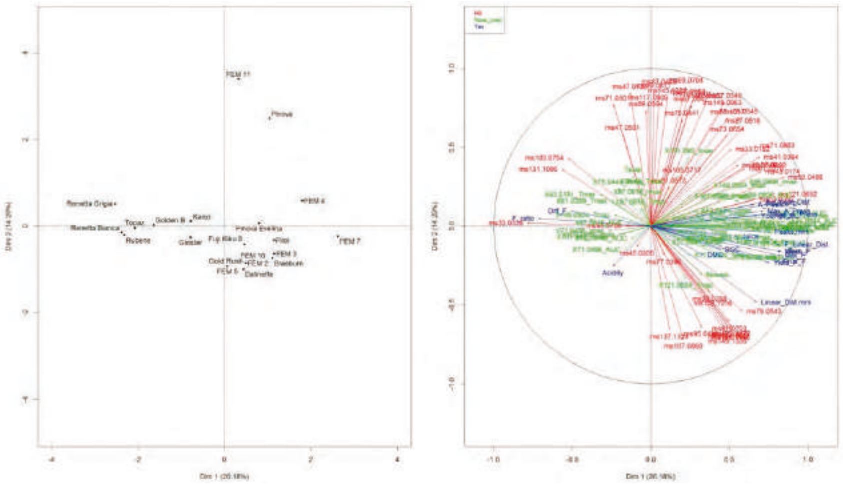

Figure 1: MFA of Dim 1-2 (A) using in vitro headspace VOCs, in vivo nosespace and swallow parameters, texture and physico-chemical properties. Abbreviations on figure legend include: HS - Headspace; Nose_swal - Nosespace and swallows; and Tex - Texture.

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A sense of spices by PTR-MS

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Abstract

Spices are important ingredients of foods and they enhance aroma and taste of a wide variety of food products on the market. In this study the volatile organic compounds of a variety of spices is compared by PTR-QMS. Furthermore, we compare good quality nutmeg and black pepper with low-grade counterparts and are able to distinguish them consistently by their volatiles. Finally, retail black pepper is compared with quality and low-grade samples and a striking 40% presents more similarity with low-grade material then with quality spices.

Introduction

Spices and herbs come from a number of different parts of plants. This include the aril (mace), bark (e.g. cinnamon), berries (e.g. peppercorn), bulbs (e.g. garlic), flower (saffron), leaves (e.g. bay leaves), roots (e.g. ginger) and seeds (e.g. nutmeg) of a plant. They have been used to flavor foods for millennia without any real understanding of the processes behind them. Spices are in particular important for the aroma and taste improvements of food. Whereas nutmeg and cinnamon for instance are valued mostly for their aroma contribution, others such as saffron and black pepper contribute to both aroma and taste. In addition to quality materials, there are also low-grade variants on the market, such as 100% light berries, spiral rejects, shells, fruit pulp, and spent which should not end up as retail products. They are considered inferior products, not meeting any of the flavor specifications of the real quality spice equivalents.

Since aroma is a very important aspect of spices, in the current study we mapped the volatile organic compounds (VOCs) of a variety of spices by PTR-QMS in order to understand natural variation between and within spice groups. Furthermore, quality nutmeg and quality black pepper was compared with low-grade alternatives and thresholds were set to distinguish the grades and to evaluate retail samples.

Experimental Methods

Samples of black pepper, chili paprika, cinnamon, coriander, cumin, nutmeg, saffron and white pepper were collected from retail outlets (6-12 of each spice) in various European countries. Furthermore, ca. 200 nutmeg and black pepper samples were collected from European spice enterprises, as well as a variety of inferior samples for both nutmeg and black pepper. Furthermore, an additional ca. 50 black pepper samples were gathered from retail outlets across Europe.

The VOC profiles of the spice samples were measured in triplicate in the headspace of the spices using a PTR-QMS instrument (Ionicon Analytik, Innsbruck, Austria). The order of sample and triplicate measurements were randomized to account for possible memory affects. All measurements were carried out under drift tube conditions of 120 – 140 Td (Td = Townsend; 1 Td = 10-17 V cm2 mol-1) over a mass range of m/z = 26 to m/z = 160 and a dwell time of 0.2 s/mass, giving a cycle time of 32 s. The flasks with the samples were connected to the PTR-MS inlet flow that was heated to 60 °C via Teflon (0.25 mm) tubing and headspace air was sampled at a flow rate of 50 mL/min. Masses were analyzed in a quadrupole mass spectrometer and detected as ion counts per second (cps) by a secondary electron multiplier. Sample measurements were performed in 5 cycles resulting in an analysis time of 3.0 min. Furthermore, background air scans of five cycles were conducted from an empty bottle before each sample measurement.

The headspace concentrations of the compounds during the cycles #2, #3 and #4 were calculated and averaged. Subsequently background and transmission corrections were applied. Then, the three averaged mass spectra of the three replicates of each sample were averaged to obtain a mean mass spectrum per sample. In this manner, a data matrix comprising mean mass spectra for all samples was compiled. Mass intensities were statistically evaluated by Mann-Whitney tests, $p<0.01$.

Results and Discussion

The spices showed distinct VOC patterns and the concentration ranges differed considerably between the various spices. Saffron showed the lowest concentrations, whereas nutmeg exhibited the highest (>10 ppmv). The latter may be due to the fact that nutmeg comprises a high volatile oil content compared to the other spices. The major class of the VOCs of the spices was the class of the terpenoids. For the spices in this study, it concerned in particular monoterpenes and sesquiterpenes. Some spices, such as saffron and cinnamon presented key character impact compounds, i.e. safranal and cinnamaldehyde. Others showed a more mixture of various VOCs, such as black pepper. More details about this comparative study have been published previously [1]. The results are useful for sensory-related specifications of spices and to understand differences occurring in the market.

Analysis of the large set of quality and low-grade nutmeg samples revealed distinct differences between the two groups. The low-grade nutmeg presented similar VOCs as the quality nutmeg, but generally in lower concentrations. The overall intensity was approximately 10% of the intensity of quality nutmeg only. From the 133 masses measured, 110 masses showed significant differences between the groups ($p<0.01$). Just a few masses rendered higher intensities in the low-grade materials, but they point in the direction of the use of solvents (e.g. methanol).

In the extended black pepper study, the group of the monoterpenes and sesquiterpenes dominated the profiles. The intensities of approximately 30% of the masses measured were present in significantly higher concentrations in the quality black pepper group compared to the low-grade material. This difference is due to the extraction of essential oils or loss of VOCs during storage. Retail black pepper samples presented significantly lower intensities for more than 50% of the masses than the quality black pepper samples (reference samples from industry). On the other hand, higher concentrations were determined for mass 33 (methanol), which was present at substantial concentration levels (300-500 ppbv). This high concentration shows similarities with the low-grade material, which points at residues from industrial extraction processes. Mass 137 (terpenoids) was used as an indicator for the quality of the black pepper. Frequency distributions of the quality and low-grade black pepper samples of the first part of the study were calculated and the concentrations associated with the 1st percentile of the quality black pepper was used to verify the retail samples. The majority of the low-grade samples presented concentrations below the 1st percentile value of the quality black pepper. It appeared that a striking ~40% of the retail black pepper samples presented intensities of mass 137 below this 1st percentile value too. This result indicates that a substantial fraction of the black pepper found in retail are not meeting usual industry specifications and are likely to have been adulterated with low-grade or other materials. The nutmeg and pepper studies have been detailed in other journal publications [2,3].

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Applications in Health Science

Real time Proton Transfer Reaction and Electronic Nose simultaneous characterization of Plasmodium falciparum released VOCs

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Abstract

In this study, we investigated the VOCs released by culture media of red blood cells (RBCs) infected by the asexual forms of the human malaria parasite *Plasmodium falciparum* and the sexual gametocytes at different stages of maturation. The analysis has been carried out with an innovative setup where a PTR-ToF has been hyphenated with a gas sensor array previously used to detect malaria infection in a murine model. In this setup the same sample was measured with both the techniques at the same time.

Introduction

The majority of malaria deaths are caused by *Plasmodium falciparum*, the most virulent of the *Plasmodium* species. Several studies showed that *Plasmodium*-infected humans are more attractive to mosquitoes than non-infected hosts, particularly when high levels of gametocytes are present.

The detection of specific malaria volatile compounds have been claimed in different kinds of samples. Recent studies point out the alteration of VOCs in murine models [1], in humans in skin [2] and breath [3]. However, it is still not clear the stage-specific emission of malaria-related compounds.

A useful bottom up approach considers the emission of VOCs from infected RBCs. Previous studies produced divergent outcomes with both negative and positive results about the different VOCs emission between infected and non-infected RBCs. Moreover, these studies missed the relationship between VOCs and developmental stage of *Plasmodium*.

Experimental Methods

A PTR-ToF MS 8000 from Ionicon has been hyphenated with a gas sensor array designed and developed at the University of Rome Tor Vergata. The sensor array was made of 12 porphyrinoids coated quartz microbalances [4]. These sensors have been used for *in-vivo* and *in-vitro* characterization of VOCs from breath, skin, and cultured cells.

Media from cultured RBCs infected with either *Plasmodium falciparum* asexual forms or gametocytes were analyzed. Samples were placed in sealed vials and measured with an automatic sampler after a thermalization period. The headspace was extracted by a constant flow of nitrogen kept at 50 sccm. Such a flow is compatible with the inlet of both instruments. Figure 1 shows the experimental setup.

Results

A total of 405 peaks were detected in the PTR-MS spectra obtained by measuring the head-space of the samples. Sensors were sensitive to the VOCs present in the headspace of culture media.

Multivariate analysis of sensors and PTR-MS data shows a clear separation of *P falciparum* gametocyte-infected RBCs from healthy and asexual-infected RBCs. Less sharp is the difference between healthy and asexual-infected RBCs

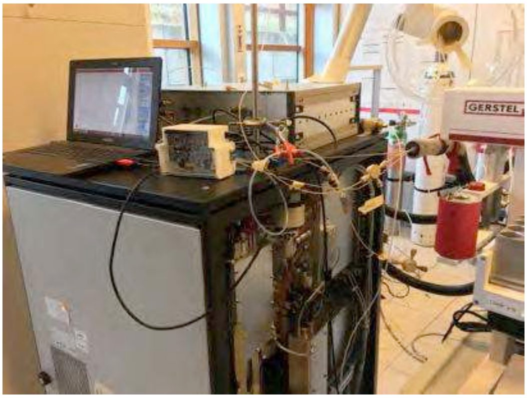

Figure 1: The experimental set-up with PTR-MS in background, conditioning oven on the right and the e-nose.

Discussion

Results evidence the presence of a specific VOC signature for gametocytes, which represent the transmissible stage of the disease. The majority of antimalarial drugs do not possess anti-gametocyte activity hence individuals may remain infectious to mosquitoes for several weeks after treatment. Thus, to eliminate/eradicate malaria, one of main objectives is the identification and treatment of these gametocyte reservoirs. In this context, the development of sensitive, non-invasive, easy-to-use and low-cost devices to detect sexual stages of parasite in asymptomatic individuals is strategic for the design of novel control measures

The simultaneous use of different analytical techniques is common in analytical chemistry where it is mainly used to compensate the limitations of individual approaches. Gas sensor arrays have been considered as a valid alternative to costly and bulky instruments. However, it is known that sensor arrays provide only scarce information about the nature of the detected compounds. On this basis, the information retrieved by PTR-ToF can be used to elucidate the working mechanism of gas sensors and may be used to support and optimize the sensor array elements.

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Guiding breath sensor development with PTR-MS

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Abstract

Breath sensors are promising as portable/wearable devices for routine and personalized health monitoring. During their development, early and continuous assessment on human breath and rigorous comparison to bench-top mass spectrometry are essential. Here, I will describe recent progress on the development of selective/single-molecule breath sensors. In particular, I will showcase our recent development on Si-doped WO_3 nanoparticles as acetone-selective breath sensors. Together with a tailor-made breath sampler[1], this sensor was tested on 20 volunteers during exercise and rest to measure their individual breath acetone concentrations in good agreement to proton transfer reaction time-of-flight mass spectrometry (PTR-TOF-MS)[2]. During exercise, this sensor revealed the onset and progression of increasing breath acetone levels. Finally, I will update on our newest development on orthogonal sensor arrays[3] and present their application to sniff breath- and skin-emitted tracers (including acetone, isoprene and ammonia) for search & rescue applications[4].

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Comparison of PTR-ToF-MS and PTR-QMS product ion branching ratios for compounds associated with peppermint oil capsules

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Abstract

The lack of standardization regarding the sampling and analysis of exhaled breath is a widely accepted issue within the breath research community. In 2016 the IABR set up a task force to tackle this issue which resulted in the Peppermint consortium. The aim of this consortium is to create a set of benchmarking data that can be used as a tool for comparing and analysing the various analytical techniques and protocols from different research institutes. Several members of the consortium use proton transfer reaction mass spectrometry with quadrupole mass filter (PTR-QMS) or time-of-flight mass analyzer (PTR-ToF-MS). We present here the primary compounds associated with the peppermint oil capsule after identification using GC-MS. Each compound was measured on a PTR-ToF8000 and PTR-QMS 500 (both from Ionicon Analytik GmbH). The compounds (menthol, menthone, eucalyptol, limonene, ɑ-pinene, β-pinene, and γ-terpinene) were analysed under normal and humid drift tube operating conditions, to investigate the effect of humidity on the product ion branching ratios and to replicate the relative humidity of a human breath sample. The samples were prepared by injecting a small volume of the headspace of the compounds into a Tedlar bag filled with 2 L of dry or humid nitrogen gas. The drift tube conditions were altered so that a reduced electric field (E/N) range measured was 80-200 Td. The results for all the above volatile compounds will be shown in the oral presentation. For illustrative purposes we present here results on menthone.

Introduction

There is currently a wide range of breath sampling protocols and analysis methods available to researchers using various types of instruments such as PTR-MS, ESI-ITMS, GC-MS, GC-IMS etc. [1-3]. A couple of successful previous endeavours towards breath standardisation for the sampling and analysis of exhaled nitric oxide [4] and exhaled breath condensate [5] have been explored so far. However, for the majority of volatile organic compounds (VOCs) there are no such agreed sampling and analysis protocols, which is a high priority issue for the breath research community [6]. During the IABR breath summit in Zurich 2016, a task force was created with the aim of collecting benchmark data that could be used to compare different breath sampling and analysis techniques. The founding members of this task force are Loughborough University, Radboud University, the Fraunhofer Institute for Process Engineering and Packaging IVV and Manchester University. The primary aim of this task force is to establish if an experiment in which the washout profile of exogenous compounds contained in a 200 mg peppermint oil capsule (Boots Pharmaceuticals, UK) can be measured in exhaled breath. There are currently 15 members in the consortium, with several instruments used to analyse the breath samples, including GC-MS, GC-IMS and PTR-MS. Before undertaking any breath analysis, it is important to ascertain what volatile components are contained in the peppermint oil capsule and then to know how these are metabolized in the human body. For the former, we have undertaken a GC-MS analysis of the peppermint oil. Following this, we have investigated how the individual compounds respond in a PTR-MS instrument, which is used in real time for the pharmacokinetic studies. These PTR-MS studies undertaken under normal and humid conditions, the latter being needed to mimic human breath samples. Due to diffusion of water vapour from the hollow cathode ion source, a dry buffer gas in the drift tube does not mean that the instrument is operating under dry conditions. Therefore, when the dry buffer gas is used we will refer to this as "normal" operating conditions. When a water saturated buffer gas is used, we will refer to that as "humid" conditions [7].

Experimental Methods

Chemicals

Menthol, menthone, eucalyptol, α-pinene, β-pinene, and γ-terpinene were purchased from Aldrich, and limonene was purchased from Fluka. All of these chemicals had reported purities of greater than 95%, and were used without further purification.

GC-MS

Headspace (15-20 ml, with a total flow of 8 ml min^{-1}) above the liquid contained in a capsule was extracted with a needle trap (NT, PAS Technology, Magdala, Germany), containing 1 cm Tenax TA, Carbopack X and Carboxen 1000 sorption materials. 7890A gas GC equipped with a 5975 C Inert XL mass selective detector (both from Agilent Technologies, Waldbronn, Germany) was used to release the analytes from the sorbent. A capillary column RXT-624 30 m × 0.32 mm × 1.8 μm (Restek Corporation, U.S., Bellefonte, PA, USA) was used. MS analysis was performed in a full scan mode with a scan range of 20–200 amu. The oven temperature was set to 40 °C for 0 min, then 5 °C/min to 150 °C for 2 min and then 10 °C/min to 240 °C for 5 min. [8]

PTR-MS

Two IONICON Analytik GmbH PTR-MS instruments were used in this study: a PTR-ToF8000 and a PTR-QMS 500. A reduced electric field, *E/N*, [9] range of 80 – 200 Td (Townsend) was applied to the drift tube. The PTR-ToF8000 was used at a mass resolution of 2400 $m/\Delta m$ and scanned from m/z 0 to 230. The PTR-QMS 500 has a mass resolution of 1 amu and was operated in bar graph scan mode from m/z 20 to 200, with a dwell time of 0.2 seconds per m/z, 5 cycles were saved per *E/N* step. Various volumes (0.1 – 5 mL) of headspace from the chemicals sample vial were taken depending on the compound being analysed and injected into a Tedlar bag filled with 2 L dry or humid nitrogen. The humid nitrogen was generated by bubbling high purity nitrogen through water into the Tedlar bag, which was kept in an oven at 50ºC to avoid condensation on the bags surface.

Results

GC-MS

The major compounds identified from the GC-MS in the peppermint oil capsule were: menthol, menthone, eucalyptol, limonene, α-pinene, β-pinene and γ-terpinene.

PTR-MS

The product ion branching ratios for all the standard compounds previously mentioned will be shown during the presentation, along with the spectrum of the headspace of the peppermint oil measured on both instruments. Owing to potential impurities from the Tedlar bag, a blank measurement was made before each sample measurement, consisting of the Tedlar bag filled with either dry or humid nitrogen. This blank measurement was subtracted from the sample measurement. For the purpose of illustration, we are only presenting the results for menthone in this abstract. Figure 1 shows the product ion branching for menthone for the two PTR-MS instruments. It shows the main product ions at *m/z 155 (*protonated parent ($C_{10}H_{18}O)H^+$*)*, and the fragment ions *m/z 137* $C_{10}H_{17}^+$ *(loss of* H_2O *from the protonated parent), 95* $C_7H_{11}^+$*, 81* $C_6H_9^+$*, 79* $C_6H_7^+$ *and 39* $C_3H_3^+$*.*

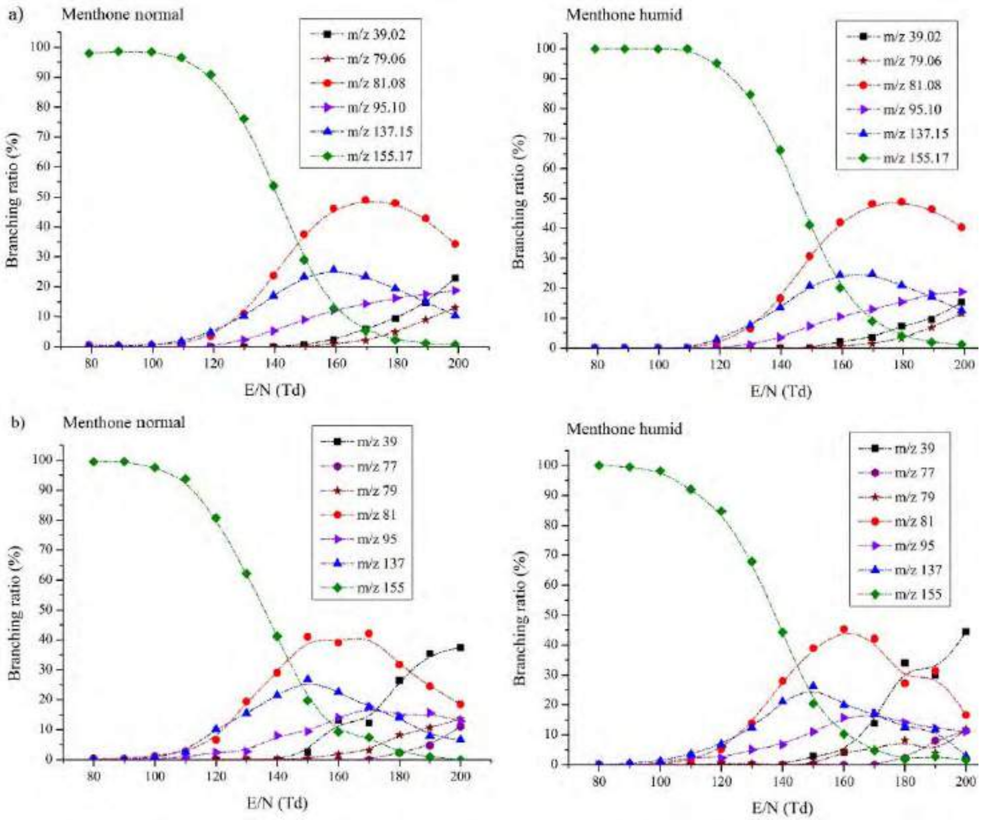

Figure 1: Product ion branching ratios of menthone under normal and humid conditions on t instruments, a) PTR-ToF8000, b) PTR-QMS 500

Discussion

The results for the other compounds will be shown during the presentation, with only the menthone results discussed here. The main difference between the instruments is the type of mass spectrometer used; therefore each instrument will have different transmission and detection efficiencies, which can result in observable differences in the branching ratio of the product ions. However, for menthone, similar product ion branching ratios are recorded for both instruments, with the largest difference coming from the high signal at m/z 39 after 180 Td on the PTR-QMS 500 compared to the PTR-ToF8000. At the lower *E/N* conditions 80-140 Td the protonated parent ion is the most abundant species. As the reduced electric field in the drift tube is increased, the protonated parent begins to fragment; above 140 Td the product ion of m/z 81 is becoming the most abundant. At the higher reduced electric field, *E/N* >180 Td, the protonated parent ion is negligible. There was no significant difference between the normal and humid samples measured using the PTR-QMS 500, which could be due to the diffusion of water vapour from the hollow cathode ion source into the drift tube, meaning that the relative humidity within the drift tube was the same under both experimental conditions. As for the PTR-TOF8000, the only difference we observe is at a higher *E/N* (above 180 Td). In case of the normal condition the fragment m/z 39 reaches 10-25% of the branching ratio, whereas in the humid conditions this is around 10-15%.

Acknowledgements

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Non-targeted analysis: Implementing high-resolution mass spectrometry to improve identification of analytical features in biomonitoring studies

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Abstract

Conventional biomonitoring studies are based on analyses using mass spectrometry (MS) instrumentation with unit Da resolution to measure trends in targeted compounds. More recently, complementary methodology has emerged referred to as non-targeted, or "discovery" analysis. This is an agnostic technique wherein as many analytical features as possible are documented within complex samples and then used to observe differences in case-control or longitudinal study designs. Ultimately, important features are investigated to achieve compound identifications. Because there can be no *a priori* external standards or calibrations for unknown compounds, non-targeted identifications using standard MS spectra tend to be ambiguous. One approach to improve analytical results is to implement high(er) resolution (HR) in the mass spectrometer. This is especially important in real-time instruments such as PTR-MS wherein there is no chromatographic separation during sample introduction. This work describes the use of non-targeted analysis in exhaled breath and urine biomonitoring studies and discusses the techniques for implementing HR strategies that are of relevance in PTR-TOF-MS analysis.

Introduction

Recent studies in environmental, occupational, and medical diagnostics have implemented non-targeted mass spectrometry analysis as an exploratory tool beyond standard targeted analytes. Most analyses are accomplished with gas chromatography (GC) or liquid chromatography (LC) separation as a preliminary step, followed by electron ionization (EI) fragmentation with single Da resolution, which together provide reasonable identification of compounds. Herein we discuss how the additional dimension of high-resolution mass spectrometry (HR-MS) can help identify ambiguous features in various applications of discovery analysis.

HR-MS technology is especially important for classifying "unknowns" into groups within samples, and ultimately for separating isobaric compounds that overlap in time. We have found that breath and urine measurements for previously undocumented metabolites can greatly benefit from HR-MS. The move from integer mass quadrupole mass filters to high-resolution time-of-flight mass spectrometers in PTR-MS over a decade ago [1] greatly elevated the power of this technology for isobaric compound identification at ≥0.015 Da separation (PTR-TOF 8000, IONICON Analytik, Innsbruck, Austria) [2].

Experimental Methods

Herein we excerpt results from three different studies to illustrate where HR-MS could benefit identification of compounds. These are drawn from recent publications of exhaled breath of firefighters [3], urinary metabolites [4], and exhaled aerosols from cancer screening [5].

The underlying methods for investigating results from these studies stem from two recent publications; the first develops the basic methods for using monoisotopic features for a preliminary assessment of potential elemental composition [6], and the second for looking more closely at high-resolution isotopic abundances and mass fragmentation [7]. The basic method revolves around the observation that atoms do not have an integer mass, but that there is a small change due to strong force that holds the nucleus together. The most common constituents of organic molecules, plus other halogens of interest, have the exact masses as shown in Table 1. As such, given sufficient mass resolution in the spectrometer, compounds with the same integer mass but different elemental composition can be separated by the sub-integer molecular masses.

Table 1: Mono-isotopic masses and nucleon numbers for common atoms in organic molecules.

Atom	Protons (#)	Neutrons (#)	Integer mass (# nucleons)	Exact mass (Da)	Mass defect (Da)
Carbon	6	6	12	12.00000	0.00000
Hydrogen	1	0	1	1.00783	0.00783
Nitrogen	7	7	14	14.00307	0.00307
Oxygen	8	8	16	15.99492	-0.00508
Phosphorus	15	16	31	30.97376	-0.02624
Sulfur	16	16	32	31.97297	-0.02793
Flourine	9	10	19	18.99840	-0.00160
Chlorine	17	18	35	34.96885	-0.03115
Bromine	35	45	79	78.91834	-0.08166
Iondine	53	74	127	126.90448	-0.09552

For example, some common mass fragments found in GC-MS volatiles analysis are 73 and 86 Da. There are a number of arrangements of prevalent organic atoms (from Table 1) that can add up to a molecular (or fragment) mass as shown in Table 2.

Table 2: Two examples of compounds with same integer mass but different elemental compositions; knowledge of exact mass allows discrimination.

Compound	Elemental composition	Integer mass (Da)	Exact mass (Da)	Mass defect (Da)
Methylisocyanate	C_2H_3NS	73	72.99862	-0.00138
Nitroethene	$C_2H_3NO_2$	73	73.01638	0.01638
N,N-Dimethylformamide	C_3H_7NO	73	73.05276	0.05276
1-Methylguanidine	$C_2H_7N_3$	73	73.06400	0.06400
Isobutylamine	$C_4H_{11}N$	73	73.08915	0.08915
Chlorodiflouromethane	$CHClF_2$	86	85.97348	-0.02652
Trifluoromethoxy	CHF_3O	86	85.99795	-0.00205
Vinyl acetate	$C_4H_6O_2$	86	86.03678	0.03678
Ethylene urea	$C_3H_6N_2O$	86	86.04801	0.04801
Pentanal	$C_5H_{10}O$	86	86.07316	0.07316

If the MS has a resolution of 0.01 Da, for example, similar to the PTR-TOF 8000, it can easily discern all of the 73 Da candidates and the 86 Da candidates within their respective groups. Given such higher resolution results, there are software packages that can provide candidate elemental compositions for any exact mass. Alternatively, one could simply add together the atomic masses for a candidate composition using the entries in Table 1. (Note, the tables are extracted [6].)

Results

The three studies mentioned above all contain highly complex datasets. However, for the purpose of this abstract there are some specific examples that illustrate how higher resolution could improve the identification of unknown compounds in non-targeted analyses. In these projects, we looked at both targeted and untargeted compounds using single Da resolution MS data via EI, but had the additional information from retention time, mass fragmentation pattern, and prior knowledge from many external calibrations. As such, we had confidence in identifications. We provide two key compounds found in non-targeted analyses as examples from the three studies:

1. VOCs from firefighters' breath: methyl tertiary butyl ether, $C_4H_{10}O$, and methyl disulfide, $C_2H_6S_2$ [3].
2. VOCs from urine headspace: heptanal, $C_7H_{14}O$, and 4-methyl-2-pentanol, $C_6H_{14}O$ [4].
3. Semi-volatile compounds from breath aerosols: formic acid, 2-ethyl butyl ester, $C_7H_{14}O_2$, and 2,2,4-trimethyl heptane, $C_{10}H_{22}$ [5].

Discussion

If these compounds were to be found in analyses from PTR-MS without benefit of chromatographic separation or EI fragmentation, they could have a number of interpretations at single Da resolution. Such identifications could be narrowed using higher resolution MS. Of the examples above, the EI product ions, integer masses and exact masses of the compounds are shown in Table 3; with the last column interpreted as the exact mass of the molecular MH^+ ion as expected in PTR-TOF-MS.

Table 3: Examples of key non-targeted compounds from three studies using EI-MS at 1 Da resolution showing the comparisons between integer and exact mass.

Study	GC-MS		Element. comp.	Int. mass (Da)	Exact mass (Da)	
	EI m/z	Compound ID			EI	PTR
1	59, 41	methyl tert-butyl ether	$C_4H_{10}O$	74	74.073	75.080
	94, 79	carbon disulfide	$C_2H_6S_2$	94	93.991	94.998
2	70, 43	heptanal	$C_7H_{14}O$	114	114.105	115.112
	45, 69	4-methyl-2-pentanol	$C_6H_{14}O$	102	102.105	103.112
3	43, 69	formic acid, 2-ethyl butyl ester	$C_7H_{14}O_2$	130	130.100	131.107
	57, 56	2,2,4-trimethyl heptane	$C_{10}H_{22}$	142	142.172	143.179

Studies relate to 1) firefighters' breath, 2) urinary metabolites, and 3) breath aerosols.

Higher mass resolution has value in narrowing down compound identifications. For example, integer mass 74 associated with methyl tert-butyl ether ($C_4H_{10}O$) could also represent CNO_3, $CH_2N_2O_2$, or CH_6N_4, among others. However, these all have different exact masses, namely

74.07322, 73.98783, 74.01164, and 74.05926, respectively. As such, with resolution of better than 0.01 Da in this mass regime, we could quickly narrow down the choices despite the many different configurations of common organic compounds. The caveat of this approach is the assumption at any given mass that the signal represents the protonated parent ion, rather than a fragment of a higher molecular weight compound, but in PTR-MS in most cases the MH^+ parent ion is observed and branching ratios are typically well characterized, so informed deductions can be made in relation to candidate compounds. On the whole, the higher mass resolving power afforded by PTR-TOF-MS, in combination with the deductions outlined above to aid compound identification, add greatly increased value to non-targeted analysis of VOCs in biological samples such as exhaled breath.

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Breath-resolved analysis of exhaled amines by PTR-TOF-MS: effects of protein intake

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Abstract

Amines represent an important class of volatile compounds in breath that can be related to diseases, metabolic processes and bacterial activity. Analysis of these compounds is hampered through their high reactivity. As they can react with any surface of sampling or calibration devices and as well as they may de-compose under certain conditions, time-resolved detection and calibration are difficult.

We developed and optimized a PTR-Tof-MS based analytical setup for continuous and breath-resolved determination of aliphatic amines.

Methyl-, dimethyl- and trimethyl-amine at low ppbV levels were analyzed with different pH and temperature conditions and different sampling line materials. Influence of these factors on the PTR-ToF response was systematically evaluated. Gaseous standard solutions were prepared by means of a liquid calibration unit (LCU). For each experimental set-up, gaseous standards were measured continuously over 10 minutes.

At pH 7.4, high temperatures and using inert materials, compound reactivity on the surfaces of the analytical system was considerably reduced and the measured intensities reached a stable plateau after 1 minute of measurement. Under these conditions, calibrations showed good linearity with correlation coefficients > 0.99. LODs of amines ranged from 0.15 ppbV to 63 ppbV and LOQs from 0.24 ppbV to 1.94 ppbV.

The applicability of the developed method was assessed by the determination of the target compounds in the breath of 15 healthy volunteers after a protein meal. Methylamine and dimethylamine breath concentrations were below LOD. Trimethylamine breath concentration ranged from 0.27 to 3.2 ppb. Mean alveolar concentration of trimethylamine, indole, methylsulphide and acetone showed significant changes (p-value < 0.05) after protein intake.

The results of our investigations confirmed that PTR-ToF-MS can be applied for breath resolved analysis of exhaled amines. Change in breath VOC concentrations may provide non-invasive insights on regular and abnormal metabolic conditions in the whole body.

Real-time monitoring of human physiology and metabolism via PTR-ToF-MS

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Abstract

Clinical breath analysis requires reliable and reproducible methodology. Apart from environmental confounders, subject's physiological and metabolic factors may have profound effects on exhaled volatile compositions.

In series of studies, we therefore investigated effects of human physiology and metabolism on VOC exhalation. In 220 healthy adult subjects, we applied online mass-spectrometry (PTR-ToF-MS-8000, optimized for breath-resolved analysis of VOCs) in parallel to breath-resolved spirometry, capnometry and non-invasive hemodynamic monitoring to evaluate immediate effects of subject's physiology such as breathing patterns, subject's postures, breathing maneuvers, sampling routes, resistances and respiratory rhythms onto VOC exhalation. Similarly, we investigated metabolic effects of natural menstrual cycles and use of oral contraception in adult women via breath analysis.

Instant effects on VOC profiles were observed in all of those study setups. Exhalation kinetics of blood-borne VOCs mirrored cardiac output, minute ventilation and end-tidal CO_2 profiles. Substance's origins, volatility and solubility played important roles. Many observed concentration changes were more pronounced than those described in cross-sectional studies for disease detection and thereby may bias clinical interpretations.

PTR-ToF-MS driven real-time monitoring enabled us to address many issues regarding sampling physiology and metabolic state of subjects during sampling. These enhanced our basic and analytical knowledge and clinical understanding of breath biomarkers. Participant's physiological attributes and metabolic status must be accounted, controlled and kept constant during any clinical measurement in relation to biomarker discovery. We are applying that knowledge in our ongoing clinical studies.

Introduction

Reductions of physiological effects and of subsequent variations in the obtained data are critical challenges that have been faced since the inception of respiratory research and breathomics. During breath sampling, normal but complex variability of respiratory physiology often screens the true and rather minute expressions of biochemical pathways, pathological conditions or metabolic processes in the VOC data [1, 2]. We have investigated sudden and profound effects from subject's breathing patterns, body positions, FEV maneuvers, oral and nasal breathing and sampling diameters onto VOC exhalation [3, 4, 5]. Due to exhaustive list of confounders and regular irregularity of sampling- and analytical standards in our field of research, validation and reproducibility of results are compromised ad nauseam. In order to realize the anticipated future of breath VOC applications in routine medical practice; subject's own physiological and metabolic effects must be realized in real-time. Therefore, we applied online PTR-ToF-MS measurements in various setups to frame many in vivo factors that may immediately affect VOC exhalation.

Experimental Methods

Continuous breath sampling (side-stream mode) was performed in 220 healthy adult human via an online PTR-ToF-MS-8000. Various physiological and metabolic effects were implied and subsequent effects on VOC exhalation were monitored. Sampling related physiological effects under different breathing patterns, postures, breathing maneuvers, sampling routes, resistances and respiratory rhythms (e.g. paced and spontaneous respiration) were monitored. Metabolic effects from natural menstrual cycle and from cycles undergoing combined oral contraception was also assessed in real-time.

Breath-resolved spirometry & capnometry was done via Oxycon Mobile device. Non-invasive hemodynamic monitoring was performed by ClearSight system.

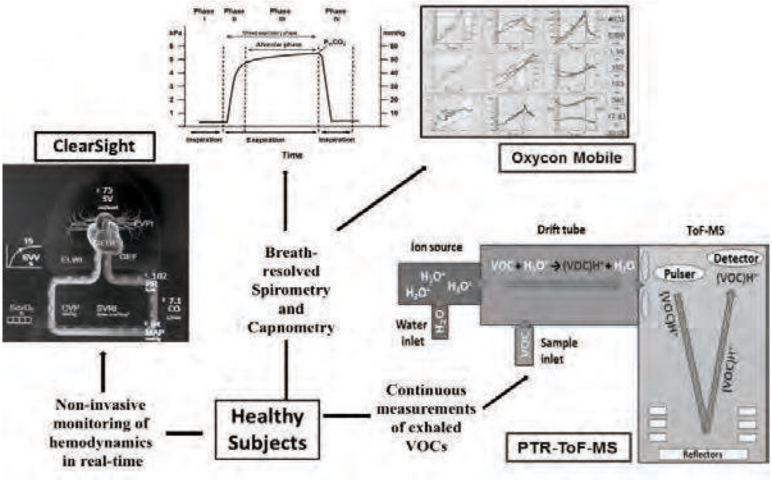

Figure 1: Schematic representation of our instrumentation and study setup.

VOC data processing

Alveolar and inspiratory breath phases were identified by "Breath Tracker". Endogenous acetone was used as tracker mass due to its higher signal intensity in expiration.

In order to track the relative changes each individual was used as his or her own control and measured data were normalized onto corresponding values in one breath. These helped us to minimize inter-individual variations.

Statistics on Sigma Plot:

Repeated Measurement-ANOVA on Ranks (Student Newman-Keuls:ˇ pairwiseˇ multipleˇ comparison) were used to for comparison of observed differences.

Results

Instant effects on VOC profiles were observed in all of those study setups. Exhalation kinetics of blood-borne VOCs mirrored cardiac output, minute ventilation and end-tidal CO_2 profiles. Substance's origins, volatility and solubility played important roles. E.g. low aqueous soluble isoprene (endogenous), furan (smoking related), C_2H_6S (gut-bacterial origin) followed hemodynamic profiles whereas high-soluble acetone remained almost unaffected. H_2S (oral-bacterial origin), C_4H_8S (diet related), exogenous benzene, acetonitrile and limonene etc. were moderately affected by physiological factors. Certain respiratory rhythms (i.e. a custom sampling maneuver) turned out to reduce physiological variations in the observed data and may contribute toward reproducibility of breath samples. Similarly, systemic and metabolic effects were observed mainly on endogenous substances during different menstrual cycle phases and those effects differed significantly (P-value ≤ 0.005) under the presence of oral contraceptive pills.

Discussion

Most of the observed changes in concentrations were more pronounced than those described in cross-sectional studies as biomarkers for disease detection and thereby, may bias and mislead clinical interpretations. Assessment of physiological and metabolic effects onto VOC profiles can enhance basic and analytical knowledge and clinical understanding of breath biomarkers. Reproducibility and variation of VOC analyses can be improved if these effects are taken into account. If disease related VOCs are to be identified and characterized, standardized sampling and basic knowledge on respiratory physiology are mandatory. PTR-ToF-MS driven real-time monitoring enabled us to address many issues regarding sampling physiology and metabolic state of subjects during sampling. At present, our state-of the art knowledge that has been gained through the above mentioned outcome, are now being applied in many of our ongoing clinical studies..

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What can we learn from the air chemistry of crowds?

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Abstract

Current PTR-MS technology allows hundreds of volatile trace gases in air to be measured every second at extremely low levels (parts per trillion). These instruments are often used in atmospheric research on planes and ships and even in the Amazon rainforest. Recently, we have used this technology to examine air composition changes caused by large groups of people (10 000-30 000) under real world conditions at a football match and in a movie theater. In both cases the trace gas signatures measured in ambient air are shown to reflect crowd behavior. By applying advanced data mining techniques we have shown that groups of people reproducibly respond to certain emotional stimuli (e.g. suspense and comedy) by exhaling specific trace gases. Furthermore, we explore whether this information can be used to determine the age classification of films.

Introduction

Human beings continuously emit chemicals into their local air environment by breath and through the skin. In order to determine whether these emissions vary predictably in response to external audiovisual stimuli, we have continuously monitored trace gases including carbon dioxide and over one hundred volatile organic compounds at a football match and then in a cinema, with multiple screenings of different films and involving over nine thousand people.

Experimental Methods

The measurements were conducted in the multiplex cinema Cinestar in Mainz (Germany) in two different screening rooms for approximately four weeks during the winter 2013/2014 and winter 2015/2016. Over the 8 weeks of measurement, 11 different films were shown multiple times resulting in a total of 135 separate screenings. The exhaust air of the cinema was measured with a PTR-TOF-MS 8000 (Ionicon Analytik GmbH, Innsbruck, Austria) and a CO2 sensor (Licorr).

Results

In the first part of this study determine whether these emissions vary predictably in response to external audiovisual stimuli. It was found that many airborne chemicals in cinema air varied distinctively and reproducibly with time for a particularly film. The film scenes were labelled for content and data mining methods applied to the combined chemical and label dataset. Remarkably, certain film scene content (e.g. suspense or comedy) was found to induce changes in specific airborne chemicals from cinema audiences, both within repeat screenings of the same film and within entirely different films.

In the second part of this study we assess the emission fluxes of VOCs from human beings under real world conditions. children. Gas-phase emission rates are analyzed as a function of time of day, variability during the film, and age of viewer. The average emission rates of CO2, acetone, and isoprene were lower (by a factor of ~1.2-1.4) for children under twelve compared to adults while for acetaldehyde emission rates were equivalent. Molecules influenced by exogenous sources such as decamethylcyclopentasiloxanes and methanol tended to decrease over the course of day and then rise for late evening screenings.

In the third part of this study we systematically examine the feasibility of using CO2 and over 60 VOCs measured in air ventilating from a cinema to classify films.. Our approach involves a random forest model built with time independent features extracted from the time series of every measured compound for every film. These features include for example peak height, peak width and the number of peaks in a film normalized to its length. Finally, a permutation test was performed to test the resulting performance measures (area under ROC curve) of the original model versus the ones calculated from randomized class labels. Of all species tested we found that isoprene performed best in predicting the different age classifications.

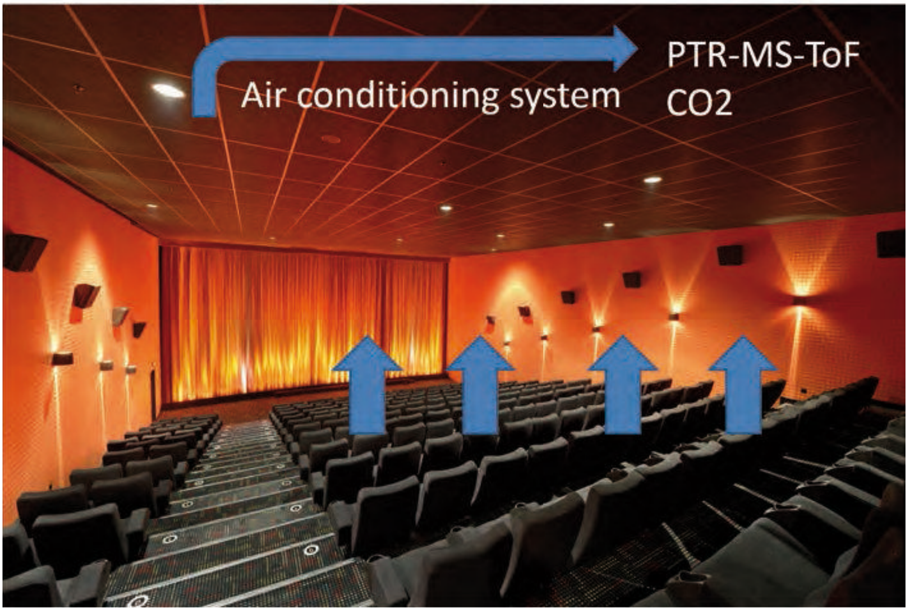

Figure 1: The cinema is a box full of people, flushed with air that enters under the seat and is extracted through the ceiling.

Discussion

In this series of studies we have reported correspondence between audio-visual stimuli and the emission of VOC from human beings. We have quantified the emissions of people in real world environments and we have assessed whether the age classification of a film can be predicted based on variations of airborne chemicals measured in a cinema. It is interesting to reflect that a chemical based approach as advocated here, would be based on directly measured responses from large test audiences, whereas the current scheme is based on a subjective appraisal of the film by relatively few people entrusted to reflect the general public sentiment.

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Instruments & Technology and Future Trends

Using collision-induced dissociation to constrain sensitivities of ammonia chemical ionization mass spectrometry

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Abstract

Chemical ionization mass spectrometers (CIMS) routinely detect hundreds of oxidized organic compounds in the atmosphere. To date, no instrument is capable of measuring the whole volatility range of organic compounds, from volatile organic compounds (VOCs), semi-volatile organics (SVOC) to low and extremely low volatility organic compounds (LVOC and ELVOC, respectively). On the one hand, classical PTR-MS instruments have predictable sensitivities to a wide variety of VOCs, but currently suffer from insufficient overall sensitivities to detect low volatility organics at sub-pptv levels. On the other hand, selective CIMS using negative ion chemistry have superior sensitivities to most LVOCs and ELVOCs, but have difficulties quantifying most SVOCs. Recent advances in PTR designs dramatically increased sensitivities, however, at the cost of higher uncertainties in measured quantities. We describe a method which predicts sensitivities for a myriad of species without direct calibration, using ammonium-water clusters as primary ions: the binding energies of formed ammonium-organics clusters are directly related to sensitivities and can be easily measured for all observed (unknown) compounds in a mass spectrum.

Methods

The instrument is based on the recently developed PTR3 [1] coupled to a high resolution time-of-flight mass spectrometer (LToF, Tofwerk AG, Switzerland). Reagent ions are generated in a corona discharge region and are extracted using a source drift region as indicated by arrows in Figure 1. The reaction chamber uses a tripole electrode configuration and is operated at typical pressures between 50 and 70 mbar. Unlike many other PTR instruments, there is no axial electric field accelerating ions towards the exit of the reaction chamber. Therefore, the reaction time is exclusively determined by the flow of the analyte gas, typically leading to a reaction time of 3 ms. Contrary to the original PTR3 instrument equipped with a single ion source, the new design comprises three ion sources, one active at a time, enabling switchable reagent ions (SRI-PTR3). Currently, we use two sources: one for producing $H_3O^+\cdot(H_2O)_n$, n=0,1 reagent ions (H_3O^+ mode), and another for producing $NH_4^+\cdot(H_2O)_n$, n = 1,2 reagent ions (NH_4^+ mode). $NH_4^+\cdot(H_2O)_n$ ions are produced in the corona discharge ion source from NH_3 and H_2O. Constant flow (0.2 sccm) of ammonium and water vapor is added to the ion source region from the head space of a 10% solution of ammonium hydroxide in water.

Figure 1 shows the instrument in the NH_4^+ mode with the active ion source on the bottom, while the two other ion sources (depicted as a single ion source on the top) are inactive. The innermost source drift plate of the active ion source and the innermost source drift plates of both inactive sources generate an electric field perpendicular to the tripole axis. In addition, another component of the electric field is generated parallel to the tripole axis by biasing the electric potential at the secondary orifice relative to the tripole offset potential. Figure 1 illustrates the resulting electric field in this transfer region. This geometry allows for effective ion guiding from the respective active ion source to the centre of the reaction tripole chamber.

The second major design change consists of replacing the straight tripole electrode rods with a helix. Simulations of ion trajectories in the original tripole showed that ions are mostly lost by exiting the device through spaces between the rods, rather than by being adsorbed by the rods themselves, probably due to inhomogeneous effective potentials generated by the tripole radio frequency (RF) fields. The helical structure effectively averages these inhomogeneities, increasing the ion transmission efficiency and therefore the overall instrument performance.

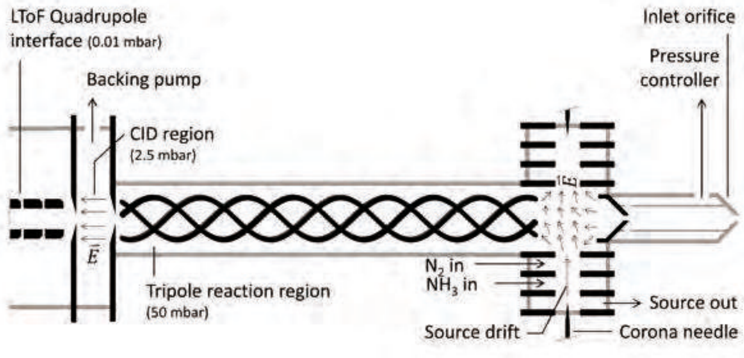

Figure 1: Schematic representation of the SRI-PTR3.

Results

Numerous VOCs can be detected though a reaction of ammonium clusters with analyte molecules [2, 3] – an ionization method generally softer than protonation via hydronium ions. In NH_4^+ mode, the primary reagent ion is $NH_4^+{\cdot}H_2O$, with minor signals corresponding to NH_4^+, higher NH_4^+-water clusters and $NH_4^+{\cdot}NH_3$. Sensitivities of 16 volatile organic compounds (VOC) were measured using a liquid calibration unit (LCU, Ionicon Analytik GmbH, Austria). All standard compounds were almost entirely detected as $NH_4^+{\cdot}$VOC clusters, with sensitivities up to 90000 cps/ppbv (decanone). Our working hypothesis – a strong correlation of the binding energy of these clusters and the observed sensitivities – was demonstrated: Binding energies were experimentally probed [2] by varying the electric field gradient in the CID region (Figure 1) between the ionization region and the mass spectrometer. Figure 2 shows normalized signals of $NH_4^+{\cdot}$VOC clusters present in the standard as a function of the kinetic energy (KE_{cm}). KE_{cm} was calculated by taking parameterized ion mobilities [4], gas pressure, maximum electric field strength and molecular weights of ions into account. Finally, Figure 2b shows the measured sensitivities plotted against the kinetic energies obtained (defined as the energy at which the signals dropped to 50%).

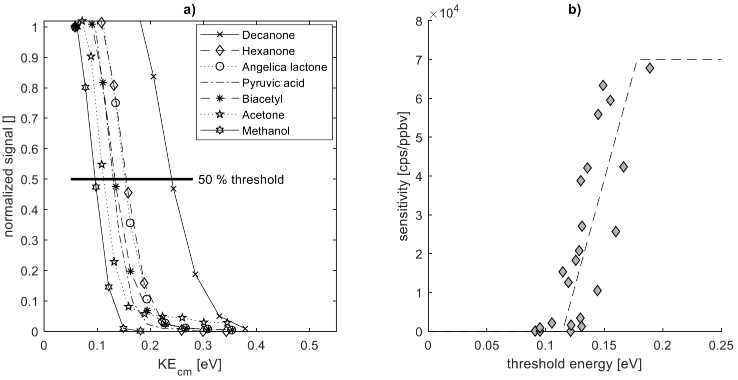

Figure 2: a) Cluster breakup for selected VOCs as a function of kinetic energy in the center-of-mass frame. b) Measured sensitivities of 16 VOCs as a function of 50% threshold energies.

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Application of PTRMS and stable isotopes to identify microbial processes in fermenters and manure

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Abstract

A quadrupole PTR-MS has been used in isotope labeling studies of two processes: Methane production from waste incl. competing microbial reactions occurring at in situ biogas upgrading, and turnover of sulfur compounds in livestock waste and atmospheric release of volatile sulfur compounds. At adequate labelling rates, the instrument was found to be useful for elucidating processes that are difficult to characterize by other means. In the case of biogas production, a competing reaction occurring as a result of H_2 reactor addition was successfully monitored by adding labelled bicarbonate, $H^{13}CO_3^-$, to reactors and measuring the formation of acetic acid via homo-acetogenesis through m/z 44 and m/z 62. For the sulfur turnover experiments, labelled sulfate ($^{33}SO_4^{2-}$) was added to livestock slurry and the formation of $H_2{}^{33}S$ was monitored at m/z 36. Furthermore, microbial methylation and demethylation was monitored by measuring m/z 50 and m/z 62, corresponding to $CH_3{}^{33}SH$ and $CH_3{}^{33}SCH_3$.

Introduction

Isotope labeling is commonly used in e.g. microbiology and biorefinery research for elucidating biochemical pathways of microorganisms. For this purpose, Isotope Ratio Mass Spectrometry (IRMS) is used for measuring end products such as CO_2 and CH_4, but for intermediates and more complex precursors it may be more challenging to measure isotope ratios. One example of a complex microbial process is the methanogenesis of organic waste, which involves a number of hydrolytic, acidogenic and acetogenic pathways. Specific isotope labeling and IRMS can be used to elucidate the mechanisms [1] ultimately leading to formation of CO_2 and CH_4, but isotope enrichment of intermediates and byproducts, e.g. carboxylic acids, is not easily measured. If the degree of labeling is sufficient (which is feasible for small sampling volumes), however, a quadrupole Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) can be used for measuring such compounds. In the current work, we haves used PTRMS to elucidate the formation of acetate by homoacetogenesis [2]:

$$2CO_2 + 4H_2 \rightarrow CH_3COOH + 2H_2O$$

This process may become important when H_2 is added to a reactor in order to upgrade the biogas and increase the yield of CH_4. The process may compete with methanogenic CO_2 reduction and the acetic acid formed serves as a carbon reservoir. This so-called in situ upgrading [3] has received increasing attention as a means of utilizing surplus electricity to produce H_2 and store this energy by upgrading biogas in situ.

Another example of complex microbial processes is the turnover of sulfur compounds in liquid waste materials. In livestock manure, sulfate is reduced to H_2S [4], which evaporates relatively easily. H_2S may be methylated to produce methanethiol and dimethyl sulfide in subsequent steps. These organic sulfur compounds may be de-methylated by methylotrophic organisms by which process sulfur is recycled to H_2S. Other sources of sulfur compounds include the amino acids, cysteine and methionine. Emission of H_2S is the main loss mechanism of sulfur and the importance of this for the atmospheric sulfur composition has been highlighted by [5].

Experimental Methods

All experiments were performed with a High-Sensitivity Proton-Transfer-Reaction Mass Spectrometer (PTR-MS) with a quadrupole mass analyzer (Ionicon, Innsbruck, Austria). The PTR-MS was run under standard drift tube conditions at 75 °C and 2.2 mbar corresponding to an E/N number of 141 Townsend. Under these conditions, protonated acetic acid fragments partly to CH_3CO^+ and partly remains as the protonated parent ion, $CH_3C(O)OH_2^+$, giving rise to two ion signals for monitoring the occurrence of the ^{12}C isotopomer of acetic acid : m/z 43 and m/z 61 [6]. The enrichment of ^{13}C was therefore monitored by measuring the increases of m/z 44 and m/z 62. Before the experiments, the minimum detectable increases in m/z 44 and m/z 62 was established as three times the standard deviation of continuous measurements on an instrument blank (clean air) and the addition of $NaH^{13}CO_3$ was designed to give isotopomer signals well above this level if significant homo-acetogenesis would occur. Measurements were done by headspace analysis of 1 ml aliquots of sludge placed in vials closed with rubber septa. A ~100 ml/min flow of N_2 was added via infusion needles through the septum for flushing the headspace and was directed to the inlet of the PTR-MS. Prior to headspace analysis, pH was adjusted to ~3–4 by addition of 1.0 M hydrochloric acid in order to increase the air-water partitioning of acetic acid and at the same time avoid high headspace concentrations of NH_3, which would otherwise potentially consume the primary ion (H_3O^+) used for ionizing acetic acid. This new method enables measurement of $^{13}C/^{12}C$ in acetate within a few minutes if sufficient amounts of labeled $NaH^{13}CO_3$ is added.

For the sulfur turnover experiments, the setup presented in [4] was used. The transmission of the PTR-MS was updated before and after the experiments with a Scott Mini-Mix (Restek) transmission gas. The hydrogen sulfide concentration was calibrated against the humidity before and after the experiments. Proton-transfer rate coefficients were calculated for each individual molecule using capture rate coefficients. Non-labelled sulfur compounds were calibrated by using authentic standard gases.

Results

The method was successfully able to monitor isotopic enrichments and depletion under the conditions applied. Examples of sulfur turnover experiments are shown in Figure 1 and 2. The isotopologue measurements together with inhibitors enabled us to calculate a sulfate reduction rate of 1.03 ± 0.18 mM/day corresponding to 76.9 ± 3.0% of the hydrogen sulfide emissions. Cysteine degradation constituted 20.2 ± 2.7% of the total hydrogen sulfide produced and the remaining hydrogen sulfide came from demethylation of methanethiol and dimethyl sulfide. Another source to methanethiol, besides hydrogen sulfide methylation, was methionine degradation, which contributed with 78.3 ± 2.5% of the methanethiol production, whereas the remaining 21.7 ± 2.5% came from hydrogen sulfide methylation.

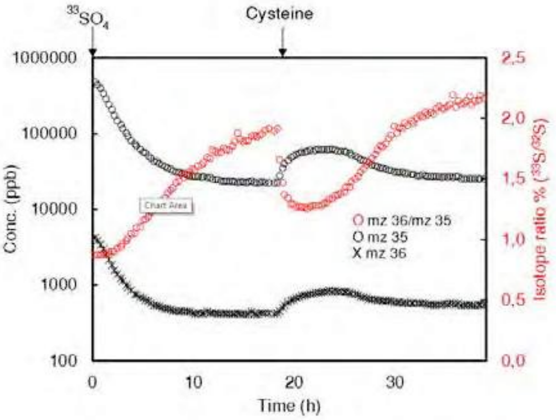

Figure 1: Isotopologues of hydrogen sulfide (m/z 35 and m/z 36) and their internal ratio measured with PTR-MS from a batch reactor with swine manure. Labelled Sulfate was amended at experiment initiation and cysteine was amended after 19 h.

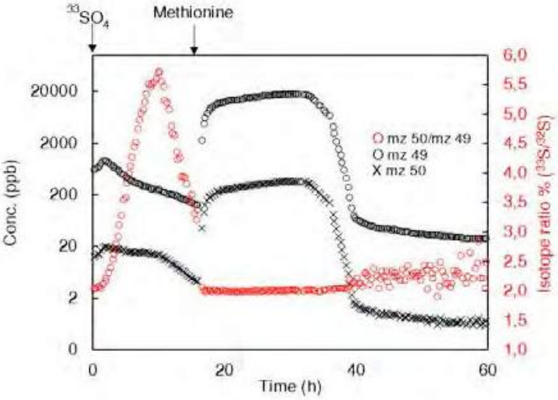

Figure 2: Isotopologues of methanethiol (m/z 49 and m/z 50) and their internal ratio measured with PTR-MS from a batch reactor with swine manure. Labelled Sulfate was amended at experiment initiation and methionine was amended after 19 h.

For the methanogenic studies, homoacetogenesis was ascribed to 20-38% of the H_2 consumption in the treatments. The contribution of homoacetogenesis to H_2 consumption decreased strongly to less than 10% in an adapted sludge. These results are in line with previous experiments, where a fast shift towards hydrogenotrophic methanogenesis was observed through microbial analysis an increase of hydrogenotrophic methanogen abundance after hydrogen injections [7].

Discussion

The experiments and data demonstrate the ability of the PTRMS to monitor microbial processes by using carefully selected isotope labeling in sufficient amounts. A conventional quadrupole PTRMS was used for these studies, nut application of high-resolution time-flight PTRMS will improve the methodology further and make it easier to distinguish isotopologues from potential interferences. The application of headspace analysis makes it relatively straightforward to apply the method for complex materials such as wastewater and livestock waste.

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A new High Resolution PTR-TOFMS instrument with RF-Drift Tube, Ion Funnel and the novel TRION Source

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Abstract

Current commercially available IONICON Proton-Transfer-Reaction – Time-Of-Flight Mass Spectrometry (PTR-TOFMS) instruments show a sensitivity of about 1000 cps/ppbv, a single digit pptv level detection limit and a mass resolution of over 6000 m/Δm [1]. Here we present the next step in PTR-TOFMS technology, namely the overall improvement of every aspect of instrumental performance. We show that with these advancements we can now reach about 10,000 m/Δm mass resolution, a sensitivity of up to 10,000 cps/ppbv and detection limits in the upper ppqv range. Furthermore, the instrument is equipped with three ion sources for extremely rapid switching between different reagent ions.

Experimental Methods and Results

The newly developed TOF mass spectrometer is of the orthogonal acceleration type and equipped with a dual stage ion mirror. The length of the TOF flight path is 40 cm longer than for the present PTR-TOF 6000 X2 [2] in order to achieve mass resolutions of up to 10,000 m/Δm. The instrument is equipped with a triple ion (TRION) source perpendicular to the axis of the drift tube. The three ion sources can continuously generate three different reagent ions (e.g. H_3O^+, NO^+ and O_2^+; [3]), respectively, wherein in each ion source one specific type of reagent ions is produced. Applying an injection voltage to a certain ion source will inject the reagent ions into the drift tube, while the ions of the two other sources are rejected. This allows for extremely rapid switching between different reagent ions in split seconds. The drift tube consists of a series of RF-driven ring electrodes and an adjacent ion funnel is installed for increasing the ion throughput. The inlet is in axis with the drift tube, while pin holes are reducing the pressure from atmospheric pressure to about 2.6 mbar in the drift tube. This in-line arrangement and the higher inlet flow compared to established PTR-TOFMS instruments, leads to a considerably lower response time and effectively avoids losses of compounds and memory effects due to condensation in an inlet line. A schematic view of the experimental setup can be seen in Figure 1.

In Figures 2 and 3 the results of a performance evaluation utilizing a certified gas standard are displayed. It can be seen that for many compounds the sensitivity even exceeds 10,000 cps/ppbv. Based on these results the Limits-of-Detection (LoDs) haven been calculated using the established 3σ-method. For an integration time of 100 ms, i.e. for a measurement frequency of 10 Hz, which is typically used for flux measurements in atmospheric chemistry, the LoDs for virtually all substances are around 10 pptv. For higher integration times the parts-per-quadrillion (ppqv) range becomes accessible, which makes this novel PTR-TOFMS instrument one of the most sensitive trace gas analyzers ever.

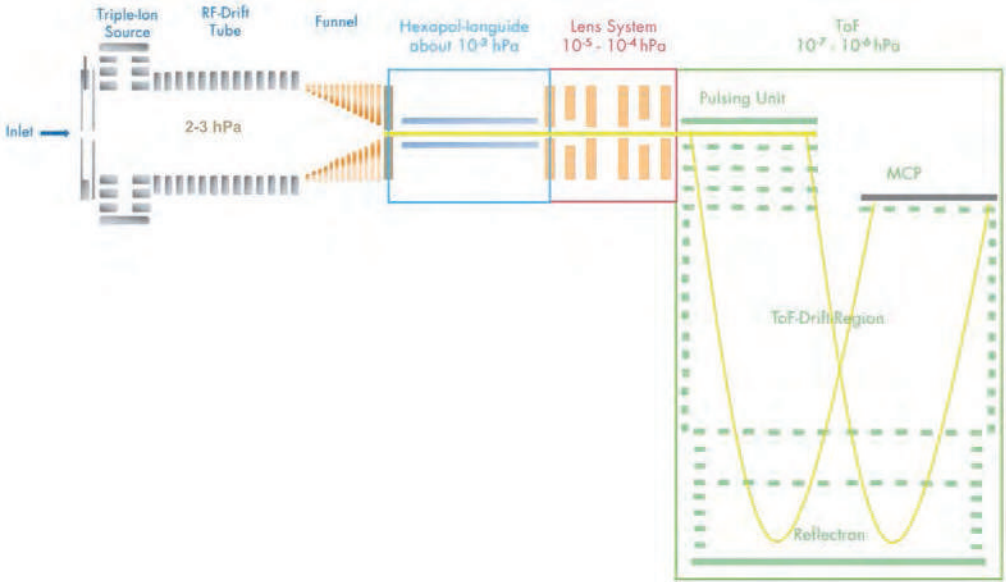
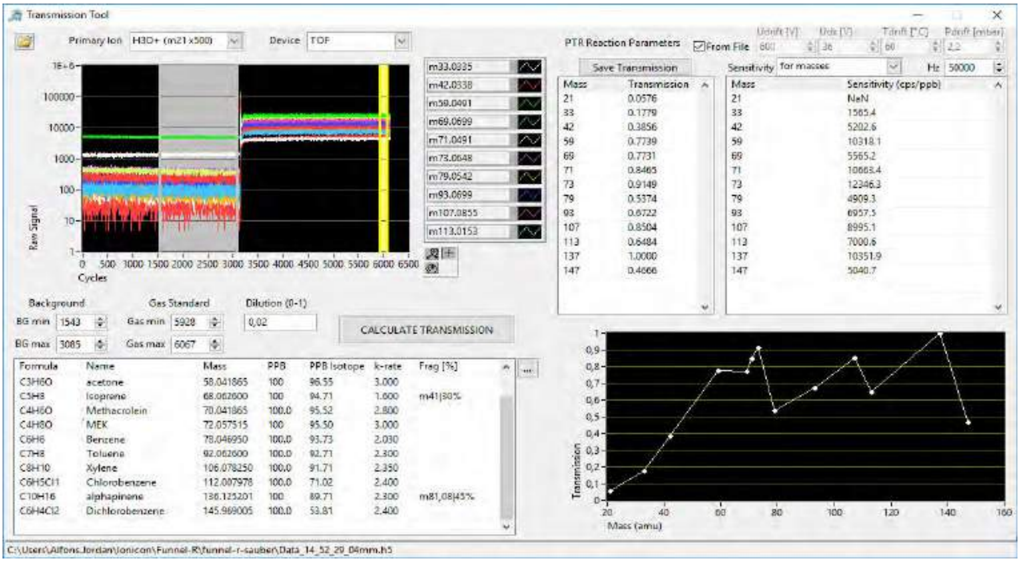


Figure 1: Schematic view of the novel PTR-TOFMS instrument.



Primary Ion: H3D+ (m21 x500)
Device: TOF

Background
BG min: 1543
BG max: 3085

Gas Standard
Gas min: 5928
Gas max: 6067

Dilution (0-1): 0,02

PTR Reaction Parameters ☑ From File
Udrift [V]: 600
Udx [V]: 36
Tdrift [°C]: 60
Pdrift [mbar]: 2,2

Sensitivity: for masses
Hz: 50000

Formula	Name	Mass	PPB	PPB Isotope	k-rate	Frag [%]
C3H6O	acetone	58.041865	100	96.55	3.000	
C5H8	Isoprene	68.062600	100	94.71	1.600	m41|30%
C4H6O	Methacrolein	70.041865	100.0	95.52	2.800	
C4H8O	MEK	72.057515	100	95.50	3.000	
C6H6	Benzene	78.046950	100.0	93.73	2.030	
C7H8	Toluene	92.062600	100.0	92.71	2.300	
C8H10	Xylene	106.078250	100.0	91.71	2.350	
C6H5Cl1	Chlorobenzene	112.007978	100.0	71.02	2.400	
C10H16	alphapinene	136.125201	100	89.71	2.300	m81,08|45%
C6H4Cl2	Dichlorobenzene	145.969005	100.0	53.81	2.400	

Mass	Transmission
21	0.0576
33	0.1779
42	0.3856
59	0.7739
69	0.7731
71	0.8465
73	0.9149
79	0.5374
93	0.6722
107	0.8504
113	0.6484
137	1.0000
147	0.4666

Mass	Sensitivity (cps/ppb)
21	NaN
33	1565.4
42	5202.6
59	10318.1
69	5565.2
71	10663.4
73	12346.3
79	4909.3
93	6957.5
107	8995.1
113	7000.6
137	10351.9
147	5040.7

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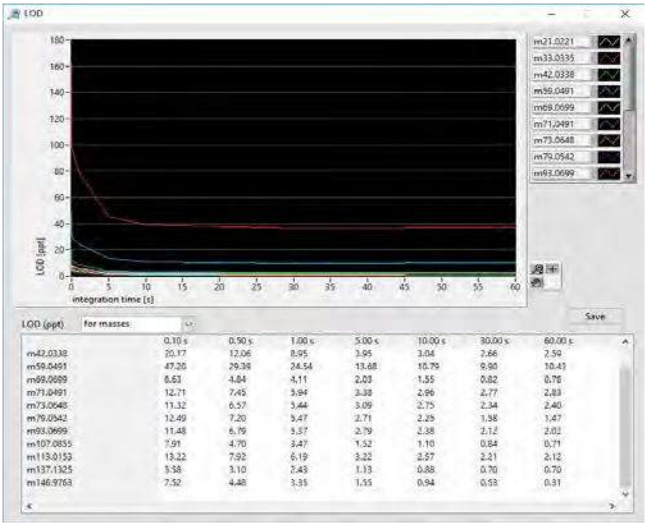
Figure 2: Determination of the instrument's sensitivity by analyzing a certified gas standard.



	0.10 s	0.50 s	1.00 s	5.00 s	10.00 s	30.00 s	60.00 s
m42.0338	20.17	12.06	8.95	3.95	3.04	2.66	2.59
m59.0491	47.26	29.39	24.54	13.68	10.79	9.90	10.43
m69.0699	6.63	4.84	4.11	2.03	1.55	0.82	0.76
m71.0491	12.71	7.45	5.94	3.38	2.96	2.77	2.83
m73.0648	11.32	6.57	5.44	3.09	2.75	2.34	2.40
m79.0542	12.49	7.20	5.47	2.71	2.25	1.58	1.47
m93.0699	11.48	6.79	5.57	2.79	2.38	2.12	2.02
m107.0855	7.91	4.70	3.47	1.52	1.10	0.84	0.71
m113.0153	13.22	7.92	6.19	3.22	2.57	2.21	2.12
m137.1325	5.58	3.10	2.43	1.13	0.88	0.70	0.70
m146.9763	7.52	4.48	3.35	1.55	0.94	0.53	0.31

Figure 3: Calculated LoDs for different integration times; calculation is based on the measurement data from Figure 2.

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Characterization of the transfer of cluster ions using hexapole ion guides in Atmospheric Pressure interface Time-of-Flight mass spectrometry

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Abstract

We developed a novel Atmospheric Pressure (AP)-interface Time-Of-Flight (APi-TOF) mass spectrometer using hexapole ion guides, the so-called ioniAPi-TOF. The instrument was characterized with regard to its transfer properties for cluster ions. The setting of the electric fields of ion guides and lenses in the AP-interface plays a crucial role for an efficient cluster ion-transfer when entering the mass spectrometer from ambient pressure. Fragmentation of weakly bond cluster ions during the transfer can complicate the interpretation of mass spectra data. We present results from the characterization of hexapole ion guides and show that a low-fragmenting ion transfer is even possible for cluster ions having a Gibbs free bond energy as low as 7 to 8 kcal/mol. In the tested configuration, the electric fields can also be set to allow elevated collision energies for Collision-Induced Dissociation (CID) studies up to Gibbs free bond energies of 23 kcal/mol. We further determined an overall ion transmission efficiency of about 1%. Experimental results from an inter-comparison with a quadrupole APi-TOF indicate that hexapole ion guides also allow the transfer of a broader mass range compared to quadrupoles.

Introduction

In the earth atmosphere, ions can contribute to atmospheric new particle formation via ion-induced nucleation. Under distinct conditions, new particle formation via the charged channel can dominate over the neutral formation pathway [1]. Ion-induced nucleation proceeds via the formation of cluster ions. To study the chemical composition of atmospheric ions and cluster ions with mass spectrometric methods, a high ion transmission efficiency and mass resolution is required as early observations with quadrupole mass spectrometers in the 1980's showed a complex picture which was only resolved for small positive ions using tandem mass spectrometry [2]. A huge step forward in the identification of atmospheric ions was done by Junninen et al. (2010) by coupling a high-resolution Time-Of-Flight mass spectrometer with an Atmospheric Pressure interface [3]. This instrument enabled the detection and identification of ions and cluster ions up to a mass range of 3000 Th with mass resolving powers of 3000-5000 leading to many important scientific discoveries in the field of atmospheric new particle formation [4]–[6].

However, uncertainties about fragmentation of cluster ions in the AP interface of APi-TOFs remain. There are indications that weakly bonded ligands like water molecules and others might be lost during the ion transfer most likely due to elevated collision energy in the AP interface caused by rather strong focusing properties of the commonly used quadrupoles [7]. Here, hexapole ion guides have a high potential as alternative ion guides as our findings indicate a less fragmenting ion transfer at comparable ion transmission efficiencies. As we will show, the application of hexapole ion guides provides further suitable properties for the ion transfer and therefore, for the study of atmospheric ions and cluster ions.

Experimental Methods

Instrument design

The ioniAPi-TOF is a Time-Of-Flight mass spectrometer with an Atmospheric-Pressure (AP) interface for the highly efficient transfer of atmospheric ions. In contrast to existing APi-TOFs, hexapole ion guides are used instead of quadrupoles for the ion transfer bridging different pressure stages. Both hexapoles are made of stainless-steel rods of a few cm in length. After the two hexapoles, an ion optical lens system focuses the ion beam. A laminar flow inlet transports ambient ions to the entrance of the mass spectrometer, see figure 1. The mass analyzer in this study is a commercial Time-Of-Flight mass spectrometer of the ioniTOF 1000 platform from IONICON Analytik GmbH with a mass resolution of 2000.

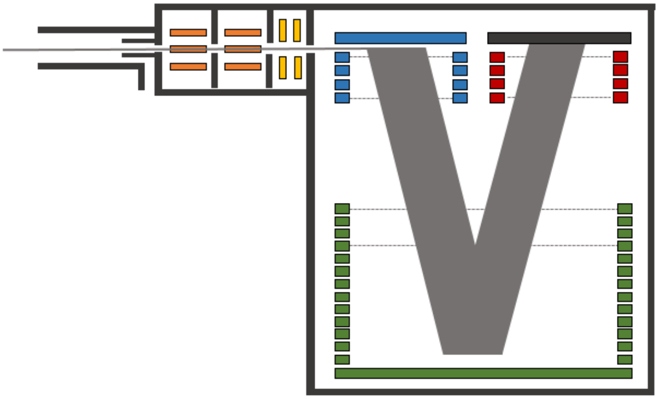

Figure 1: Schematic of the ioniAPi-TOF mass spectrometer. On the left, starting with the laminar flow inlet, followed by the Atmospheric Pressure interface with two pressure stages consisting of hexapole ion guides and another stage with the ion optical lens system. The Time-Of-Flight mass analyzer indicated with a V-shaped ion trajectory is a commercial ioniTOF 1000 from IONICON Analytik GmbH.

Experiment design

Characteristic instrument properties like mass resolution, transmission efficiency and fragmentation potential of cluster ions was determined with the so-called Cluster Calibration Unit (CCU). The Cluster Calibration Unit enables the generation of ions of various sizes depending on the selected calibration compound. The calibration standards used in this study are tetra-alkyl-ammonium halides [8]. The calibration standards are ionized via Electrospray-Ionization (ESI) and further size selected in terms of their ion mobility with a Vienna-type Differential-Mobility-

The ion count rate of the mass spectrometer can be compared to a Faraday Cup Electrometer (FCE) for determination of the mass dependent ion transmission efficiency.

Results

To characterize the fragmentation properties of hexapole ion guides, experiments with the voltage settings revealed that in the current configuration, the electric potential difference between the two hexapoles is most critical. Here, the combination of low pressure and electric field gradient can under certain settings lead to collision-induced dissociation. From the change of the distribution of $H_3O^+(H_2O)_{n=1-3}$ cluster ions for the different settings, we estimate that clusters with Gibbs free bond energies of 7 to 8 kcal/mol can be transferred without significant fragmentation. Another important characteristic of the ioniAPi-TOF is the transmission efficiency. With the CCU, we determined an overall ion transmission efficiency of about 1 % for a broad mass range.

In the course of the CERN CLOUD experiment in fall 2017, we conducted an inter-comparison with a quadrupole APi-TOF from the University of Eastern Finland, Kuopio. The results of this inter-comparison are shown in figure 2. Here, the mass spectra for an α-pinene and isoprene ozonolysis experiment are compared. The transmission efficiency of the hexapole based ioniAPi-TOF is comparable to the one of a quadrupole APi-TOF as can be seen from the comparable ion signal intensities. The striking feature in this figure is the absence of small ions in the lower panel, that shows the mass spectrum of the quadrupole APi-TOF. In the course of the campaign, this instrument was set to optimized transmission for high mass ions. Due to the low-mass cut-off property of the quadrupole, ions below 120 Th cannot be detected. Here, the ioniAPi-TOF demonstrates the potential of hexapole ion guides. Hexapole ion guides cannot only be set to transmit cluster ions with a lower fragmenting electric potential, but also allow the transmission of a broader mass range at comparable ion transmission efficiencies.

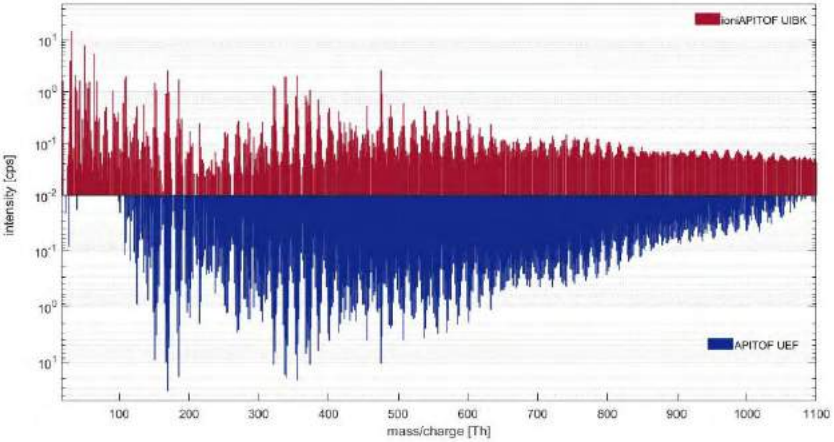

Figure 2: Inter-comparison of the mass spectra of both APi-TOFs during an isoprene and α-pinene ozonolysis experiment at the CERN CLOUD facility in fall 2017.

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Aerosol Chemistry Investigations by CHARON PTR-TOF

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Abstract

Herein we present a detailed characterization of CHARON PTR-TOF based on the detection of a set of pure compounds including ionic fragmentation, sensitivity and response times. We present a recipe on how to quantitatively and qualitatively measure the organic fraction of aerosol in real-time. Intercomparison studies with alternative instruments show great agreements for urban aerosol and secondary organic aerosol (SOA) formed in various oxidation reactors. We will show first results of the characterization of SOA produced from the ozonolysis of a set of monoterpenes. These results include the chemical composition as well as the volatility of the bulk SOA and individual constituents.

Introduction

Scientific progress in organic aerosol chemistry is still hampered by the lack of analytical methods that comprehensively and quantitatively characterize the organic composition of particulate matter in the atmosphere. Recently, the "Chemical Analysis of Aerosol Online" (CHARON) particle inlet has been introduced, enabling proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF) instruments to characterize particulate-bound organics down to <100 pg m^{-3} levels. [1,2] Herein, we show a detailed characterization of CHARON PTR-TOF based on pure chemical compositions. We further apply the derived information to aerosol chemistry and physics studies including urban aerosol and thermo-denuder aerosol-flow-tube measurements of secondary organic aerosol formed by the ozonolysis of α-pinene, 3-carene and limonene.

Methods

In the following the experimental methods used for this study are briefly introduced.

CHARON PTR-TOF

For the presented results the CHARON particle inlet was coupled to a PTR-TOF 8000, a PTR-TOF 4000 X2, or a PTR-TOF 6000 X2 instrument (all IONICON Analytik GmbH, Austria). The CHARON inlet consists of a gas-phase denuder for stripping off gas-phase analytes (efficiency >99.999%), an aerodynamic lens system for particle collimation, an inertial sampler for the particle-enriched flow and a thermodesorption unit for particle volatilization. Proton transfer from hydronium ions quantitatively ionizes almost the full range of organic analytes in the intermediate to low volatility range. The high mass resolution (R > 6000, PTR-TOF 6000 X2) and mass accuracy (< 10 ppm) allows assigning elemental compositions to organic analyte ions over a large mass range. With enrichment factors between ~25 (PTR-TOF 6000 X2) and ~44 (PTR-TOF 8000) for particle diameters (D_P) between 150 nm and >1000 nm (lower enrichment for particles in the 80-to-150 nm diameter range), particulate organic matter is measured online and in real-time down to 0.1 µg m^{-3} and 1.4 µg m^{-3}, respectively.

Pure Compound Characterizations

PTR-MS is a soft chemical ionization technique. Nevertheless, proton transfer reactions under the thermal conditions of a drift tube reaction chamber lead to a certain degree of fragmentation. This is especially the case for complex molecules found in secondary organic aerosol (SOA) that often include multiple groups. To study the effects of this ionic fragmentation on the interpretation of CHARON PTR-TOF data, around 30 pure compounds of atmospheric relevance were aerosolized, preselected by a differential mobility analyzer to transmit a monodisperse particle size-distribution and were finally detected by CHARON PTR-TOF (Leglise et al., in preparation). Side by side measurements with a condensation particle counter also allowed for a direct feedback on the quantification capabilities of CHARON PTR-TOF for selected compounds.

As this set of compounds covers a wide range of volatilities (from intermediate to low volatility), we have additionally quantified the response times of a (CHARON) PTR-TOF 4000 X2 for samples in the gas- and particle phase (Piel et al., in preparation).

Results and Discussion

Based on the results of the pure compounds characterization we will show how qualitative (elemental composition) and quantitative analyses (mass concentrations) can be efficiently corrected for biases caused by analyte ion fragmentation in the PTR-TOF analyzer. We have therefore developed a correction recipe to correct for ionic fragmentation simply based on the measured bulk chemical composition of the aerosol. In addition, parameterizations of reaction rate-constants based on the detected chemical compositions [3] plus Su and Chesnavich's parameterized capture rate theory [4] have demonstrated to show promising quantification results for pure compounds as well as ambient aerosol [2].

In addition we have characterized the 1/e response times that were typically in the range of 3-5s for IVOCs, 5-20s for SVOCs and up to one minute for LVOCs.

Applications of CHARON PTR-TOF

We apply the fragmentation correction recipe to a set of measurements. We will show how bulk elemental ratios (O:C, H:C) of urban aerosol and monoterpene-derived SOA compare with parallel time-of-flight aerosol-mass-spectrometer (Aerodyne Inc, USA; TOF-AMS) measurements and reported literature values.

We will present the detected mass spectra of SOA produced from the ozonolysis of α-pinene, limonene and 3-carene, respectively, in an aerosol flow tube reactor after 30 min of residence time. We will compare the volatility of this monoterpene-derived SOA on a molecular level as directly measured in thermodenuder experiments and predicted from parametrizations like the 2D-volatility basis set using the CHARON PTR-TOF-derived chemical composition. The implications for the aerosol chemistry of monoterpene-derived SOA will be discussed.

Acknowledgement

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Combining a PTR3-TOF-MS with a Nitrate-CIMS: Quantifying initial nanoparticle growth over a wide tropospheric temperature range

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Abstract

New particle formation by gas-to-particle conversion could account for more than 50 % of global cloud condensation nuclei concentrations and therefore directly impacts climate. After nucleation of small molecular clusters, high initial growth rates are required that the newly formed particles reach sizes where they can act as cloud condensation nuclei. The vapors responsible for that growth in the atmosphere are sulfuric acid and maybe more important, organics produced by the oxidation of volatile organic compounds (VOCs). This oxidation process and the subsequent nanoparticle growth might be heavily influenced by ambient conditions, e.g. by temperature. Here we present results from the CERN CLOUD experiments, where a PTR3-TOF-MS was combined with a Nitrate-CIMS in order to identify the organic species responsible for growth at warm (+25°C) and cold temperatures (-25°C). We observe that the lesser extend of autoxidation at cold temperatures is compensated by the decrease of volatility of all oxidation products. Organics might therefore be responsible for initial growth over a wide range of tropospheric conditions and could for example contribute to upper tropospheric new particle formation over areas with high biogenic VOC emissions like the Amazon Basin.

Introduction

New particle formation and subsequent nanoparticle growth has been identified as the main contributor to the global budget of cloud condensation nuclei (CCN), significantly impacting the Earth's radiative balance [1]. In order to reach CCN sizes, high initial particle growth rates are crucial for the survival of freshly formed nanoparticles, as they rapidly coagulate with pre-existing aerosol [2]. Characteristics of particle growth depend largely on the abundance of different condensable vapours and parameters such as temperature and relative humidity. Detailed studies exploring this wide parameter space are missing so far.

While sulfuric acid was thought to be the major compound responsible for new particle formation, recent studies have shown that the oxidation products from alpha-pinene ozonolysis can efficiently grow nanoparticles [3]. Vegetation and its emissions of various types of volatile organic compounds might therefore be responsible for a large part of the pre-industrial cloud condensation nuclei budget [4]. However, the oxidation chemistry of monoterpenes is rather complex and might be heavily influenced by temperature [5].

Here we use the CERN CLOUD experiment in order to investigate the behaviour of alpha-pinene ozonolysis and the subsequent particle formation under a wide range of tropospheric temperature conditions. We find that new particle formation from biogenic vapors can proceed at warm and cold temperatures efficiently. Therefore this process might be of significant importance throughout the troposphere [6].

Experimental Methods

We use a Nitrate-CI-APi-ToF-MS [7] together with the PTR3-ToF-MS [8] in order to quantify the condensable vapor species which contribute to nanoparticle growth. While the Nitrate-CI is able to quantify highly oxygenated molecules (HOMs) with high precision due to selectiveness of the ionization technique. The PTR3 measures VOCs, modestly oxygenated compounds as well as some (HOMs). We use several molecular ion species unambiguously identified in both mass spectrometers to bring the instruments into agreement.

Measurement of the particle growth rates in the sub-10 nm regime is performed with a DMA-train [9]. With this recently developed instrument we are able to measure nanoparticle growth down to 1.8 nm, i.e. close to the critical cluster size. It is especially that size-range which is important for the survival probability of newly formed particles [2].

Experiments were conducted at the CERN CLOUD experiment, which can be kept at constant temperature with ± 0.1K precision. It achieves extremely low contaminant levels using air mixed from boil-off liquid nitrogen and oxygen. Trace gases like alpha-pinene or ozone can be added precisely at the ppt level and have been monitored with a PTR-TOF-MS. Sulfuric acid contamination was below $10^5\,\mathrm{cm}^{-3}$ throughout the experiments and all experiments were performed without NO_x and in absence of any other OH source than the ozonolysis of alpha-pinene.

Results

In the combined mass spectra observed during the alpha-pinene ozonolysis experiments the PTR3 introduces more than 200 previously undetected molecular ion signals. Most of them are not HOMs, (defined as O:C >0.7 for monomers), but mostly compounds with a lower state of oxidation. In order to simplify considerations about gas-particle-partitioning, a volatility was estimated for every organic compound and thereafter they were grouped into a volatility basis set. At low temperature, fewer polar functional groups and therefore a lower degree of oxygenation is required for a compound to have a low volatility. Therefore, at e.g. -25°C, the species observed by the PTR3 contribute substantially in the low volatility range and therefore to growth.

Observed nanoparticle growth rates can be modelled with the estimated volatility basis set from the combination of both mass spectrometers. Due to the additional information from the PTR3, growth at cold temperatures can be precisely reproduced by the model. This is supported by measurements of the particle phase composition, with a FIGAERO-CIMS (Filter Inlet for Gas and Aerosols), using O_2^- as reagent ion. Also in the particle phase more and more less oxygenated species appear at lower temperatures.

However, the yield of highly oxygenated species significantly drops at cold temperatures, due to a reduction in autoxidation rates [5]. Both effects seem to be at least in the same order of magnitude as the measured growth rates are similar at similar precursor (alpha-pinene) reaction rates, which is shown in Figure 1. This yields the conclusion that growth by organics is important in warm and cold environments throughout the troposphere due to the compensating effects described above.

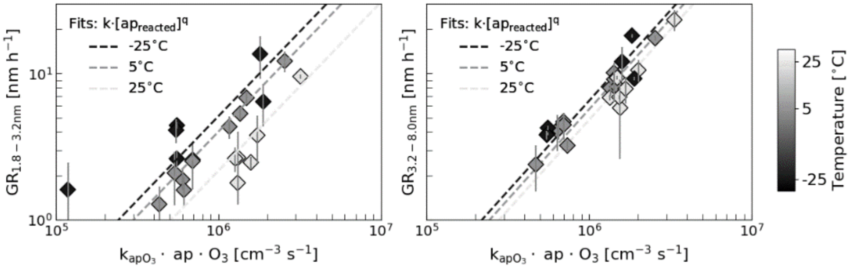

Figure 1: Measured growth rates from alpha-pinene ozonolysis over a wide tropospheric temperature range versus precursor reaction rates. Growth proceeds similarly at cold and warm temperatures at equal precursor reaction rate constants, especially at larger sizes (right panel). The small size range (left panel) shows some differences as it is very sensitive to the volatility distribution of the oxidation products.

Discussion

We demonstrate that by combining two complementary ionization techniques we can obtain detailed insights into condensable gas phase species from alpha-pinene ozonolysis over a wide temperature range. Due to the compensating effects of reduced autoxidation but decreased volatility of all oxidation products, growth can proceed equally fast at cold temperatures compared to elevated temperatures. This could point towards an important contribution of organics to nanoparticle growth at high altitudes over regions with large biogenic VOC emissions like the Amazon Basin.

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A revolutionary new method for the production of NH_4^+ reagent ions and its applications

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Abstract

The ample advantages of using NH_4^+ as reagent ions in Proton-Transfer-Reaction – Mass Spectrometry (PTR-MS) have been known for a long time, but due to the requirement of toxic, corrosive and environmentally hazardous NH_3 for NH_4^+ production, this reagent ion has not found its widespread use yet. We present a novel method for the production of NH_4^+ which makes the use of problematic NH_3 obsolete, only requires H_2O and N_2 and achieves reagent ion purities of about 98%. With this method the infamous explosive TATP can be detected with a more than 20 times increased sensitivity. For the first time H_3O^+ and NH_4^+ studies on nine organophosphorus chemical warfare agents have been conducted and the advantages of NH_4^+ reagent ions in terms of sensitivity and selectivity will be demonstrated.

Introduction

In PTR-MS traditionally H_3O^+ is used as reagent ions. However, recent PTR-MS instruments are additionally capable of utilizing alternative reagent ions, e.g. NO^+, O_2^+, Kr^+ and other positively or negatively charged reagent ions [1-3] and thus are sometimes called Selective-Reagent-Ionization – Mass Spectrometry (SRI-MS) instruments.

All of these reagent ions used in PTR-MS have distinct advantages, which make them particularly suitable for certain applications. An especially beneficial reagent ion is the ammonium cation NH_4^+. NH_3 has a Proton Affinity (PA) of 854 kJ/mol, whereas H_2O has a PA of 691 kJ/mol. Proton transfer is energetically only possible if the PA of the analyte is higher than the PA of the reagent ion. Thus, some of the advantages of using NH_4^+ are:

Improved selectivity: In PTR-MS often two or more compounds are detected at the same nominal *m/z* (e.g. isobars or isomers). If they share the same exact *m/z* (isomers) or if the mass resolution of the mass spectrometer is insufficient to separate isobars, additional measures have to be taken to distinguish them. In [4] for example pinene ($C_{10}H_{16}$; PA < 854 kJ/mol and > 691 kJ/mol) and 2-ethyl-3,5-dimethylpyrazine ($C_8H_{12}N_2$; PA > 854 kJ/mol) are mentioned. The protonated molecules of both compounds share nominal *m/z* 137 when using H_3O^+ as reagent ions. However, with NH_4^+ as reagent ions, only 2-ethyl-3,5-dimethylpyrazine gets protonated whereas pinene does not react. That is, if only one of these two compounds is present in a sample and ions are detected at *m/z* 137 with NH_4^+ as reagent ions, the compound can be identified as 2-ethyl-3,5-dimethylpyrazine. If ions are detected at *m/z* 137 with H_3O^+ as reagent ions, but not with NH_4^+, the compound can be identified as pinene.

Simplification of mass spectra: If, for example, in a complex sample only compounds with a PA higher than the PA of NH_3 need to be detected and quantified, using NH_4^+ reagent ions will blank out all analytes with a PA lower than the PA of NH_3 and thus will lead to a mass spectrum which is considerably easier to interpret than a mass spectrum generated with H_3O^+ reagent ions.

Less fragmentation: Compounds with high PAs (> 854 kJ/mol) often show high levels of fragmentation upon PTR ionization from H_3O^+, which makes identification and quantification difficult. According to [5] the explosive TATP ($C_9H_{18}O_6$) does not form the characteristic ion TATP.H^+, but many fragment ions when reacting with H_3O^+ at a reduced electric field strength (E/N) which is typically used in PTR-MS. When switching to NH_4^+ as reagent ions the protonated TATP molecule as well as TATP.NH_4^+ are formed at high abundance and thus detection and identification of this explosive is improved. Another example is the Chemical Warfare Agent (CWA) sarin ($C_4H_{10}FO_2P$), which also shows a high level of fragmentation upon H_3O^+ ionization [6]. Using NH_4^+ as reagent ions effectively suppresses fragmentation and produces the protonated sarin molecule as well as [sarin+NH_3].H^+ clusters.

Despite of these advantages, so far NH_4^+ has found only limited application among PTR-MS users. Most probably this is because all known methods for the production of NH_4^+ reagent ions involve the introduction of NH_3 to at least some parts of the instrument, which comes with a series of serious disadvantages:

- NH_3 is toxic, corrosive and environmentally hazardous.
- The use of NH_3 gas cylinders requires a high level of safety precautions and is prohibited in some areas.
- The use of ammonia solutions as an NH_3 source does not provide a stable NH_3 concentration over time.
- NH_3 can damage important parts of the instrument, such as lines, lenses, vacuum pumps, valves, flow controllers, etc.
- The exhaust of the PTR-MS instrument is contaminated with NH_3 and needs to be properly disposed.
- The surfaces inside the PTR-MS instrument get covered with NH_3 which desorbs very slowly after switching to a different reagent ion, i.e. switching from NH_4^+ to H_3O^+ takes tens of minutes if not hours.

Here we present a novel method of producing NH_4^+ reagent ions without the need of any NH_3, but solely N_2 and H_2O. Thus, this method eliminates all of the above-mentioned disadvantages while all advantages, such as improved selectivity and sensitivity, are preserved. We apply the PTR-MS instrument equipped with this feature to the extremely sensitive detection of TATP and, for the very first time, to a series of organophosphorus CWAs.

Experimental Methods and Discussion

We utilized the commercially available high-resolution and sensitivity PTR-TOF 6000 X2 (IONICON Analytik GmbH., AT) for a first test of the novel NH_4^+ production method. In normal H_3O^+ mode the instrument was operated with a H_2O source gas flow of 6.5 sccm. At a drift tube voltage of 600 V and a drift tube pressure of 2.3 hPa the H_3O^+ reagent ion yield was measured being about 22 x 10^6 cps. The relative amount of parasitic ions originating from the ion source was determined being about 4.6% plus about 2.4% water cluster $2(H_2O).H^+$ at m/z 37, which is of course dependent on the drift tube voltage.

However, when the H_2O flow was reduced to 3 sccm and additionally 3 sccm N_2 flow was added as a source gas, immediately the production of NH_4^+ reagent ions could be observed. The switching time took about 3-5 s and is mainly limited by the response time of the mass flow controllers controlling the source gas flows. The purity of NH_4^+ production can be considerably improved by increasing the pressure in the source drift region and increasing the voltage for extraction of the reagent ions from the ion source into the drift tube. With these optimized settings and a drift tube voltage of 650 V at 2.3 hPa, a NH_4+ reagent ion yield of about 19 x 10^6 cps, i.e. a comparable intensity to the H_3O^+ mode, was achieved. The relative amounts of parasitic ions were about 2.4%, i.e. the reagent ions are even more pure than in H_3O^+ mode, plus about 0.1% $2(NH_3).H^+$ at m/z 35, which is again dependent on the drift tube voltage.

Switching back to H_3O^+ by applying the settings for H_3O^+ mode again just takes seconds and the relative amount of remaining parasitic NH_4^+ drops below 10% nearly instantaneously and below 4% after about 10 s.

In order to confirm these first results and test the advantages of NH_4^+ with a real-life example, we put one TATP EMPK (ExploTech GmbH., DE) into a sampling bag. EMPK are small aluminum foam test bodies coated with explosives in the µg region, thus no special licenses or handling precautions are required. Figure 1 shows the detected ion yield for *m/z* 223 (protonated TATP). After about 5 s the sampling bag is connected to a compact and high-sensitivity PTR-TOF 1000 *ultra* being operated in H_3O^+ mode at an extremely low E/N setting. The recorded ion yield is about 2400 cps. After about 18 s the settings for NH_4^+ mode are applied, i.e. N_2 is added to the ion source, pressures and voltages are adjusted. Within 2 s the $TATP.H^+$ yield jumps to about 13,000 cps and after about 10 s the signal reaches a plateau of about 50,000 cps. That is, switching from H_3O^+ to NH_4^+ boosts the instrument's sensitivity for $TATP.H^+$ detection by more than a factor of 20. It should be noted that for this example the N_2 source was ambient air (which contains about 80% N_2) so that no additional source gas containers were necessary.

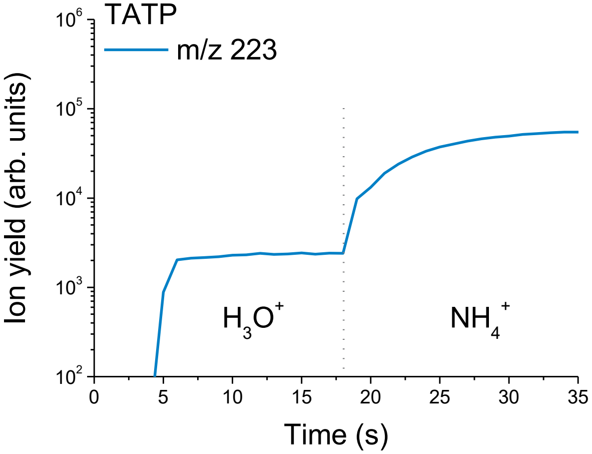

Figure 1: Ion yield for $TATP.H^+$ (m/z 223) with the PTR-TOF 1000 being operated in H_3O^+ and then switched to NH_4^+ mode.

Recently, we performed a measurement campaign at a facility specialized and licensed for CWA handling, where nine of the most important CWAs (including sarin, tabun, soman, VX, etc.) have been investigated with H_3O^+ and NH_4^+ reagent ions, respectively. These results show a dramatic increase in selectivity and sensitivity and will be presented.

In summary our novel development enables the powerful capability of operating a PTR-MS instrument with NH_4^+ reagent ions, while no NH_3 or any other harmful, toxic, environmentally hazardous, corrosive, etc. compounds are necessary. The only compounds needed for extremely pure NH_4^+ production are N_2 and H_2O.

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The CHARON inlet for online sampling of atmospheric particles by PTR-MS: basics and recent developments

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Abstract

Particulate organic matter in the Earth's atmosphere is difficult to measure, especially if analytes are reactive and/or semivolatile. Offline sampling techniques based on particle collection onto a filter or impactor often suffer from sampling artefacts caused by reactive transformations on the collection substrate as well as adsorption and desorption of semivolatile analytes. Online sampling without sample pre-collection, as for example implemented in the aerosol mass spectrometer (AMS), has greatly reduced such sampling artefacts. AMS measurements do, however, suffer from the decomposition of organic analytes during particle vaporization at 600 °C and hard (70 eV electron) ionization.

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a well-established online measurement technique for gaseous organic analytes. Chemical ionization via proton transfer from hydronium (H_3O^+) ions greatly reduces fragmentation of organic molecules and thus often allows identifying the elemental composition of analytes. We have recently developed a particle inlet system for PTR-MS instruments [1]. The CHARON ("*Chemical Analysis of Aerosol On-line*") inlet consists of a gas-phase denuder, an aerodynamic lens and a vaporization unit. The activated carbon monolith denuder removes gaseous analytes from the sampling flow. The aerodynamic lens enriches the particle concentration in the instrument subsampling flow by a factor of 30 to 50. In the vaporizer, particle-bound organics are evaporated at reduced pressure (few mbar) and relatively low temperature (~150 °C) which reduces thermally induced decomposition of analytes. The CHARON inlet was originally conceived and prototyped at the University of Innsbruck and is nowadays being commercialized by Ionicon Analytik. Ionicon has developed CHARON from a laboratory prototype into a rugged and fully automated particle sampling system for PTR-ToF-MS instruments. Automated operation allows to alternately sample through CHARON or through the conventional gas inlet in 10-minute intervals. Ionicon has also achieved significant improvements in detection limits (~0.1 ng/m³) and time response (3-5 s for IVOC, 5-20 s for SVOC, < 60 s for LVOC).

Published work relying on the CHARON technique includes i) the investigation of organic particle emissions from a marine diesel engine [2], ii) ambient air measurements in three European cities including a measurement comparison with an AMS instrument [3],

iii) an atmosphere simulation chamber study on biogenic secondary organic aerosol [4, 5], iv) an atmosphere simulation chamber study on secondary organic aerosol (SOA) formed from the OH-induced degradation of an amine [6]. Our ongoing work includes v) the development of a fragmentation correction algorithm for deriving total organic mass as well as bulk O:C and H:C ratios (Leglise et al., *in preparation*), vi) the analysis of the first airborne CHARON-PTR-ToF-MS measurements conducted in summer 2018 (Piel et al., *in preparation* – see separate abstract in this book), vii) the analysis of a measurement comparison with an EESI-MS instrument (Zhou et al., *in preparation*), viii) the analysis of aerosol flow tube studies conducted on anthropogenic and biogenic SOA (Martinez et al., *in preparation*; Leglise et al., *in preparation*), ix) the analysis of chamber experiments conducted on SOA formed from amines (Tan et al., *in preparation*)

The long list of recent applications demonstrates that CHARON PTR-ToF-MS is rapidly evolving into a successful analytical technique for monitoring the organic composition of submicrometer particles in real time. In my talk, I will present the basics of the CHARON technique and show the highlights of our recent work.

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Applications in the Industry

Trace gas analysis with PTR-MS at Carl Zeiss SMT for quality control and root cause analysis

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Abstract

Organic contamination inside optical systems of semiconductor lithography tools could lead to transmission loss and lens heating issues. But where does this contamination come from? What is the critical level? Two examples for root cause analysis of contamination issues are described here. In addition a more general cleanliness quality control set-up is presented.

Introduction

Until now TENAX analytics has been used for detection of volatile and non-volatile organics in gases. This method has several disadvantages: online analysis is impossible (takes at least 2 days), large sample volumes are needed for low limits of detection and localization of outgassing is difficult. Because of these drawbacks a novel approach for the root cause analysis of optical systems was needed. It delivers fast quantification and localizes the contamination directly: *P*roton *T*ransfer Reaction *T*ime *o*f *F*light *M*ass *S*pectrometry (PTR-TOF MS).

Experimental Methods

PTR-MS uses soft ionization technology with low fragmentation rates. By proton transfer from H_3O^+, all compounds with a higher proton affinity (PA) than water get ionized (this means almost all organic substances!). Common constituents of air, such as N_2 , O_2 , Ar, CO_2 etc. have lower PAs than H_2O and are therefore not detected and do not disturb the measurement. Due to precisely controlled ion source and drift tube parameters, absolute quantification of VOC (*v*olatile *o*rganic *c*ompounds) concentrations is possible. Not only trace volatile organic compounds are detected by PTR TOF-MS but additionally also very important, inorganic substances, i.e. SO_2 can be detected and quantified with the same instrument. As all ionizing agents are produced in a hollow cathode discharge ion source with good purity no additional mass filter is needed for reagent ion selection (as in other analytical methods employed) and remaining reagent ion impurities can be clearly distinguished from isobaric sample compounds due to the high mass resolution of the time-of-flight mass spectrometer used.

Results

PTR-MS is used for localization of contaminants inside optical tools. With its high sensitivity and fast answer times it is well suited for finding contamination sources. Because of its capillary design at the inlet, localization of organic substances becomes possible which are usually inaccessible like blind holes, tubings or undercuts.

Additionally a semi-automatic cleanliness trace gas control of litho-tools is possible. Time and cost consuming alternative chemical analyses are replaced by one method which can be done by one trained worker in less than one hour. This process will be presented (prearrangement, measurement, data acquisition, automatic alarming (depending on concentration levels), reporting and data management).

Figure 1: Contamination Analysis of Gas Manifold of an Optical Lithography Tool.

Verification of odor abatement technologies for livestock production based on measurements by PTR-MS

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Abstract

In Denmark, it has recently been accepted that chemical measurements by PTR-MS can be applied in the verification of odor abatement technologies for livestock production. The aim of the present study was to identify key odorants in air from pig houses. PTR-MS results from a number of studies with pig houses were compiled and based on the relation between the OTV and concentration range key odorants were identified. The results demonstrate that even though a number of odorants are found in air from pig houses it is only a relative limited number of odorants that should be included in the verification of odor abatement technologies. For pig production nine odorants within sulfur compounds, amines, carboxylic acids, phenols and indoles were identified as key odorants.

Introduction

A number of studies have been concerned with the conversion of chemical measurements into an odor value that could replace odor measurements by dynamic olfactometry [1-5]. However, it is a challenge to achieve a high correlation between dynamic olfactometry with a high variability and chemical measurements of odorants with a relatively low variability. In the study by Hansen et al. [4] both dynamic olfactometry and chemical measurements of odorants by PTR-MS were performed on-site without bias from sample bags. In this study a fairly high correlation (r2 = 0.77) was achieved and this indicates that chemical measurements can be used as an alternative to dynamic olfactometry. However, the application of prediction models is depending on the sample matrix and therefore application of odor activity value (OAV) based on odorant concentrations and odor threshold values (OTV) has been suggested as a method. The advantage of this method is that it resembles dynamic olfactometry in the sense that olfactometry estimates the detection threshold for the whole air sample and the OTV is the detection threshold for the individual odorants. In Denmark it has recently been accepted that chemical measurements of odorants can be used to verify the effect of odor abatement technologies for livestock production using OAV. The aim of the present study was to identify key odorants to be included in verification of odor abatement technologies for pig production.

Experimental Methods

During recent years, the Air Quality Engineering group at Aarhus University has examined the emission of odorants from pig houses and the effect of different abatement technologies by PTR-MS [4, 6-8]. In these studies, a high-sensitivity PTR-MS was applied for measuring odorants. The PTR-MS was operated under standard drift conditions with a drift voltage set at 600 V, a drift tube pressure between 2.1 – 2.2 mbar and a drift temperature at 60 – 75 °C. The sensitivity of the compound of interest was estimated using the rate constants for proton transfer, estimated drift tube residence time, and the mass-specific transmission factor [9]. Furthemore, GC measurements were used for compound assignment. Based on these studies the results for the untreated air (ex. before air cleaner) was extracted and evaluated in relation to the OTV's estimated in the study by Hansen et al. [10].

In the studies by Feilberg et al. [6] and Liu et al. [8] the emission of odorants was measured from an experimental facility with 32 growing-finishing pigs and fully slatted floor. In the study by Hansen et al. [7] the emission of odorants was measured from a commercial pig production house with 350 pigs and fully slatted floor. In the study by Hansen et al. [4] the emission of odorants was measured from three commercial pig house with 1) 650 pigs and fully slatted floor, 2) 270 pigs and partly slatted floor, and 3) 350 pigs and fully slatted floor.

Results

In Table 1, the most commonly found odorants in air from pig production facilities are listed along with their OTV and concentration range. The applied OTV's were based on a study by Hansen et al. [10] where measurements were combined with values found in literature. The studies that were included in the study by Hansen et al. [10] were all based on measurements where the actual exposure concentration during measurements was estimated.

Table 1. Odor threshold values and measured concentration range for odorants found in air from pig houses.

Odorants	**m/z**	**OTV, ppb$_v$**	**Concentration range, ppb$_v$**	**Key odorants, ±**
Hydrogen sulfide	35	0.8	100 – 1000	+
Methanethiol	49	0.03	2 – 20	+
Dimethyl sulfide	63	2.3	2 – 15	-
Trimethylamine	60	0.08	5 – 30	+
Acetaldehyde	45	1.5	10 – 25	-
Acetone	59	42000	5 – 15	-
2-butanone	73	440	2 – 5	-
2,3-butandione	87	0.06	1 – 2	-
Acetic acid	61 + 43	8.3	200 – 500	+
Propanoic acid	75 +57	5.7	50 – 250	+
Butanoic acid	89 +71	0.23	40 – 120	+
Pentanoic acid	103+85	0.2	5 – 30	+
Phenol	95	8.4	1 – 10	-
4-methylphenol	109	0.02	5 – 20	+
4-ethylphenol	123	0.4	0.5 – 2	-
Indole	118	0.06	0.1 – 2	-
3-methylindole	132	0.003	0.1 – 1	+

The results in Table 1 shows that even though a number of odorants are found in air from pig houses only a limited number of odorants will have a significant influence. Based on the relation between OTV and the concentration range nine odorants were identified as key odorants that should be included in evaluation of abatement technologies for pig production. The significant odorants are found within sulphur compounds, amines, carboxylic acids, phenols and indoles.

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Real-time Characterization and Quantification of Electronic Cigarette Aerosol and VOC using Proton Transfer Reaction Mass Spectrometry

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Abstract

To date, the analysis of aerosol and gas phase volatile organic compounds (VOC) emitted by Electronic Nicotine Delivery Systems (ENDS) relies on a variety of standardized but time-consuming off-line technologies. Conventional methods typically involve sampling of aerosol from multiple sequential puffs on a filter pad, or in an impinger solution, followed by extraction and derivatization. These procedures are resource intensive, result in low time-resolution prohibiting puff-by-puff analysis, and may lead to sample alteration due to evaporation, or chemical reactions on the filter. Real-time aerosol and VOC characterization methods can overcome these limitations and enable the direct assessment of multiple key components simultaneously. Recently, Blair *et al.* [1] demonstrated that proton transfer reaction mass spectrometry (PTR-MS) can be employed to achieve on-line quantification of VOC emitted from ENDS while Breiev *et al.* [2] introduced a dilution system which facilitated the online measurement of aerosol from ENDS.

The PTR-MS technique has been described previously [3]. For this study a PTR-TOF 6000 X2 (IONICON Analytik GmbH, AT [4]) was employed in combination with a 3-stage dilution system, developed by Ionicon (IONICON Analytik GmbH, AT). ENDS were vaped with a Borgwaldt LME1 smoking machine, generating 70 ml 3 s long puffs in a 30 s interval. For exhalation studies a breath sample interface with disposable mouthpiece was used. The inlet line and drift tube chamber were heated to 150 °C to avoid condensation. In order to determine the exact concentrations of the studied compounds, we used a calibration gas for volatile compounds and a Liquid Calibration Unit (LCU [5], IONICON Analytik GmbH, AT) to calibrate the PTR-TOF 6000 X2 for the most common harmful or potentially harmful constituents (HPHCs).

In this study, we evaluated the described set up for applicability and stability to perform reliable, real-time measurement of HPHCs. We characterized and quantified key aerosol and VOC constituents of ENDS products directly and simultaneously and assess their LODs with a dilution factor of ~1000, concentrations of several compounds were determined puff-by-puff and were compared to results obtained from conventional off-line methods. Lastly, we compared exhaled breath following the inhalation of mainstream aerosol from different ENDS devices and a combustible cigarette. We demonstrate that PTR-MS may be used as an alternative to off-line methods for simultaneous quantification and characterization of most HPHCs found in aerosol as well as VOCs, puff-by-puff, and even intra-puff to enable immediate assessment of new nicotine containing formulations, changes in device design, and validation of product designs.

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Automated Measurement Software for Industrial Applications

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Abstract

The AME software is a framework to set up a PTR-MS for monitoring of a complex set of compounds by Automating Measurement, data Evaluation, and visualization. A pattern matching algorithm combined with a compound library greatly enhances compound selectivity and specificity. Together with a simple front-end and data interface to industrial systems, a PTR-MS with AME software becomes an ideal industrial monitoring solution.

Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is one of the most sensitive methods for real-time gas analysis. The ‘soft’ PTR ionization largely avoids fragmentation, providing the molecular (protonated) ion. The mass of the compound is the most important parameter for its identification. High resolution PTR-TOF was a major step towards unambiguous identification. PTR-TOF measure the exact mass of a compound, therefore resolve isobars and identify the chemical composition of a compound. However, the separation of isomeric molecules remains challenging.

Additional information on a sample can be gathered by applying a variety of ionization modes. PTR-MS systems provide several possibilities: by selecting different pre-cursor ions (SRI) AND the variation of the collisional energy (E/N).

The AME software automates the measurement in different ionization modes and consolidates this data. The analysis part employs a pattern matching algorithm in combination with a compound library to enhance selectivity and specificity, which also allows the separation of overlapping molecules including isomers.

Methods

A PTR-TOF acquires a complete mass spectrum in a split second, which provides extensive information on the composition of the analyzed sample. Nevertheless, this information can be multiplied by analyzing the sample using different ionization modes. IONICON PTR-TOF systems provide several possibilities, by selecting different pre-cursor ions (SRI), the variation of the collisional energy (E/N), and combinations thereof.

SRI

PTR-MS systems with SRI can use H_3O+, NO+, O_2+, NH_4+, Xe+ and Kr+ ionization modes [1, 2]. For AME typically the first three modes are used. H_3O+ is the most universal. O_2+ is primarily employed to detect compounds that cannot be ionized in H_3O+. Combining these two modes gives access to all compounds typically of interest.

To separate isomers the application of different pre-cursor ions is just a partial solution. Mainly H_3O+ in combination with NO+ can be used to separate isomeric aldehydes and ketones, but typically not structural isomers.

E/N

In addition to different pre-cursor ions, PTR-MS offers the possibility to tune the collisional energy (E/N) in the ionization process, by simply changing the drift voltage. This change is instant and can be made in many discrete steps. Changing E/N enhances or suppresses fragmentation [3] and reveals highly compound specific information that can be used to separate compounds, especially structural isomers.

Combining SRI and E/N

In principle, each ionization mode (SRI) can be operated at several E/N levels. We have tested up to 8 different ionization modes that add additional information, see fig. 1.

H_3O+: Up to 5 (typically 3) different E/N settings are used in combination with H_3O+, where altering the E/N has the strongest influence on fragmentation and thus directly contains information about the compounds molecular structure.

NO+: In NO+ ionization the E/N mainly influences which product ion is formed. The product of ionizing compound R (especially for ketones) can be shifted from R.NO+ to R+. This is valuable compound specific information. Two (typically one low) E/N levels are used for NO+.

O_2+: The high ionization energy of O_2+ allows to ionize a variety of compounds that cannot be ionized by the other modes. Due to the already high energy in the ionization process E/N has a negligible influence. Only one E/N level is used in combination with O_2+.

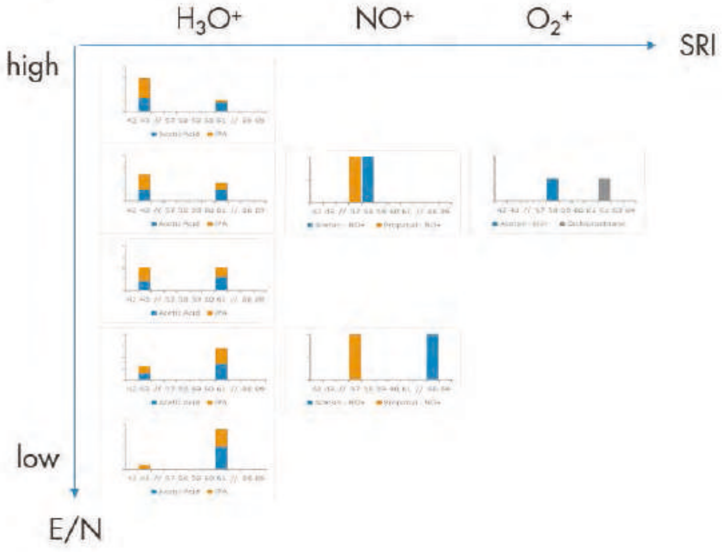

Figure 1: Ionization modes used in AME are a combination of different pre-cursor ions and E/N levels.

Automated Measurement

The AME software automatically alternates through different ionization modes. Data directly after switching to another mode is ignored to allow for stabilization. The subsequent data in each mode is averaged. The averaged data of all modes is consolidated and is fed into the data evaluation.

Automated Evaluation

The analysis part of the AME software allows to process the consolidated data of all modes using different mathematical procedures. As a typical first step, a previously acquired background can be subtracted from the measured mean values. For further processing, different procedures are available. In the simplest case, this can be used to report concentrations of compounds that are measured in H_3O+ mode in the same table as such measured in the O_2+ - a process that is tedious if not automated.

Simple calculations can be used to generate sum values, such as “BTEX” (sum of Benzene, Toluene, Ethylbenzene and Xylene) or “Total VOC” values, e.g. the sum of all (or selected) m/z in a certain mass range and in a particular mode. These simple calculations can also be used to measure the pre-cursor intensity and purity, specifically for each mode to monitor the system performance.

Pattern matching algorithm

As a general approach to analyse the combined spectral information from all different modes and to enhance specificity, we have implemented a pattern matching algorithm. For a growing number of compounds we have established compound libraries: These contain a compounds ‘features’, i.e. their reaction products, molecular ions and fragments, and the respective ratios over all ionization modes. Isotopes can automatically be added wherever the sum formula is known.

The AME software can be set-up for a pre-defined set of compound libraries. The pattern matching algorithm uses the library information of all these compounds to best fit the measured spectra of all modes combined. This algorithm is able to separate isomers and interferences and quantify the contributions of different compound to the same m/z in complex samples. It is largely robust against interference from unknown compounds.

As an added benefit, a compound library can be normalized to a particular mode including the fragments and isotopes, which eliminates these factors in the quantification and thus enhances the accuracy, when no calibration gas is available. For those compounds that can be calibrated experimentally, a calibration factor can be applied.

Figure 2: Schematic of the AME software data flow (left) and the user interface displaying the calculated concentrations.

Simple User Interface

The user interface of the AME software is easy to use without any prior knowledge about PTR-MS or trace gas analysis, see figure 2. A touch-screen ready interface allows to select a pre-defined measurement recipe which controls ionization modes and the set of compounds.

Different measurement recipes can be set-up. A recipe could contain different lists of compounds or a fast measurement for highly dynamic processes or longer averaging for higher precision etc. The calculated concentration values are displayed on the touch screen interface.

In addition, alarm levels can be flexibly defined that e.g. alert the user of a low or high concentration levels or low pre-cursor ion count. AME concentration data is stored in easily readable ASCII tables. Online access to this data is possible by a MODBUS over TCP interface.

Conclusion

A PTR-TOF in combination with the AME software collects a maximum of information from a sample, by analyzing in different ionization modes. Here we do not restrict this to different pre-cursor ions or E/N levels, but combinations thereof. Consolidating and processing the combined data is, to our knowledge, the first approach of this kind in PTR-MS data processing. Several approaches have been tested to separate interfering compounds and the described pattern matching algorithm has been selected due to its universality and robustness against unknown interferences.

This high level of expertise and elaborate data processing is packaged in a simple to use software that does not require an expert for operation or data analysis. PTR-TOF with AME software is currently employed successfully in several industrial processes for automated monitoring.

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PTR-MS in commercial applications using a mobile laboratory

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Abstract

PTR-MS is widely used for environmental analyses and atmospheric science applications in primarily academic settings. Few commercial analytical laboratories in the USA offer this type of instrumentation in their portfolio, partially due to the lack of EPA approved methodology and partially due to the rather steep investment up front. RJ Lee Group as an industrial forensics company has partnered with Montrose Environmental to pursue leads for specific niche applications where low-cost sensors and even traditional analytical instrumentation are insufficient in sensitivity and selectivity. The RJ Lee Group mobile laboratory has been developed over the last ten years and is currently in use in its third iteration. Examples of applications presented will include emission assessments of industrial stack exhaust systems, fugitive emissions from industrial sites, and vapor intrusion, but also indoor air assessments, materials characterization and illicit substance identification and tracking.

Mobile PTR-TOF Laboratory for Real-Time Industrial Health Applications

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Abstract

TerraGraphics Environmental Engineering has built and deployed a Mobile Laboratory (ML) to monitor Volatile Organic Compounds (VOCs) and chemicals listed on the Hanford Tank Farm Vapors Chemicals of Potential Concern (COPCs) list in real time, in and around the Hanford Tank Farms.

Organic compounds were used in the processing of nuclear materials at the Hanford Site. Due to radiolysis, these compounds decompose over time. Chemical vapors from the decomposition products accumulate in the tank headspace (the unfilled area above the waste in the underground storage tanks). Vapor emissions are influenced by the weather, maintenance activities, or work activities that involve disturbing the tank waste, including retrievals and tank-to-tank transfers.

Some chemicals may cause more concern because they appear in higher concentrations than others. Occupational Exposure Limits (OELs) are set based on strict criteria, and the Hanford site takes a more conservative approach than many in similar industries when it comes to limiting worker exposure with engineering, administrative, and personal protective equipment controls.

The ML provides the ability to analyze and characterize vapors emanating from tanks, fence line monitoring, source characterization and fingerprinting, odor investigations and plume tracking, with fewer sources of error and lower detection limits than traditional industrial hygiene techniques used in the field. Samples can be collected by the ML for offline analysis using traditional analytical techniques for validation or analysis that goes beyond the real-time capabilities. The ML has been deployed to monitor stack emissions, tank farm fence line monitoring, area monitoring during waste disturbing activities, fugitive emission source location and characterization, and general ambient air monitoring.

Introduction

The TerraGraphics Mobile Laboratory has been used for a number of applications in and around the Hanford Site. These include monitoring for chemicals of potential concern in the tank farms, odor investigations, plume tracking, detailed background studies, and source characterization and chemical fingerprinting. In addition, detailed background studies have been performed for low OEL compounds in order to more accurately characterize ambient concentrations at a number of locations.

Chemical gases in Hanford's waste storage tanks may, from time to time, enter the workers' breathing zone. The vapors reside in the tank headspace and the area above the liquid waste in the underground storage tanks contain a large number of chemicals produced from Hanford's days as a weapons production facility.

Some chemicals present in the tanks cause more concern because they appear in higher concentrations or are more harmful than others. These COPCs are of particular interest and exposure limits are based on strict criteria. The COPC list and the associated OELs were determined in 2006 and recently reevaluated and revised. The OELs were established based on 8-hour time-weighted averages (TWAs) to represent the limit to which a worker could be exposed during a normal shift without experiencing an appreciable health risk. The current COPC list contains 61 chemicals, with widely varying OELs and chemical characteristics. The diverse nature of this list provides a unique analytical challenge in terms of detection and quantification.

The primary instrument housed in the ML is the IONICON PTR-TOF 6000 X2 for VOC measurements. This instrument can detect 53 of the 61 COPC at 1-second time resolution at levels below the OELs. Traditional analytical techniques can offer good selectivity and sensitivity, but do not offer this level of temporal resolution, thus making the two types of approaches complimentary.

The Mobile Laboratory

The ML is outfitted with numerous instruments for monitoring a wide range of species and capture meteorological conditions. This includes an IONICON PTR-TOF 6000 X2 for VOC measurements; a Picarro Cavity Ring Down Spectrometer for ammonia (Model G2103); a LI-COR instrument for CO_2 (Model 840A); an AirMar Weather Station with GPS (Model 200WX); and a sampling system for the collection of sorbent tube and canister samples for offline confirmation and validation of results. The PTR-TOF and Picarro NH_3 contain their own internal data acquisition systems. The data acquisition and system control software DaqFactory®[1] is utilized to record the LI-COR CO_2, AirMar, and the sorbent/canister sampling. The ML is capable of full operation while the vehicle is in motion and an operator can monitor and control the laboratory from the passenger seat. The instrumentation racks utilize properly rated shock absorption to protect against damage from large mechanical shocks. A wireless router (CradlePoint®[2]) in combination with a Verizon®[3] wireless card is used to allow remote connection to the ML.

The sampling inlet consists of ~20’ of 3/8” outside diameter (OD) Perfluoroalkoxy (PFA) tubing wrapped in heating tape that controls the temperature to ~60˚C.≈The≈LI-COR CO_2, Picarro NH_3, PTR-TOF, and alternative media sampling systems subsample from this main inlet using a combination of heated 1/8” and 1/4" OD PFA tubing and fittings. The main sample line is connected to a mass flow controller (MFC) that allows for additional controlled flow if a higher flowrate or reduced residence within the sampling line is desired. This line is connected to a mast that allows the inlet to be raised approximately 3’ above the height of the roof.

The alternative media sampling system is capable of sampling up to four sorbent tubes and a canister simultaneously and autonomously. This is accomplished using four MFCs to control the flow through the sorbents and a calibrated orifice to control flow to a canister. Each of the four sorbents and the canister can be run individually or in any combination that can be triggered autonomously or remotely once the media is attached.

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[1] DaqFactory is a registered trademark of Azeotech, Inc., Ashland, Oregon.

[2] CradlePoint is a registered trademark of CradlePoint, Inc., Boise, Idaho.

[3] Verizon is a registered trademark of Verizon Trademark Services, LLC, Arlington, Virginia.

Beyond the instrumentation, the ML has a zero air calibration system that can be fully automated or triggered remotely. It consists of four MFCs to control the flow of CO_2, NH_3, a VOC mixture, and ultra-zero air from cylinders. Valves are used to control the configuration of the flow to allow for an individual instrument to sample a single diluted gas standard or multiple instruments to sample a diluted mixture of gas standards.

Data collected with the ML is processed at the TerraGraphics office. The PTR-TOF data are mass calibrated and converted from ion counts into concentrations. Typical deployment produces 0.5 Hz (one measurement every 2 seconds) concentration data for roughly 280 ion signals. Typical ML measurements can last anywhere from 6 – 20+ hours, resulting in datasets that contain roughly 10,000 – 40,000 data points per ion signal (280,000 – 11,200,000 unique data points per dataset). Correlating auxiliary data such as ambient CO_2, NH_3, and meteorological data collected on other ML instrumentation are time-synchronized to PTR-TOF data via interpolation. These data are synthesized into time-series plots and statistical tables spanning broader times.

Results

The data discussed here relate to better understanding VOC sources around the Hanford site to aid in interpretation of live data for use in ensuring worker safety. After spending some time on the Hanford site, two sources of VOC in the Hanford area were observed frequently enough to characterize in more detail; septic tank emissions and VOC drift from an onion processing facility.

Septic Tank Emissions

Vapors from the septic tank(s) are hypothesized to travel downwind and result in workers smelling an unknown substance. The ML has spent 7 days focused on characterization and tracking of the septic tank odors. The ML has used the side port with the 35’ line to sample at the emission point of the septic tanks. Figure 1 shows the response of methyl mercaptan and the sum of dimethyl sulfide and ethanethiol on August 7, 2018. The 35’ line sample intake was next to one of the septic tanks between 8:33 and 9:25 am. The methyl mercaptan and dimethyl sulfide + ethanethiol were found to be among the most abundant species within the septic emissions.

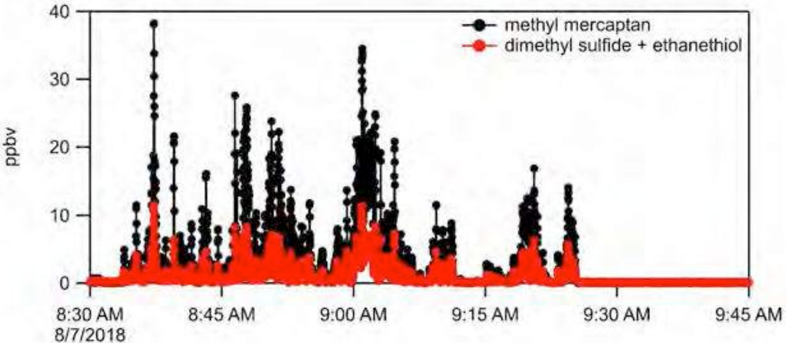

Figure 1: Time Series of Methyl Mercaptan and Dimethyl Sulfide + Ethanethiol when the Mobile Laboratory was Sampling near the Source of the Septic Plume.

A percent abundance was calculated for all resolved peaks within the data set. This is achieved by taking the average of the largest plume observed between 09:00 and 09:02 then subtracting the ambient mixing ratios approximated by the average between 09:30 and 09:45. The plume average was then summed to get a total response and each species divided by this total response to get a percentage contribution of the total abundance for each species. This list of compounds and relative abundances serves as a fingerprint to identify septic tank emissions during other ML deployments around the Hanford site.

Onion Processing

Multiple days were spent identifying a fingerprint of onion emissions. Figure 2 shows the results of holding a fresh onion near the sample inlet, followed by a partially rotten onion. Similar sampling was done on onions of various stages of rotting to determine the evolution of onion emissions over time. Methyl acetate and ethyl acetate were in high concentrations for all stages of onion decay. The difference in magnitude shown in Figure 2 is not attributed to the relative abundances between the two emissions and is a result of variable sampling conditions. The distance at which the onion was held from the inlet is the primary factor in the observed magnitude.

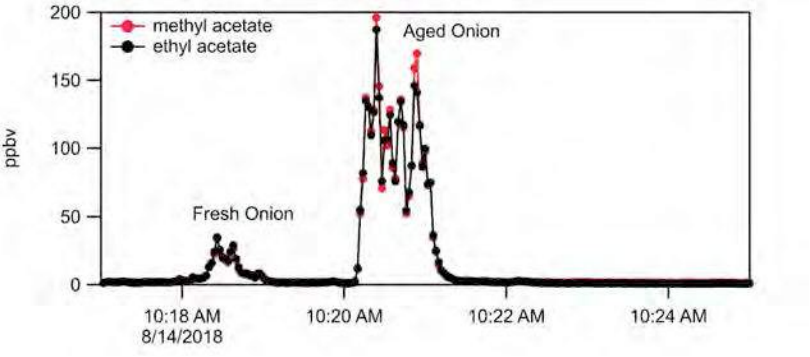

Figure 2: Time Series of Methyl Acetate and Ethyl Acetate while Sampling a fresh onion and an aged onion near the Inlet.

Unique signatures of various stages of rot were determined by averaging the signals of each plume and subtracting the average ambient background signal (10:23 to 10:25) to result in an emission plume average. The signal was then summed to get a total response and each species divided by this total response to get a percentage contribution of the total abundance for each species.

Conclusion

The TerraGraphics ML has been used for a number of applications in an around the Hanford Site including monitoring for chemicals of potential concern in the tank farms, odor investigations, plume tracking, detailed background studies, and source characterization and chemical fingerprinting. All of these forms of deployment are only possible due to the sensitive, near real-time nature of the ML. The examples provided here are brief but demonstrate the ability discriminate between the fingerprint of known VOC sources from those from hazardous sources in the worker environment.

Importance of background in the analysis of complex industrial gases.

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Abstract

In this work, we focus on the analysis of background measurements with and without humidity taken from different inert gases and gas qualities commonly used for the dilution of industrial process gases by means of a commercial Proton-transfer-reaction Quadrupole interface time-of-flight mass spectrometer (PTR-QiTOF-MS). This work is carried out as an attempt to stablish a clear assignment for the origin (artefact, impurity or memory effect) of peaks in the mass spectrum, which later may be relevant in the analysis of industrial gases, before and after a purification system and their application in subsequent catalytic processes. We present a simple procedure to differentiate instrumental artefacts, such as parasitic ions, memory effects and real trace impurities contained in the inert gases. This work was carried out in a mobile lab-container, which is located on-site in a steel mill plant with the main aim of characterizing all trace compounds present in metallurgical gases (Coke oven gas, converter gas and blast furnace gas). This project is part of the bigger project Carbon2Chem® [1], which has the goal to apply these metallurgical gases as a feedstock for the production of valuable chemicals, thus contributing to the reduction of CO_2 emissions.

Introduction

The recent global commitment to reduce carbon dioxide (CO_2) emissions and the growing strictness of environmental regulations in the European Union are causing an increase in the costs for CO_2 emissions, which are making products and processes less competitive and therefore, a search for more sustainable ways of operation is needed. Recycling of waste gases or even their subsequent utilization is a promising way but requires a profound knowledge of not only the main components and their temporal concentration fluctuations but also of all trace components, since many common volatile organic compounds (VOCs) even at the trace level can hinder the utilization of waste gases due to damages [2] (e.g. corrosion, abrasion) of downstream units or to deactivation of catalysts in downstream processes (e.g. after a purification process), which results in high operational costs. Therefore, the online characterization of trace components at the ppt level is necessary as input for the development of adequate purification processes. Proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS), a technique developed for the analysis of VOCs in air [3] has proven to be a powerful technique for the analysis of VOCs at low concentrations with short time responses and high resolution [4]. In the analysis of traces in industrials gases and catalytic processes, the background is of paramount importance, since a wrong estimation may result in the underestimation of purification units or even the choice of inadequate materials, and thus, incurring in higher operational costs.

Experimental Methods

Measurements were performed with a new generation mass spectrometer, a Proton-Transfer-Reaction Quadrupole interface Time-Of-Flight Mass Spectrometer (PTR-QiTOF-MS), acquired from IONICON Analytik GmbH, Innsbruck (Austria). Our state-of-the-art instrument is a prototype, which is equipped with additional features like the so-called Selective Reagent Ionization (SRI) [5] and a FastGC. Prior to measurements of background, an optimization of the instrument using the Thuner Software (Tofwerk AG, Switzerland) was carried out, in order to find optimum parameters for substances of interest and to minimize the intensities of the parasitic ions like $N_2.H^+$, NO^+, O_2^+ and fragmentation products. By means of a commercial gas calibrator (HovaCal, IAS GmbH, Oberrursel, Germany) a constant toluene concentration of 100 ppbv was used for the optimization process, thus the protonated mass of toluene (m/z 93), the mass fragment at m/z 91, the protonated mass of benzene (m/z 89) and the masses of the internal standard 1,3-Diiodobenzene at m/z 204 (fragment) and at m/z 331 (protonated) were taken for the iteration process. For the determination of traces in background measurements, two different gas qualities (5.0 and 6.0) from the same inert gas (nitrogen) were used and for the highest gas quality an additional filter was employed. In order to check for differences in traces among typical inert gases, helium and argon were also analyzed. In order to help the identification of instrument specific compounds, a comparison measurement was carried out using two less sensitive PTR instruments (PTR-TOF1000) also from IONICON Analytik GmbH. The gas flows used were normally of 1,0 l/min, from which the PTR-QiTOF-MS took between 100-200 ml/min. Typical instrument parameters were: drift tube temperature 60°C, pressure 3,5 mbar and voltage 900 V, resulting in a E/N of 131 Td. The PTR-QiTOF-MS was connected near the exit of a heated multiport valve (MPV) by means of a t-piece, thus allowing the excess flow to the vent. The inlet consisted of PEEK tubing heated at 120°C. Although switching between the three primary ions H_3O^+, NO^+ and O_2^+ within the same measurement is possible, background measurements were carried out in separate measurements. Variations of E/N were carried out by changing the drift voltage in order to analyze its influence on the background compounds. Similarly, variations in humidity were done using the gas calibrator in order to study the influence of humidity on the sensitivity of background compounds.

Results and Discussion

Regarding the typical parasitic ions in this kind of PTR instrument ($NH_3.H^+$, $N_2.H^+$, NO^+, O_2^+) the most important effect observed was by the change of humidity in the system. It was observed that some of these parasitic ions, such as N_2^+ and $N_2.H^+$ showed a significant signal reduction in the presence of humidity, whereas ions like $NH_3.H^+$ and NO^+ showed no change. Up to date only the parasitic ions NO^+, O_2^+ and water cluster $H_3O^+.(H_2O)n$ have been considered in the literature as the most dominant. In our case, the most dominant parasitic ion is $N_2.H^+$ and even after the optimization process, this ion remains as the predominant parasitic ion. With the straightforward methodology developed here, the gathered observations helped to assign the origin of the ions, thus, parasitic ions that are independent of the gas quality are produced in the ion source, whereas some parasitic ions with humidity dependency may be produced in the quadrupole interface. In general, for most VOCs the presence of humidity showed a remarkable increase in sensitivity but just for a few compounds the observed trend was reverse, like for instance for formaldehyde. This can be mainly assigned to the lower fragmentation due to the collisional cooling caused by the higher concentration of water molecules. For benzene no significant change was observed, probably due to their nonpolar character, which is somehow in disagreement with the previous results of Warneke et al. [6]. In contrast, toluene exhibited a positive humidity dependency. Although a comparison measurement with nitrogen 5.0 using the two PTR-TOF1000 was carried out to help identify instrument specific peaks (e.g. memory effects), it was observed that by using a filter a straightforward identification for most instrument specific peaks was possible. It could be observed that for instrument specific compounds like Fe^+ or FeO^+ the presence of humidity decreased their signals, whereas for ions like $FeOH.H^+$ a clear increase in signal was observed. However, other instrument specific ions like $FeOOH.H^+$ showed the opposite behavior, probably because they act as intermediates. The gases used with the PTR-QiTOF-MS were from a supplier company A, whereas the N_2 5.0 used with the PTR-TOF1000 was purchased from a different supplier B. A direct comparison between the gas qualities of the two companies was not the goal of the study and moreover due to the lower resolution of the PTR-TOF1000, it would be very difficult to identify and assign compounds to all peaks, since the measurements are carried out around the detection limits of the instruments. For typical “sticky” compounds, such as polyaromatics or siloxanes, which could be expected as “memory effects” and thus, as instrument specific substances, no such trend was observed.

To a good approximation, quantification with PTR-MS is possible if the reaction rate coefficients of the reactants with the primary ions are known, although a reaction rate coefficient of $2{,}0 \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1} can be used in cases when no values are available in literature or no gas standards can be used. Thus, quantification for all identified traces in all the gases is provided. As a quality control, toluene was used for calibrations by means of the gas generator, which enables the calibration of typical VOCs under dry and humid conditions. During the measurements with humidity, the relative humidity was varied in the steps 0%, 20%, 50% and 80%. Over 900 peaks were identified, although many of them are assigned to the most abundant isotopologues.

The implications of these contaminants by the utilization of these inert gases are quite considerable. For most applications, these gases are regarded as pure and therefore, no further analysis is normally carried out. With conventional techniques, such as GCMS a characterization is not possible, since the signals of traces in these gases are not higher than the background. Since typical catalyst poisons were identified, it becomes clear that even if the concentrations lie in the ppt-range, in catalytic processes using several m^3 per hour, a significant deactivation may take place, especially if the experiments are run for several days. For instance, a common practice in catalytic processes is to purge the reactor with inert gases, after that the catalyst is reduced or activated in-situ in gas mixtures containing these inert gases. Depending on the reaction, after switching to the reactants, the inert gas may still be present in considerable amounts. This could drive to irreproducible results.

Conclusions

Background measurements using inert gases of different qualities, which are commonly used in the analysis of industrial gases or in catalytic processes by means of a high-sensitive proton-transfer-reaction time-of-flight mass spectrometer delivers information not only for the identification of the trace contaminants but also helps to estimate their concentrations. A straightforward methodology was introduced, which helped to identify peaks that are assigned as instrument specific artefacts. By changing the humidity in the system it was possible to sense substances, which in dry conditions due to fragmentation were no measurable. A small database with the identified contaminants in the typical inert gases nitrogen, helium and argon was delivered. Some contaminants appeared to be gas specific, whereas others were present in all gases. By changing the collision energy in the drift tube, those contaminants, which are prone to fragmentation showed the expected behavior but it was humidity, the predominant factor that controlled in most cases fragmentation and sensitivity. Humidity was also observed to be necessary in order to reduce the presence of parasitic ions generated in the quadrupole ion guide (interface). Identification at the ppt-level with low resolution instruments like PTR-TOF1000 appears to be difficult, since multi-peak fitting is necessary in order to extract some valuable information. The big challenge is to assign peaks when no comparison measurements are available.

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Online monitoring of amines in the flue gas of a post-combustion carbon capture plant by a PTR-QMS 300 instrument operated in the NH_3 mode

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Abstract

As of 2018, the technologically most mature solution for removing carbon dioxide (CO_2) from the flue gas of a fossil fuel-operated power plant is to chemically absorb it into an aqueous amine solution. However, while CO_2 is efficiently captured as an amine carbamate salt, amines are partly volatilized, entrained into the flue gas stream and emitted to the atmosphere. In many countries, environmental authorities require industrial amine emissions to be monitored continuously. The use of a Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) for this task is expensive and time intensive. In this work, we will demonstrate how a smaller, cheaper and easier to operate Proton-Transfer-Reaction Quadrupole Mass Spectrometer (PTR-QMS 300) can be used for online and real-time monitoring of amines in treated flue gas at ppb to ppm levels. The use of ammonia as a source gas greatly simplifies the detection of amines, making it possible to use a low-end mass analyzer for ion analysis. We characterized the analytical performance of the instrument (sensitivity, limit of detection, precision, matrix effects) for nine solvent amines (monoethanolamine, dimethylaminoethanol, aminomethylpropanol, methyldiethanolamine, diglycolamine, piperazine, aminoethylpiperazine, methylpiperazine, N-(2-hydroxyethyl)piperazine) and of three amines resulting from degradation of the solvent (methylamine, dimethylamine, trimethylamine). The new analyzer was tested and validated in side-by-side measurements with established emission monitoring techniques at the Technology Centre Mongstad (TCM) in Norway [1]. After validation, the instrument was permanently installed on top of the absorber tower and is since then delivering real-time amine emission data to the plant information management system.

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Contributed Papers (Posters)

Investigation of volatile compounds in fermented cocoa beans and corresponding dark chocolates by direct injection mass-spectrometry (PTR-ToF-MS)

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Abstract

The organoleptic characteristics of dark chocolates depend on cocoa origin, cocoa variety and fabrication process. These parameters influence the composition in volatile compounds of dark chocolates and determine their sensory perception.
A previous sensory analysis performed on 206 dark chocolates produced from 206 different cocoa beans batches of different varieties and origins but with the same fabrication process classified them into four sensory categories based on the ratings of 36 flavour attributes.

By investigating the volatile compounds (VOCs) of the 206 fermented cocoa beans and corresponding dark chocolates using direct injection mass spectrometry (PTR-MS), the primary objective of this study was to examine the potentiality of PTR-MS to predict the aroma-based sensory categories previously defined. A second objective was to investigate the filiation between cocoa and chocolate in terms of VOCs related to the observed categorization.

The fermented cocoa beans powder (0.2 g) mixed with 1 mL of ultrapure water, the dark chocolates (1 g) mixed with 1 ml of artificial saliva were placed in 20 mL vials. The vials were maintained under stirring for 2 hours equilibration time at 36.2°C. Headspace analyses of the 206 affiliated samples (cocoa beans and chocolates) were done in triplicates using Proton Transfer Reaction – Time of Flight – Mass Spectrometry (PTR-ToF-MS). The average areas under the curves obtained for significant ions present in the mass spectra during 2 mn release time were used to perform multivariate data analyses: an unsupervised analysis (Principal Component Analysis PCA) allowed data exploration and a supervised one (Partial Least Squares Regression-Discriminant Analysis PLS-DA) allowed building classification models.

The results showed that the headspace analyses of dark chocolates and corresponding fermented cocoa beans allowed discrimination between the four sensory categories, *i.e.* the sensory classification of dark chocolates could be explained by the composition in volatile compounds released by dark chocolates [1] and corresponding fermented cocoa beans, revealing discriminative compounds already present in fermented cocoa.

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The effects of extended heat waves and drought on the emission and pattern of monoterpenes from Douglas fir

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Introduction

Forests are the major emitters of biogenic volatile organic compounds of which monoterpenes are quantitatively the second most important compound group emitted from trees [1]. Under future climatic conditions trees will be exposed to more extreme weather conditions, including heat waves and drought [2], which is expected to alter emission and composition of monoterpenes with potential consequences for air quality and atmospheric chemistry. Yet, the knowledge on the magnitude of monoterpene emissions and composition changes in response to heat waves, especially in combination with drought is limited.

Experimental Methods

Monoterpene emissions and composition of *Douglas fir* during heat stress and in combination with drought were observed by proton-transfer-reaction mass spectrometry (PTR-MS) and by gas chromatography mass-spectrometry (GC-MS). The gas exchange of monoterpenes and CO_2 was quantified using a branch chamber system automatically switching between branches of three different trees (n=3) in the control, heat and heat-drought treatment.

Two different heat waves (14 days each) were simulated within the greenhouse facility of the Karlsruhe Institute of Technology in Garmisch-Partenkirchen, increasing temperatures by approximately 10°C above ambient. Each heat wave was followed by a recovery period of at least 7 days. Drought was simulated supplying the trees in the respective treatment with 50 % less water than trees in the control treatment

Results and Discussion

During severe heat stress or heat stress in combination with drought, *Douglas fir* trees showed a strong emission burst of monoterpenes that resulted in two orders of magnitude larger daytime emissions compared to values measured before stress. Towards the end of the first heat wave and during the second heat wave the emissions declined and were just moderately higher than the control, suggesting that a major fraction of the emissions originated from storage pools which depleted quickly after being affected by high temperatures (> 45°C) at the onset of the stress.

Alpha- and beta-pinene dominated the monoterpene emissions. The relative contribution of alpha-pinene to total monoterpenes decreased during stress compared to before stress conditions, while the contribution of beta-pinene did not change significantly. This observation suggests that alpha-pinene is partially synthesized de-novo during heat and heat-drought stress, while beta-pinene originated mainly from storage-pools. Generally, heat and heat-drought stress caused very similar responses on monoterpene emission patterns of Douglas fir trees.

Using a time-dependent emission factor, changes of monoterpene fluxes in heat and heat-drought trees were successfully simulated with the typical exponential temperature function, which was introduced for emissions from storage organs [3].

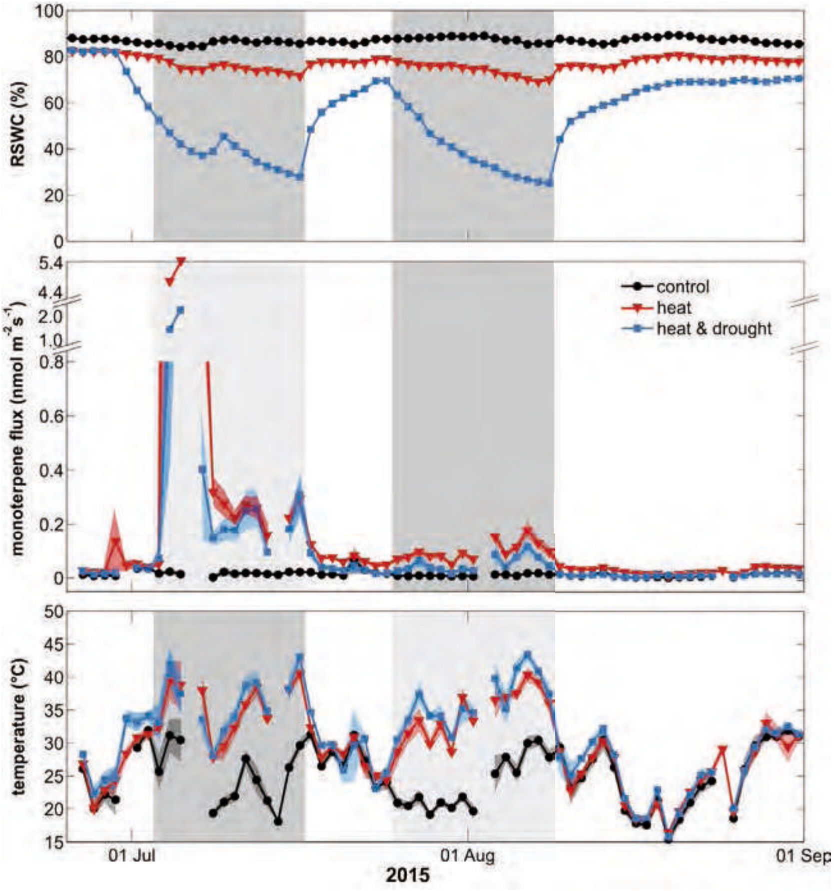

Figure 1: Temporal dynamics of temperature, monoterpene flux and relative soil water content of control (circles) heat (triangles) and heat-drought (squares) treated Douglas fir trees. Time periods, when the stress trees were exposed to heat-waves are shaded in grey.

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Linking photosynthesis and BVOC emissions in Pinus sylvestris by $^{13}CO_2$ labelling in response to drought

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Introduction

Plants are one of the major contributors to the carbon exchange between the biosphere and the atmosphere. Furthermore, they are the most important source for reactive hydrocarbons (volatile organic compounds) which play a crucial role in plant interactions and atmospheric chemistry.

Despite increased efforts in quantifying emissions and temporal dynamics of biogenic volatile organic compounds (BVOCs), the link between plant photosynthesis and the investment of carbon in the emissions of reactive hydrocarbons, especially under adverse environmental conditions, is still poorly understood [1]. Although, ^{13}C labelling turned out to be a powerful method to receive advanced information on carbon allocation and the partitioning of carbon sources used for the isoprenoid production in plants [2,3,4], there are still a lot of questions to be resolved. Especially, on the less abundant reactive hydrocarbons, or on changes of biosynthetic pathways under less favorable environmental conditions there is next to no information.

Here, we investigate biosynthetic pathways of VOC production in *Pinus sylvestris* making use of position specific labelling of central metabolites.

Experimental Methods

Pyruvate is known to be tightly involved into the primary and secondary metabolism (e.g. BVOC production) of trees. Thus the approach of position-specific pyruvate labelling offers a unique possibility to increase our understanding of the biosynthesis of BVOCs in plants and their link to the CO_2 exchange.

In order to gain a better insight in the carbon partitioning and dynamics of trees, we conducted ^{13}C labelling experiments on well-watered and drought impacted *Pinus sylvestris* saplings and recorded the carbon exchange of CO_2, BVOCs in real-time using $\delta^{13}CO_2$ laser spectroscopy and a proton-transfer-reaction time-of-flight mass-spectrometer (PTR-TOF-MS). For this purpose, we set up a system consisting of a zero air generator, providing pure air for measurements, several branch chambers, attached to the tree saplings, and the corresponding analyzers for VOC, CO2, and $\delta^{13}CO_2$ measurements [1]. We used position-specific ^{13}C pyruvate labelling and captured VOC emissions and ^{13}C dynamics of the trees in real-time to elucidate different biosynthetic pathways of VOCs.

Results, Discussion & Conclusions

While feeding the branches with pyruvate, labelled at the first carbon position led to increased $^{13}CO_2$ emissions, it was observed that pyruvate labelled on the second carbon position was rapidly incorporated into emissions of acetaldehyde (m/z 45.03) and acetic acid (m/z 61.03) indicating primarily *de novo* emissions of these volatiles.

In contrast, the effect of pyruvate labelling on other biogenic hydrocarbons emitted from *Pinus sylvestris*, e.g. monoterpenes, was less pronounced. This is probably due to increased emissions of these compounds from storage organs, like resin ducts. Generally, drought impacted trees did, compared to well-watered plants, incorporate less ^{13}C into VOC biosynthesis, which indicates an increasing use of stored carbon for VOC production.

Simultaneous measurements of BVOCs and $\delta^{13}CO2$, in combination with position-specific labelling of central metabolites, turned out to be a useful tool for biochemical research, which offers unique options to disentangle pathways of BVOC synthesis.

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Chemical characterization of volatile organic compounds emitted from selected indoor activities

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Abstract

In this study three common activities responsible for indoor air pollution in residences - cleaning, painting and candle burning have been performed in a full-scale model room in order to characterize the chemical composition of the emitted volatile organic compounds (VOCs). VOCs were measured by Proton Transfer Reaction - Time-of-Flight - Mass Spectrometry (PTR-ToF-MS). The highest number of different compounds and highest concentration of VOCs was measured during painting with 44 different compounds/molecular formulas assigned to the detected ions. Monoterpenes and different alkane fragments characterized the cleaning test. During candle burning, two specifically emitted compounds were tentatively identified as dimethyl sulfoxide (m/z 79.0214) and $C_4H_8O_2S$ (m/z 121.0280).

Introduction

Indoor air quality in buildings has great influence on human health and comfort. An important parameter for defining indoor air quality is the concentration of volatile organic compounds (VOCs). Building materials, furniture, and electronics are important sources of VOCs to the indoor environment. Additionally, occupant related activities such as cooking, cleaning, painting and use of consumer products can introduce large quantities of VOCs to indoor air. Some VOCs found in indoor air can directly cause hazardous effects on human health because of their toxicity, allergenic or cancerogenic effects.[1] Accordingly, it is important to identify the emission sources and chemical reactions that generate indoor VOCs. In order to follow the rapid changes in emission of VOCs, high time resolution measurements are needed. Proton Transfer Reaction - Mass Spectrometry (PTR-MS) has been widely applied in indoor environments because of its mobility, robustness, high sensitivity and capability of simultaneous monitoring of multiple compounds at high time resolution[2]. PTR-MS has been recently used to characterize specific emissions from human bodies[3-5], cooking[6], and painting[7].

The study presented here is part of a larger project that aims to evaluate different types of VOC sensors used to control ventilation systems in dwellings. Among the different activities investigated in the project, the results from PTR-ToF-MS measurements from three selected activities typical for residences are presented in this abstract: cleaning, painting and candle burning.

Experimental Methods

Site description

The measurements were performed in an EnergyFlexOffice (EFO) at the Danish Technological Institute consisting of one room with a floor area of 31.5 m^2 covered with wall-to-wall carpet, 2.5 m room height with a total room volume of 80 m^3. The room was equipped with a mechanical ventilation system regulated at an air exchange of 0.5 h^{-1}. Room temperature and relative humidity were kept at 23ºC and 50%, respectively. Indoor air was well mixed using 3 fans.

VOC measurements with PTR-ToF-MS

Real-time measurements of VOC concentrations were performed with a PTR-ToF-MS 8000 (Ionicon Analytik, Innsbruck, Austria) operated in H_3O^+ mode. Pressure, temperature and voltage conditions were kept constant within the drift tube in order to obtain an E/N value around 130 Td. Mass spectra were recorded up to 250 amu at 1 scan/sec intervals. Volume mixing ratios were quantified using the kinetic calibration method. Before starting a specific activity, the background of the empty room was measured overnight.

Results and Discussion

Cleaning was performed with an all-purposes cleaning agent with lemon scent diluted in water according to the label. The test procedure consisted in cleaning the walls and the doors of the room and lasted for about 15 minutes. As expected the ion with the largest increase during cleaning was m/z 137.1325 corresponding to the monoterpene group, in this case most probably limonene, which was added to the cleaning agent. Moreover, different alkane fragments ($C_3H_4^+$, $C_6H_8^+$, $C_7H_{10}^+$) were also observed to increase, but to a lesser extent. A slight increase in concentrations was also observed for isoprene and acetone. These two compounds might come from the person, who performed the cleaning.

For the painting gypsum boards (total area: 11.6 m^2) were transferred to the room and painted with a water-based acrylic white paint containing max 10 g/L VOC according to the label. The painting procedure lasted 22 minutes. The painted gypsum plates were kept in the room for the following 2 days in order to monitor the time evolution of the concentration of the emitted compounds. The PTR-ToF-MS measurements showed that 44 ions (m/z) increased during painting. For these compounds a molecular formula and a tentative identification were assigned. The identified compounds included several oxygenated compounds (carbonyls, acids and alcohols), aromatic compounds (benzene, toluene) and several alkenes. VOC concentrations rapidly decreased just after painting, but after 2 days of measurements the concentrations of almost all compounds were still above the average concentrations measured before painting. Figure 1 shows the concentrations over time of 4 selected compounds, 2 aldehydes (acetaldehyde and benzaldehyde) and two aromatic compounds (benzene and toluene), which are considered hazardous for human health.

For the candle burning 3 stearin-based candles were burned over a period of 1.5 hours. During the first 30 minutes the candles were protected with a metal screen to avoid that the flame was affected from air movements in the room (steady burning). During the next 30 minutes the screen was removed (flickering of the flame with production of sooting). After 30 minutes the flame was shielded again and the measurements continued for 30 minutes. The concentrations increased during candle burning only for 10 compounds. Most notably, two compounds were only emitted during candle burning and were tentatively identified as dimethyl sulfoxide (m/z 79.0214) and $C_4H_8O_2S$ (m/z 121.0280).

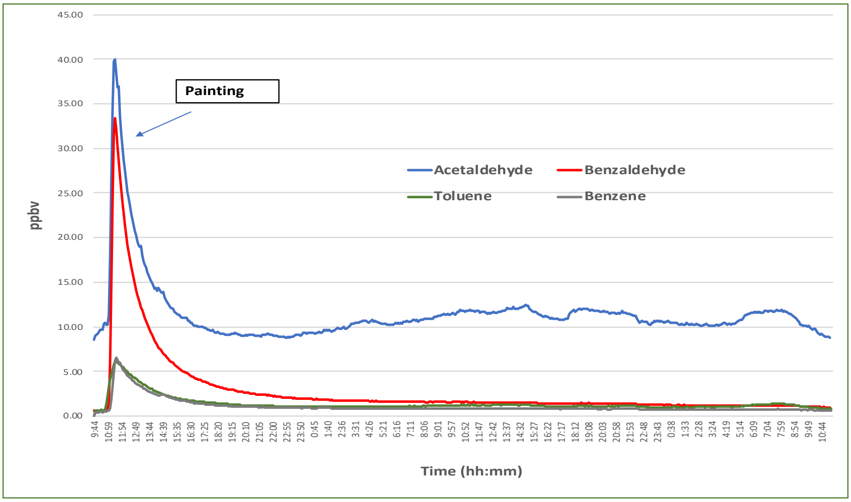

Figure 1: Concentrations of acetaldehyde, benzaldehyde, benzene and toluene during and after painting

Acknowledgement

The Villum Foundation is acknowledged for funding the PTR-ToF-MS as part of the construction of Villum Research Station at Station Nord. Christel Christoffersen is gratefully acknowledged for technical assistance during the measurements.

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PTR-ToF-MS measurements of volatile organic compounds in the atmosphere of the high Arctic

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Abstract

Volatile Organic compounds (VOCs) have been measured for the first time at the remote high Arctic station Villum Research Station (VRS) at Station Nord in north Greenland using a Proton Transfer Reaction-Time of Flight-Mass Spectrometer (PTR-ToF-MS). The results presented cover one week in April and one week in May 2018. Seven different m/z were measured over quantification limit and tentatively identified. The measured concentrations were correlated to meteorological parameters and wind speed was found to be the main meteorological parameter associated with VOC concentrations at VRS. Air mass back trajectories performed with Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) suggested that residence time over snow/marginal zones was a determining factor for VOC levels. This relationship highlights the importance of cryosphere-atmosphere interactions regarding organic compounds emission from the snowpack and the marginal ice zones.

Introduction

VOCs are emitted in large quantities to the troposphere most of which originate from biogenic emissions followed by anthropogenic emissions. Most organic compounds are removed from the atmosphere by oxidation initiated by photochemically formed radicals, where ·OH is the most important. VOCs play a crucial role in the troposphere chemistry and are associated with oxidative capacity, e.g. tropospheric ozone formation and formation of secondary organic aerosol (SOA), which affect human health, regional air quality, and the global climate [1]. Despite recent progress in our understanding the chemistry behind SOA formation, current models based on parameterizations of laboratory experiments cannot fully explain the evolution of atmospheric SOA and appear to underestimate the total mass of particles in the atmosphere. This is especially true in the High Arctic [2]. During the winter and spring, the Arctic is influenced by accumulation mode aerosols originating from midlatitude regions creating Arctic Haze [3]. During late spring and summer, nucleation and Atkien mode aerosols dominate due to less efficient transport from midlatitudes, so local formation of aerosols takes over [4]. These nucleation mode aerosols grow through the condensation of organic vapours and can have a pronouced effect on the Artic radiative balance through their role as cloud condenstation nuclei (CCN) [5]**.** Atmospheric particles are the most important short-lived climate forcers (SLCFs) and are expected to significantly influence the Arctic climate [6]. The identification and characterization of the processes leading to particle formation is important to improve the assessments of biosphere-aerosol-climate feedback mechanisms and the air quality and climate effects of biogenic emissions in general.

Experimental Methods

The experimental work was carried out at VRS, in north Greenland (81°36’ N, 16°40’ W; 24 m a.s.l.). VRS is located at the Danish military base, Station Nord, approx. 2 km from the sampling location. Sampling campaigns at VRS occurred from March 29th to April 7th, 2018 and April 28th to May 5th, 2018. On-line VOC measurements were performed with a PTR-ToF-MS 1000 (Ionicon) operated in H_3O^+ mode. Volume mixing ratios (VMR) were quantified using the kinetic calibration method.

Results and Discussion

A total of seven m/z were detected over quantification limit (LOQ) and tentatively identified by PTR-ToF-MS, of which five of them were oxygenated compounds, one an aromatic compound, and one a nitrogen-containing compound (Table 1). On average, higher mixing ratios were observed during the April campaign, except for acetone, which exhibited similar mean and median mixing ratios for both campaigns. Formic acid displayed the most significant decrease from April to May, although only two daily samples were above LOQ in May. Two long-lived compounds, acetonitrile and benzene showed little variation between campaigns; however, only one sample of acetonitrile was above LOQ during the April campaign versus seven in May. Benzene and acetonitrile are both considered either natural (biomass burning) or of anthropogenic origin (automotive exhaust) [7,8]. Air mass back trajectories showed no air mass arriving from areas affected by forest fires. For April, the one sample above LOQ (0.15 ppb) and average levels below LOQ (0.08 ppb) for acetonitrile were in close agreement with the upper and lower limits of background levels over the Atlantic Ocean (0.10-0.15 ppb) [9]. Therefore, the presence of acetonitrile could be the result of the global circulation of emissions from mid-latitudes and subsequent transport to the Arctic. Inter-campaign mixing ratios of benzene showed a marked decrease while intra-campaign values displayed little variation. Benzene has an estimated lifetime of 20 days. Therefore, the presence of benzene could be the result of long-range transport, although local emission from the military base cannot be ruled out. However, this is unlikely to be observed due to the daily time resolution.

Table 1. Mixing ratios (ppb) of compounds measured by PTR-ToF-MS

Compound	**m/z**	**Mean**		**Median**		**Minimum**		**Maximum**	
		April	**May**	**April**	**May**	**April**	**May**	**April**	**May**
Acetonitrile	42.017	0.08	0.07	0.08	0.07	0.07	0.05	0.15	0.09
$C_2H_3O^+$	43.013	1.46	0.68	1.40	0.67	1.31	0.45	1.77	0.94
Formic Acid	47.013	2.06	0.76	1.95	0.76	1.65	0.70	2.70	0.83
$C_3H_5O^+$	57.034	0.81	0.24	0.78	0.25	0.69	0.12	1.01	0.34
Acetone	59.063	0.63	0.65	0.65	0.70	0.53	0.35	0.71	0.98
$C_4H_9O^+$	73.075	0.09	0.05	0.09	0.05	0.08	0.03	0.10	0.06
Benzene	79.067	0.09	0.04	0.09	0.04	0.08	0.04	0.11	0.05

The VOC concentrations measured in the two campaigns at VRS are in the same order of magnitude as concentrations measured at other Arctic sites [10] or Arctic cruises [11] for most compounds. A direct comparison of these different campaigns is difficult considering the low mixing ratios, different locations around the Arctic, different times of the year, different sampling methods and analytical techniques.

To elucidate the controlling factors of VOCs at VRS this study employed a comparison of the measured concentrations and meteorological data. Wind speed showed a negative correlation with total VOC (TVOC) levels ($R^2 = 0.35$-0.95) during the April campaign. This negative correlation between TVOC (Total VOC) and wind speed prompted further investigation of air mass history through back trajectory analysis using HYSPLIT. A new 72-hour trajectory was calculated every 6 hours during the sampling period using GDAS meteorological data with modeled vertical velocity. The negative correlation of TVOC with wind speed, a visual inspection of air mass history, and a priori knowledge about VOC sources suggest a combination of two factors that might control VOC levels at VRS: wind speed and residence time over snow/marginal zones. Lower wind speeds and the longer residence times of air masses over snow-covered areas and marginal sea ice zones lead to enhanced daily VOC levels (Fig. 1). The converse relationship is also applicable, higher wind speeds and longer residence times of air masses over areas of sea ice lead to reduced levels of VOCs.

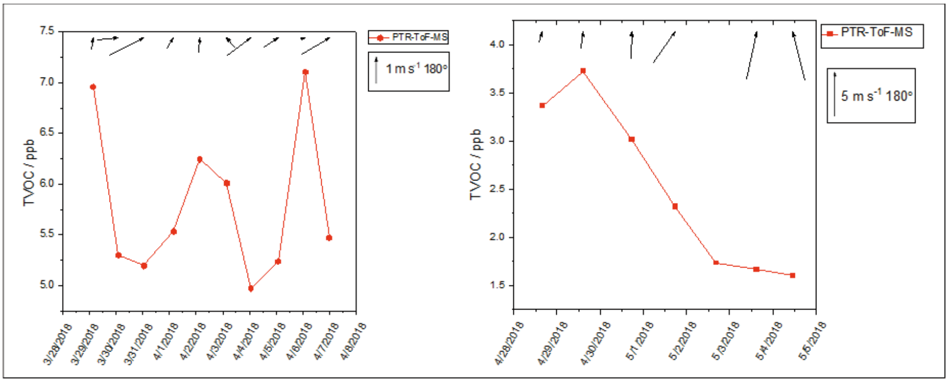

Fig. 1. Time series of TVOCs measured by PTR-ToF-MS for April (left) and May (right). Wind vectors shown in the legends correspond to the respective speeds arriving from directly south.

Recent studies have proven a link between residence times of air masses over marginal zones and leads (areas of open water on top of sea ice) and new particle formation from oceans emissions (e.g. from DMS and DMSP) [12-14]. This relationship highlights the importance of cryosphere-atmosphere interactions regarding organic compounds emission from the snowpack and the marginal zones.

Acknowledgments

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Monoterpenes chemical speciation with high time resolution using FastGC/PTR-MS: First results from the COV3ER experiment on *Quercus ilex* during summer 2018

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Abstract

Plants emit significant amounts of monoterpenes into the earth's atmosphere, where they react rapidly to form a multitude of gas phase species and particles. Although BVOCs emissions are strongly modulated by the biotic and abiotic environment, studies showed that monoterpenes emissions can be genetically fixed, highlighting the possible existence of distinct chemotypes within a tree species [1], [2]. Within the activity of the COV3ER project (Biogenic volatile organic compounds (BVOC) emissions by managed ecosystems: new references over French crops and forest and management effects), the emission of biogenic volatile organic compounds, especially monoterpenes, from *Quercus ilex* was studied in the forest of Puechabon, south of France. Measurements were carried out from mid of June to mid of July, 2018 using a fastGC/PTR-MS system connected to dynamic branch enclosures. The deployed fastGC is an upgraded version of the one adopted by Materic et al., 2015, added to a PTR-MS and tested in order to optimize the separation of monoterpenes depending on their volatility. Investigations focused mainly on characterizing the diurnal variability of monoterpenes chemical nature and concentration, with a fine time resolution from different sources on this natural site. Data analysis revealed the presence of three different genetically fixed emission patterns, known as chemotypes in this forest ecosystem. As reported in previous studies, *Quercus ilex* emissions increased with light. However, the chemical speciation as well as the rate of monoterpenes emissions dependency on temperature and light still need to be investigated.

Introduction

Terrestrial vegetation is considered to be the largest source of VOCs in the global atmosphere. With 1150 TgC/yr, they drive the chemistry of the atmosphere via the reaction with oxidants like the hydroxyl radical and thus influence the composition of the atmosphere by the formation of secondary pollutants. BVOCs, including terpenoides (isoprene, monoterepenes, …), S and N containing compounds (DMS) and oxygenated compounds (methanol, acetone, acetic acid, …) can be emitted by a variety of sources in terrestrial ecosystems including flowers, stems, roots, soil microbes though most of the global emissions stem from foliage [3].

VOC analyses have been largely done using gas chromatography (GC) techniques. Despite their high degree of selectivity and sensitivity, GC measurements are not suitable to follow rapid changes in atmospheric conditions. To overcome these disadvantages, PTR-MS emerged as a tool allowing real-time measurements of VOCs with a high sensitivity. Due to the low selectivity of PTR-MS unambiguous identification of trace gases is not possible. Additional efforts such as manipulation of drift tube parameters and using other primary ions than H_3O^+, have been made to improve the selectivity of the PTR-MS technique so that isomers can be distinguished. However, monoterpenes, representing a significant part of BVOCs from plants and in some ecosystems the main emitted compounds, could not be separated in this manner [4].

In order to progress in plant emissions research, a PTR-MS coupled to a fastGC was introduced as a sensitive system, allowing near real-time measurements of monoterpene isomers [5], [6].

The study presented herein aimed at determining, with a high time resolution, the chemical nature as well as the emission rate of monoterpenes emitted by branches of four different Holm oak trees (*Quercus ilex*) growing in a forest 35 km north-west of Montpellier, France. *Quercus ilex* is a common oak species in the Mediterranean vegetation. It is a strong emitter of monoterpenes with a-pinene, b-pinene, sabinene, myrcene and limonene representing more than 80% of total monoterpenes emitted by this species **[7].**

Experimental Methods

An upgraded version of a fastGC was deployed on a PTR-QuadMS from Ionicon in order to measure atmospheric mixing ratios of VOCs in the PTR-MS mode and to determine the chemical nature of individual monoterpenes in the fastGC mode. The pre-separation before the drift-tube, was done using a non-polar MXT-1 column. The temperature ramp was optimized and helium was adopted as carrier gas.

Continuous online monitoring of VOC emissions was made during the period from the 29th, June to the 2nd, July and from the 6th to the 9th, July, 2018 on four different branch chambers.

Results

Preliminary results show that monoterpenes level from the first branch chamber exhibited a diurnal cycle, with a maximum of 30 ppb during day-time in agreement with the maximum of temperature and light and a minimum during night-time where the level in the air out of the chamber was similar to the level of monoterpenes in ambient air. The same variability was seen on the other branches.

Regarding the chemical nature of monoterpenes (Fig. 1), chromatograms of the first branch exhibited five peaks that were identified, after calibrations, as α-pinene, sabinene, β-pinene, myrcene and limonene/ocimene with myrcene as the major one. The second branch showed four peaks with α-pinene, β-pinene and sabinene as the main emitted compounds. Finally, the 3rd and the 4th branch showed six peaks with limonene/ocimene as the highest peak.

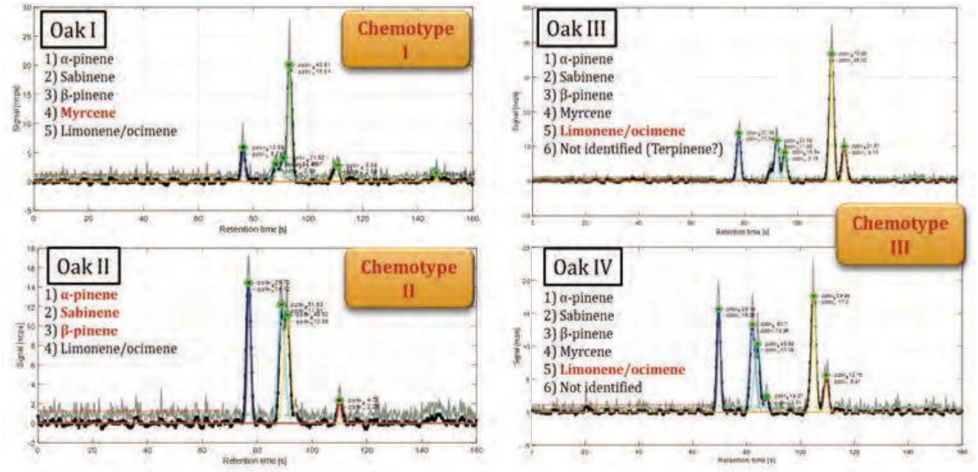

Figure 1: Chromatograms from four different branch measurements showing the existence of three different chemotypes of green oak trees in the forest of Puechabon, based on the monoterpenes signature. Compounds marked in bold present the major emitted ones.

Discussion

These results suggest the presence of three different chemotypes of green oak in the same ecosystem, based on the monoterpenes signature.

Further work is required to analyze all the chromatograms in order to follow, with a fine time resolution, monoterpene's chemical speciation and see if it is stable or variable during the day with different external factors like temperature and light. This information could be an important parameter to take into account in future modelling work on emissions from green oak trees as well as in studies on the reactivity and fate of BVOCs in the atmosphere.

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Adventures of monoterpenes and ketones in the NH_4^+ wonderland

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Abstract

In a laboratory study we investigated ammonia (NH_4^+) as precursor ion to chemically ionize three small ketones (acetone, methyl vinyl ketone, methyl ethyl ketone), methyl salicylate and eight globally most common monoterpenes using a Selective Reagent Ion Time of Flight Mass Spectrometry (SRI-ToF-MS). Additionally, we studied the effects of absolute humidity and varying collision energies on the ionization product distribution and reactivity, respectively. Reaction enthalpies and proton affinities were calculated by high level quantum chemical calculations. For compounds with a lower proton affinity than NH_3 (204 kcal/mowe observed prevailingly association reactions with NH_4^+ forming NH_4^+M adduct ions at low collision energies (KE_{cm}= 55 meV) with low reaction efficiencies. With an increased collision energy (KE_{cm} = 88 meV) the adduct ions dissociated. The monoterpenes underwent proton transfer and association reactions, where the product yields correlated with the calculated reaction enthalpies and proton affinities.

Introduction

Chemical ionization is a central tool in the analysis of volatile organic compounds in the atmosphere. Several studies investigated the reactions of NH_4^+ with varying molecules and found that NH_4^+ undergoes proton transfer with molecules having a higher proton affinity than NH_3 [1]. As the proton affinity of NH_3 is relatively high with 204 kcal/mol [2], the range of molecules which can be ionized is limited. NH_4^+ can also undergo association reactions with an analyte A in the form of $NH_4^+ + A + M <=> (NH_4^+A)^* + M => NH_4^+A + M$, with M being a third collision partner [3]. In a first step an energetically excited transition complex $(NH_4^+A)^*$ is formed. During the lifetime of the complex stabilizing collisions with a third partner M that removes the excitation energy may occur. Most recently Hansel et al. [4] showed that ammonia-water clusters can undergo fast ligand switching with organic molecules. Until today the majority of the ammonia chemical ionization studies focused on the reaction of NH_4^+ with organic molecules containing functional groups [4], [5]. Monoterpenes were never in the focus of ammonia studies, besides a study of Lindinger et al. [1] who used NH_4^+ to distinguish between the isomers pinene and pyrazine. We present here a study which investigates the reactions of three small ketones, methyl salicylate and eight monoterpenes.

Experimental Methods

Experimental Setup

To produce a defined air flow containing a constant amount of each monoterpene and methyl salicylate, we used a temperature stabilized diffusion source. A droplet of the liquid substance was placed at the bottom of the diffusion source which was placed in a temperature controlled water bath (~30°C). The diffusion rate from the diffusion source to the bypassing constant airstream is controlled by temperature, pressure and characteristics of the substance. To humidify the air stream with a specified amount of water, we used a Liquid Calibration Unit (LCU, Ionicon Analytik). For studying the reactions of the three ketones, we dynamically diluted two different calibration gas standards (Apel-Riemer). Subsequently, the water content of the air stream was analyzed with an Infrared Gas Analyzer (IRGA). The chemical ionization reactions were studied with a selective reagent ion time of flight mass spectrometer (SRI-ToF-MS).

SRI-ToF-MS

The SRI-ToF-MS is an advanced version of the instrument described in [6]. It offers the possibility of switching between different reagent ions. In a hollow cathode helium is ionized which subsequently ionizes the introduced reagent gas. Additionally, the SRI-ToF-MS is equipped with conductive peeks rings instead of metal drift rings. To reduce contaminations from the ion source region entering the drift region, the airstream is pumped backwards through the instrument. The collision energies within the drift region of the instrument were set to 55 meV and 88 meV, respectively. For studying collision induced dissociation occurring in the lens system connecting the drift tube with the mass spectrometer we ramped the extraction voltage for each collision energy in 5 steps.

Quantum Chemical Calculations

To fill the gap of missing literature values of monoterpene proton affinities, we performed high level quantum chemical calculations on the proton affinities of all used compounds. Additionally, reaction enthalpies and adduct geometries were calculated.

Results

Due to the low proton affinities of the ketones, proton transfer reactions are energetically not possible. As expected acetone, methyl vinyl ketone and methyl ethyl ketone underwent adduct formation and were only detected on the ion adduct mass (NH_4^+A). Quantum chemical calculations show that NH_4^+ is forming rather strong bonding with the carbonyl group of the ketones.

Although methyl salicylate offers a carbonyl and a hydroxyl group, it was mainly observed on the protonated mass. However, the proton affinity of methyl salicylate is higher than the one of NH_3 allowing exothermic proton transfer to occur efficiently.

Among the monoterpenes we observed great variations in their chemical ionization pattern in collisions with NH_4^+. The quantum chemical calculations show that most of our monoterpenes have just slightly higher proton affinities than NH_3. The only exception is limonene which offers no protonation site with a proton affinity higher than NH_3. Thus, limonene shows the highest adduct ion yield, followed by 3-carene. In contrast, camphene undergoes nearly 95% proton transfer and shows a negligible adduct ion yield at all collision energies. Correlating the adduct ion yield to the stability of the cluster reveals a good linear relationship (see figure 1).

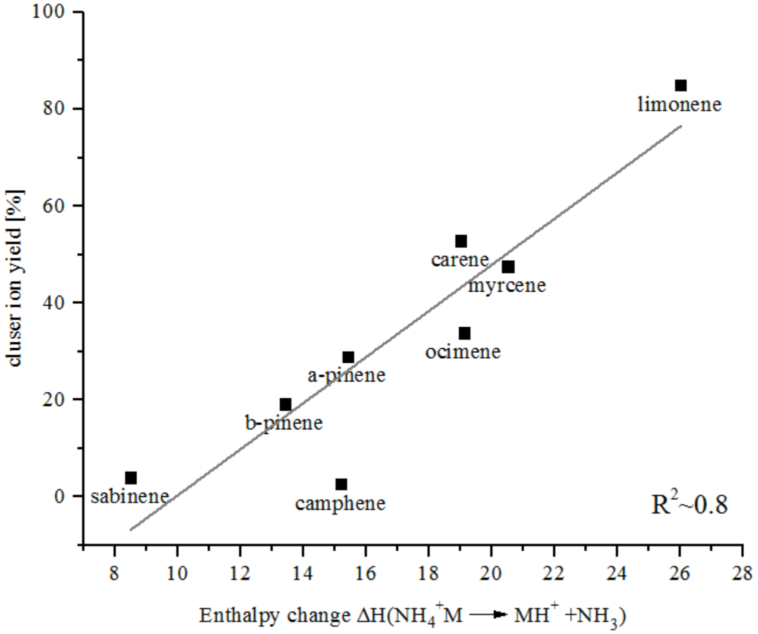

Figure 1: The cluster yield of the monoterpenes shows a good linear correlation with the calculated standard enthalpy change for fragmentation of the cluster to the protonated mass.

Discussion

The present study sheds new light on the ionization mechanism of ammonia chemical ionization mass spectrometry. The molecules having lower proton affinities than NH_3 were able to undergo association reactions with NH_4^+ forming stable adduct ions where ammonia attaches to the carbonyl group via a rather strong bonding. The association reactions show at low collision energies an efficiency of ~12% at humid conditions compared to the upper limit of the collision rate. For the monoterpenes the measured varying ionization patterns can be associated to their theoretical calculated formation enthalpies and proton affinities. Monoterpenes which obtain two or more carbon double bonds can form stronger adducts to NH_4^+. The reaction efficiency of the monoterpenes reachs approximately 20-40% of the calculated collision rate coefficients.

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Biogenic VOCs in the Arabian Sea during the AQABA ship cruise

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Abstract

Over the past decades, multiple field and laboratory studies concerning dimethyl sulfide (DMS) oxidation were conducted. Nevertheless, several relevant atmospheric chemistry questions remain open. Large regional differences in oxidation pathways have been reported [1], most probably due to the large range of environmental conditions. For a better understanding of DMS oxidation pathways in the atmosphere, more measurements of DMS and related compounds in different marine environments are important.

The AQABA (Air Quality and Climate Change in the Arabian Basin) cruise took place during July and August 2017. The ship *Kommandor Iona* was equipped with a wide range of instrumentation for trace gas and particle measurements. The expedition started near Toulon (France), proceeded via the Mediterranean, the Suez Canal, the Red Sea, the Arabian Sea and the Arabian Gulf to Kuwait, thereafter returning by the same route. Most regions were characterized by strong anthropogenic influence except for parts of the Arabian Sea/Northern Indian Ocean. There, significant biogenic VOC concentrations were detected, including DMS (nominal protonated mass 63 m/z), which is known to be emitted by phytoplankton. Higher DMS mixing ratios were observed when passing through regions of enhanced biological activity (confirmed with satellite-aided detection of chlorophyll). In addition to DMS we observed the DMS oxidation product dimethyl sulfone (DMSO2: nominal protonated mass 95 m/z) and a previously unknown compound at a nominal mass of 96 m/z, closely correlated to the DMSO2 signal. The exact mass of the unknown species corresponds to CH3S(O2)NH2 and a spike test of this pure compound was found to correspond to the mass detected on the ship. This marine emission unusually links both the marine nitrogen and sulfur cycles.

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First ambient flux measurements with the novel PTR3-TOF on top of a measurement tower in Hyytiälä, Finland

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Abstract

We demonstrate the capabilities of the new PTR3-TOF presenting first outdoor measurements of volatile organic compounds (VOCs) and their oxidation products. Concentration and eddy covariance flux results give new insights on the evolution of biogenic and anthropogenic emissions over the canopy of a boreal forest at the SMEAR II station in Hyytiälä, Finland. The new instrument was equipped with a dedicated inlet developed for reduced wall contact, enabling the quantitative measurement of many VOCs as well as highly oxidized compounds (HOMs) observed during several nucleation events in spring 2016.

Introduction

In previous work[1] PTR-MS proved to be a valuable tool for highly time resolved measurements of VOCs in the atmosphere down to concentrations in the parts per trillion (pptv) range. Combining its soft ionization method with a fast response time renders the PTR-MS capable of observing fast concentration changes of a large variety of compounds in ambient air. With our latest development, the PTR3-TOF mass spectrometer[2], we pushed the limits even further. With a limit of detection in the parts per quadrillion (ppqv) range and a wall contact reduced inlet design, we can now measure even HOMs and condensable vapors contributing to new particle formation and aerisol particle growth[3]. Bridging the gap between selective atmospheric pressure chemical ionization techniques and traditional low pressure PTR-MS, we gain higher sensitivity while trying to preserve most of the humidity independence valued by the PTR-MS community. We pick up a most demanding application, direct eddy covariance flux measurements[4], to demonstrate the performance of the new PTR3-TOF under ambient conditions.

Experimental Methods

The measurement site

The SMEAR II station (61°51 N, 24°17 E, 181 m a.s.l.) in Hyytiälä, Finland, is located in the south boreal sub-zone. Vegetation at the site is dominated by 40 year old Scots pine (Pinus sylvestris) trees. The canopy height is approximately 15 m, the ground vegetation mostly consists of lingonberry (Vaccinium vitis-idaea), blueberry (Vaccinium myrtillus), and mosses (Pleurozium scheberi; Dicranum polysetum).

Data collection and calibration

The PTR3-TOF as described by Breitenlechner et al.[2] was positioned inside a container on top of a tower at the measurement site in Hyytiälä. Humidity dependent sensitivity on selected VOCs was regularly calibrated with a setup including a humidified zero air generator and a mixing stage with a bottled gas standard (Apel Riemer Inc.). Internal humidity measurements with an infrared gas analyzer (LICOR LI-840A) ensured consistent humidity during calibration and measurements. Wind data was collected from two independent sonic anemometers (METEK USA-1), one mounted on a boom 40cm above the PTR3 inlet, the other one as reference and for flow distortion analysis at the same height, pointing in a 90° different direction. For good time syncronisation, acquisition of PTR data and sonic wind data was done on the same computer. PTR data was taken at 10Hz, wind data at 20Hz. A variety of environmental variables and concentration measurements including vertical profiles of wind, temperature, humidity, ozone, NO and NOx are available from the permanent measurement network of the SMEAR II station.

Inlet core sampling setup

In order to avoid wind flow field distortion and surface contact of sampled air with the tower structure, the air was sampled in a horizontal distance of 5m, heading ~170° south. A lined and insulated stainless steel tube with an inner diameter of 20cm guided an ambient air stream with a flow velocity of 3m/s towards the tower, where the sample flow to the PTR3-TOF was extracted perpendicular from the center. Allthough the Reynolds number of this setup well exceeds the laminar limit (~40.000), turbulence develops starting from the walls of the structure and propagates to the center described by the entrance cone. Assuming total loss at every wall collision for HOMs, we modeled a transmission of >95% at the point of perpendicular sampling.

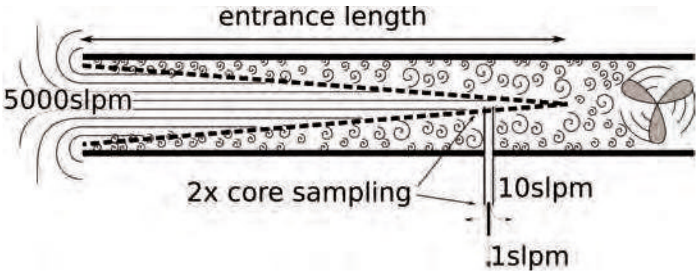

Figure 1: ***Core sampling inlet design****, taking advantage of the turbulence entrance cone. Typical parameters: Flow velocity 3m/s, ID 20cm, Reynolsnumber ~40.000, length to core sampling 5m, transmission (calculated) 95%.*

Results

During the measurement period of six weeks, we captured the time evolution of several hundred VOC signals including biogenic and anthropogenic precursors, oxidized species and organonitrates. More than 140 mass traces showed food correlation to the vertical wind speed indicating flux information. For the first time the emission flux of sesquiterpenes and prominent oxidation products could be measured. Several new particle formation events were recorded by the stationary equipment of the SMEAR II station during the campaign, further analysis of air mass trajectories and precursor composition might give insight into the responsible mechanisms of these events.

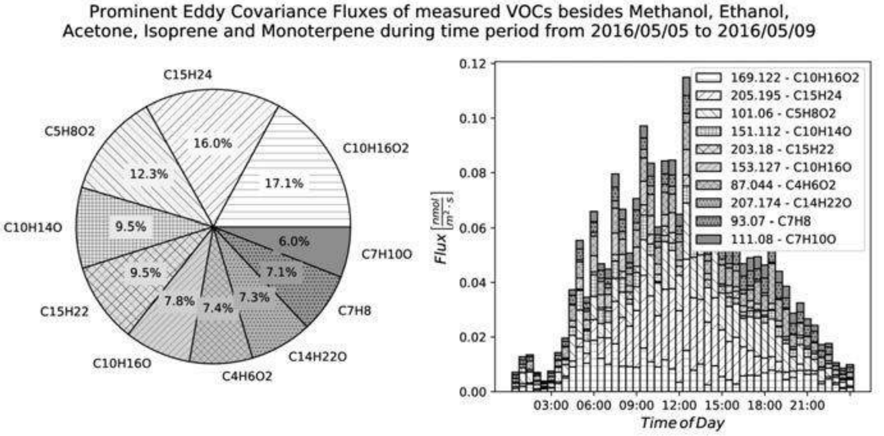
Prominent Eddy Covariance Fluxes of measured VOCs besides Methanol, Ethanol, Acetone, Isoprene and Monoterpene during time period from 2016/05/05 to 2016/05/09

Figure 2: ***Eddy covariance flux results,*** *ommiting the out-of-scale contributions of Methanol, Ethanol, Aceton, Isoprene and Monoterpene. Relative abundance is shown to the left, diurnal cycle on the right panel.*

Discussion

Our new setup provides new insights into the dynamics of emission, transport and reaction of hundreds of compounds with concentrations ranging from several parts per billion down to several hundred ppqv. We demonstrated, that the PTR3-TOF is capable of measuring eddy covariance flux data of semi-volatile compounds due to its high sensitivity and its improved inlet design.

Acknowledgements

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Combination of VOC, NH_3 and CO_2 measurements to characterize chemical fingerprints in cow and sheep barns during an on-site farm experiment

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Abstract

The project AGRIMULTIPOL (funded by the French agency ADEME, 2017-2020) aims to identify and quantify major atmospheric pollutants (ammonia, volatile organic compounds, pesticides and particles) emitted by agricultural activities. The project is based on a substantial experimental deployment work using PTR-Qi-TOF-MS, ACSM, DT-GC-MS, NOx and NH3 instruments. Measurements were performed at a conventional farm located 40 km to the west of Paris, which combines crops and livestock (~200 cows and 400 sheep). The first objective was to determine chemical profiles from typical agricultural sources, namely livestock, feed storage and pesticides. For this purpose, the instrumentation has been deployed as close as possible to the sources. Specifically, measurements were carried out in two livestock areas –with cows and sheep, respectively- as well as at a few meters downwind from the crop residues storage area. The second objective was to investigate the impact of some key agricultural practices on atmospheric composition, especially nitrogen and pesticide application in the field at the end of the winter and beginning of spring (a period often associated with particle pollution events at the regional scale). In this second phase, dedicated instrumentation measured the atmospheric composition at a site close to the farm (on a wheat crop field).

Preliminary results from the first phase of measurements taken at the sources (livestock and crop residues storage) in November 2017 are presented here, whereas preliminary results from the second phase are presented by Kammer et al. (this conference).

Introduction

Agricultural activities are essential for human population but also a significant source of atmospheric pollutants (in the gas and particulate phase) and greenhouse gases. Whereas many studies have already led to an estimation of greenhouse gases emissions, our knowledge concerning other pollutants is still associated with a high degree of uncertainty. This is especially the case for aerosol compounds, but also for their gaseous precursors, volatile organic compounds (VOCs) and ammonia (NH3). A recent study (Bauer et al., 2016, [1]) has shown that in three regions of the world (namely Europe, North America and China), agricultural activities are a significant PM2.5 source (contributing to about 1/3 of total PM2.5), which shows the importance of better characterizing their precursors, especially ammonia .Although not well documented yet, VOCs emissions by agricultural activities could also have a significant impact on air quality, especially in proximity from cities where NOx are also available (Gentner et al., 2014, [2]).

In this context, the ADEME-Agrimultipol project aims to identify and quantify some key pollutants (VOC, NH3, pesticides and aerosols) emitted by different activities linked to the agricultural sector. Characterization of volatile emissions fingerprints by livestock areas (a cow and a sheep barn) is determined by combining measurements of VOCs, NH3 and CO2.

Experimental Methods

The experiment took place at the AgroParisTech farm about 40 km west from Paris from November 15 to 30, 2017. The instrumentation was located in a van which was successively installed in a cow barn (see figure 1), in a sheep barn, outside the sheep barn and then again inside the sheep and cow barns. Measurements of NH3 and CO2 were performed during the whole time, whereas VOCs measurements were performed only from November 15 to 24th.

A proton transfer reaction - time of flight - mass spectrometer (PTR-Qi-TOF-MS, Ionicon, national instrument within the ANAEE-France framework) was used for on-line detection of VOCs (Abis et al.[3]). Blanks and calibrations were performed daily using high purity zero air and a toluene gas standard (102±10 ppb, Messer), respectively. During the experiment, full mass spectra up to m/z 510 were recorded every second. The identification of VOCs was performed on 30 min mean mass spectra, and based on several criteria such as the proximity with the theoretical m/z and the coherence with the theoretical isotopic distribution.

VOCs were also sampled by adsorption on Tenax cartridges during several hours (3 to 5 hours) at 0.5 L/min. Then, VOCs were analyzed using thermal desorption gas chromatography mass spectrometry (TD/GC-MS). This analysis was not quantitative, but provide a complementary identification of VOCs.

6-L stainless steel flasks were filled regularly in the sheep and cow barns (15 minutes sampling time) and were analyzed later on at the laboratory. Non-methane hydrocarbon (NMHC) measurements of C2 to C8 were made with an HP 6890 gas chromatograph equipped with a FID detector. The concentration of each compound was calculated from the response of a standard certified by the National Physical Laboratory (NPL) containing 32 NMHCs compounds.

Ammonia was measured using a laser-based photoacoustic ammonia analyzer (LSE Monitors, the Netherlands) with a detection limit of 1 ppb and a time resolution of 1 minute. A 1.4 m, 1/8 inch, heated Teflon line was used for sampling via a pump and a Teflon filter to retain particles.

The CO2 concentration was measured with an open path infrared gas analyzer (Li-COR 7500A, Li-COR, USA) that was calibrated a few days before the campaign. Wind speed and direction were measured using a 3-D sonic anemometer (R3-50, Gill, USA). Both instruments were placed over a mast close to the van and the inlets (Figure 1).

Additional measurements (NOx, filter sampling for aerosol chemical composition) were also performed during these experiments.

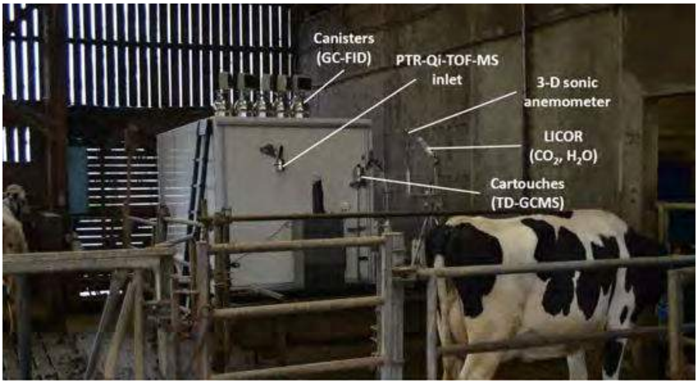

Figure 1: Instrumented van inside the cow barn

Results and discussion

Figure 2 shows the time series of NH3 and CO2 in the three studied environments (cow and sheep barn and outside air). As expected, we note for both compounds much higher levels inside the livestock areas, with ammonia values up to 10-15 ppm inside the sheep barn, comparing to outdoor levels below 20 ppb. The similarity of NH3 and CO2 data (in terms of signal intensity and variability/dynamics) inside the cow/sheep barns between the two studied periods allows to consider that PTR-Qi-TOF-MS measurements performed in each studied environment could characterize them, respectively.

More than 300 compounds were identified during the whole experiment. About 300 masses in the stable and ~150 masses in the cow and sheep barn measured by PTR-Qi-TOF-MS have shown significant levels. In both buildings, half of the identified compounds were oxygenated compounds. One specificity is that nitrogen-containing compounds, such as trimethylamine (Fig. 3) represented 13% of the identified compounds in the cow barn, and 20 % in the sheep barn, respectively.

The temporal variability of the compounds inside the sheep barn shows a clear diurnal cycle driven by the closing of the main gate every evening, leading to the accumulation of NH3 and CO2 during the night (Figure 2). This feature allows to clearly identify the compounds emitted by the sheep barn and to establish a chemical fingerprint of this specific source. For the cow barn, the building was open on several sides and therefore the establishment of the source signature was based on the behavior of VOCs in comparison with CO2 (high CO2 as indicative of the presence of the cows inside the building) and NH3 (high NH3 as indicative of indoor air).

Results from VOC source signature inside these two different livestock areas (cow and sheep barn) will be presented together with an estimation of their emission ratios based on a CO2 mass balance model.

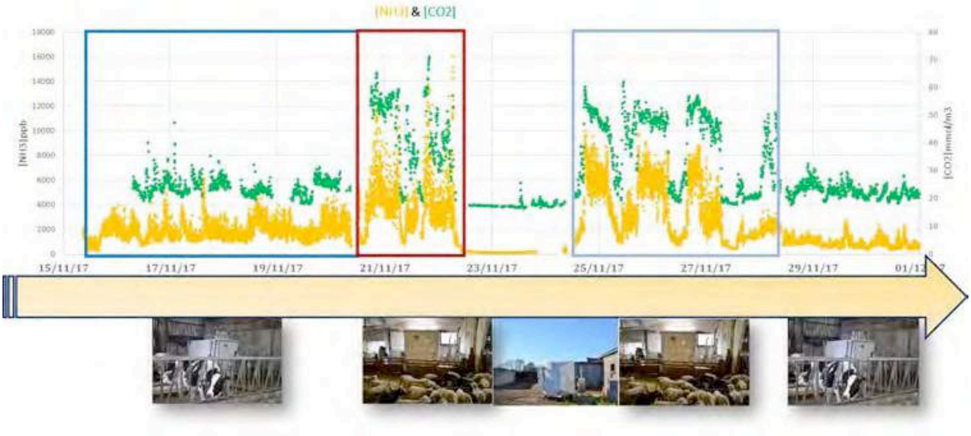

Figure 2: NH_3 and CO_2 mixing ratios measured in different environments (cow barn, sheep barn and ambient air as shown by the corresponding pictures)

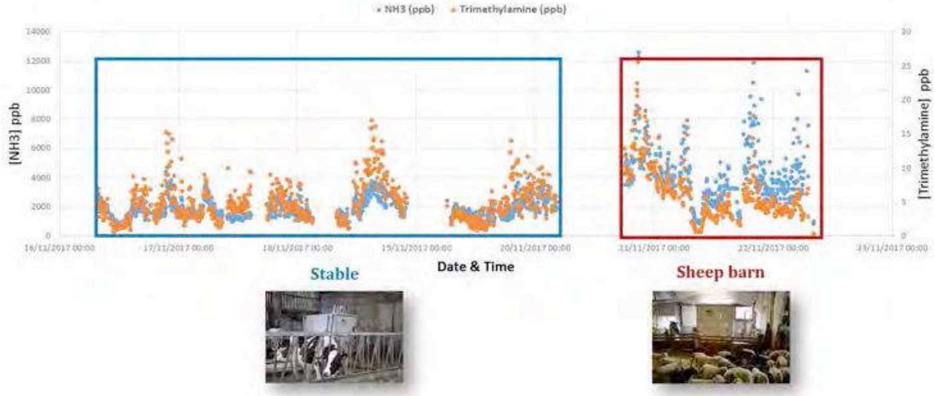

Figure 3: NH3 and trimethylamine measured in the cow and sheep barn

Acknowledgments

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A preliminary study of non-radioactive chemical ionization mass spectrometry using acetic acid-acetate cluster as a reagent ion for the real-time measurement of acids and hydroperoxides

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Abstract

We have developed a non-radioactive chemical ionization mass spectrometry method using acetic acid-acetate cluster as the reagent ion. By electron impact onto an acetic anhydride-Ar gas mixture, a strong and single ion peak of the acetic acid-acetate cluster was observed. We demonstrated that the reagent ion can ionize carboxylic acids (RC(O)OH) and hydroperoxides (ROOH) produced in ethylene ozonolysis through the formation of adduct ions of these species and acetate. This technique could be used for the detection of various organic hydroperoxides as well as organic and inorganic acids in the atmosphere [1].

Introduction

Alkenes are an important component of the anthropogenic and biogenic emissions of volatile organic compounds (VOCs) into the atmosphere. Ozonolysis is a major sink of alkenes due to the reactivity of the C=C bond toward ozone (O_3). Alkenes are converted to oxygenated produces which have lower volatility and contribute to the secondary organic aerosols (SOAs) [2]. Generally, reactions of O_3 with alkenes proceed via initial addition to the C=C bond to form energy-rich ozonides, which rapidly decompose to carbonyls and initially energy-rich Criegee intermediateds (CIs). The energy-rich CI can either undergo unimolecular decomposition or be stabilized upon collision with air. Then, the stabilized CI (sCI) is believed to be able to react with many kinds of organic compounds such as carboxylic acids and hydroperoxides to hydroperoxides which are produced by an insertion of sCI into an OH group of the compounds.

Mass spectrometry has become a ubiquitous tool in identifying and quantifying atmospherically relevant organic compounds. Chemical ionization usually permits the soft ionization of chemical species, allowing the time-resolved measurement of multiple VOCs, even when they are present in a complex sample containing a mixture of various kinds of VOCs. Proton-transfer reaction mass spectrometry (PTR-MS), where the proton transfer occurs between hydronium ions (H_3O^+) and the chemical species (M) that have a proton affinity greater than that of water, to form the protonated molecule ($M•H^+$), has been world-widely used for the purpose. However, when detecting oxygenated organic compounds in carboxylic acids and hydroperoxides, which are key players in the formation of SOAs, fragmentation involving the H_2O elimination≥from≥$M•H^+$ has been reported.

Negative-ion chemical ionization mass spectrometry (NI-CIMS) is a suitable method for the detection of oxygenated organic compounds. In fact, organic acids and hydroperoxides, besides inorganic acids such as HONO and HNO_3, are detectable by NI-CIMS using CF_3O^-, acetate ($CH_3C(O)O^-$), $I^-•(H_2O)_n$, and $SO_2•Cl^-$ as the reagent ions. However, all these reagent ions, with the exception of SO_2Cl^-, are produced via radioactive ion sources. In Japan, safety regulations limit the use of an instrument using a radioactive isotope, making it difficult to bring such an instrument for on-site measurements.

Non-radioactive NI-CIMS was developed by Hirokawa's group using $SO_2•Cl^-$ or Cl^- as the reagent ion. Because chlorine has the two principal stable isotopes, ^{35}Cl and ^{37}Cl, present in approximately 3:1 ratio, the product ions are observed as two peaks in a mass spectrum with a possibility of overlap between the peaks. In the present study, we have succeeded in preparing a reagent ion, acetic acid-acetate cluster (AcOH•AcO$^-$) without the use of radioactive isotopes. We have confirmed the detection of carboxylic acids and hydroperoxides produced during ethylene ozonolysis using this method.

Experimental Methods

Figure 1a shows a schematic diagram of the NI-CIMS instrument used in this study, which is the same as the instrument that uses SO_2Cl^- or Cl^- as the reagent ion. Here, the reagent ion was generated by the electron impact (~40 eV) from a resistively heated filament onto the acetic anhydride ($CH_3C(O)OC(O)CH_3$, Ac_2O)-Ar gas mixtur. About 2 sccm (standard cubic centimeter per minute) of pre-mixed acetic anhydride-Ar mixture (~0.1%) was introduced into an ion source, mixed with an additional 2100 sccm of Ar.

Figure 1b shows a mass spectrum of the reagent ion obtained without air sampling. Contradictory to expectation, the signal intensity of the $CH_3C(O)O^-$ ion (AcO$^-$), which is a major ion produced in a ^{210}Po ion source with a flow of acetic anhydride-N_2 mixture, at *m/z* 59 was significantly low. Instead, a strong peak was observed at *m/z* 119, which was assigned to acetic acid-acetate ion (AcOH•AcO$^-$). As shown in Figure 1, the intensities of AcO$^-$ (*m/z* 59) and (AcOH)$_2$•AcO$^-$ (*m/z* 179) peaks were less than 3% of that of the AcOH•AcO$^-$ (*m/z* 119).

To test the validity of the acetic acid-acetate cluster as a reagent ion, the detection of products in ethylene ozonolysis using our "AcOH•AcO$^-$ CIMS" was investigated. The experiments were conducted using a 100 L pillow-shaped bag made of FEP Teflon. The initial mixing ratios of ethylene and ozone were ~5 ppmv and ~3.5 ppmv, respectively. An OH radical scavenger was not used in these experiments. The gas in the Teflon bag was sampled into the NI-CIMS instrument at a flow rate of approximately 0.8 L min^{-1} through a 0.25 mm diameter orifice. The sampled gas flow from the bag was mixed with the reagent ion flow in a reaction flow tube.

Results and Discussion

The solid line in Figure 2a represents the mass spectrum obtained after 80 min of ethylene ozonolysis under dry conditions. New peaks were observed at *m/z* 105, *m/z* 137, *m/z* 151, *m/z* 183, and *m/z* 197, which could be attributed to the reaction products of the ethylene ozonolysis. Ethylene ozonolysis produces a Criegee intermediate, CH_2OO, which isomerizes to formic acid (HC(O)OH, molecular weight (MW) 46) and formaldehyde (H_2CO, MW 30). The HC(O)OH further reacts with CH_2OO to form hydroperoxymethyl formate (HPMF, $HC(O)OCH_2OOH$, MW

92). In the absence of OH radical scavengers, ethylene reacts with an OH radical to produce 2-hydroxyethyl hydroperoxide (2-HEHP, $HOCH_2CH_2OOH$, MW 78). The observed ions corresponding to *m/z* 105, *m/z* 137, and *m/z* 151 can be assigned to the adduct ions of these respective products and acetate. Since there is no information on the charge distribution of the resultant adduct ions, they can be speculated to arise from the elimination of a proton from the neutral adduct of the ozonolysis product and acetic acid, *i.e.*, $[AcOH{\bullet}HC(O)OH-H]^-$, $[AcOH{\bullet}(2\text{-}HEHP)-H]^-$, and $[AcOH{\bullet}HPMF-H]^-$.

The peaks observed at *m/z* 183 and *m/z* 197 can also be assigned to adduct ions of ethylene ozonolysis products and acetate. The peak at *m/z* 183 is attributed to a product with MW 124, considered as an insertion product of one CH_2OO into 2-HEHP, namely, $(HO)CH_2CH_2OOCH_2OOH$. Similarly, the peak at *m/z* 197 can be assigned to a product with MW 138, which may be produced from a subsequent reaction of HPMF with CH_2OO, as $HC(O)OCH_2OOCH_2OOH$. The production of these oligomeric hydroperoxides have been reported in our previous studies. It should be noted that the peak at *m/z* 197 can be alternatively assigned to an adduct ion of acetic acid-acetate and 2-HEHP, namely, $[(AcOH)_2{\bullet}(2\text{-}HEHP)-H]^-$. To summarize, the acetic acid-acetate cluster ionizes an analyte, M, such as an organic acid and a hydroperoxide, via the following reaction:

$$AcOH{\bullet}AcO^- + M \rightarrow [AcOH{\bullet}M-H]^- + AcOH \quad (1)$$

Under humid conditions (RH ≈ 25 %), the increase in the ion signal of water-acetic acid-acetate cluster ($H_2O{\bullet}AcOH{\bullet}AcO^-$, *m/z* 137) was not obvious while the increase in the ion signal of the water-acetate cluster ($H_2O{\bullet}AcO^-$, *m/z* 77) was clearly observed. But the signal intensity of $H_2O{\bullet}AcO^-$ at *m/z* 77 was still small compared to that of $AcOH{\bullet}AcO^-$. The ion signal intensities at *m/z* 105, *m/z* 123, *m/z* 139, and *m/z* 183 increased, indicating that water vapor does affect the ethylene ozonolysis reaction. The ion signal at *m/z* 123 is assigned to an adduct ion of acetate and hydroxymethyl hydroperoxide (HMHP, $HOCH_2OOH$), which is produced from the reaction between CH_2OO and water vapor. Since the molecular weight is the same for HMHP and SO_2, the former cannot be detected by $SO_2{\bullet}Cl^-$ CIMS. In addition, the reaction between CH_2OO and water vapor produced formic acid, resulting in the observed increase in the peak intensity of $[AcOH{\bullet}HC(O)OH-H]^-$ at *m/z* 105. The ion signal at *m/z* 139 can be attributed to hydroperoxymethyl hydroperoxide ($HOOCH_2OOH$), which is a possible product of the reaction between CH_2OO and H_2O_2. Previous studies have suggested that H_2O_2 is generated from the decomposition of HMHP. Although under dry conditions the ion signal at *m/z* 183 is assigned to $[AcOH{\bullet}(HO)CH_2CH_2OOCH_2OOH-H]^-$, the experiments under humid conditions showed an increase in the intensity at *m/z* 183; therefore, this signal may be ascribed to a different ion produced from a process involving water vapor. The most likely candidate is an adduct of acetic acid-acetate and HMHP, namely, $[(AcOH)_2{\bullet}HMHP-H]^-$. Because water vapor reacts with CH_2OO, the reactions between CH_2OO and other molecules are expected to be inhibited under humid conditions. In fact, the signal intensity at *m/z* 151, assigned to HPMF produced from the reaction between CH_2OO and formic acid, was found to decrease on addition of H_2O, as shown in the figure.

As a reference, a mass spectrum of gaseous products obtained by PTR-QMS after 120 min reaction of ethylene with ozone under dry conditions is shown in Figure 2b. Major product ions were observed at *m/z* 31 and *m/z* 47, which were assigned to formaldehyde and formic acid, respectively. Secondary ozonide ($CH_2O_3CH_2$, MW = 76) and hydroperoxymethyl formate ($HC(O)OCH_2OOH$, MW = 92) were possibly detected as an $M{\bullet}H^+$ ion at *m/z* 77 and *m/z* 93, respectively. Products from the OH reaction with ethylene such as 2-HEHP, glycolaldehyde ($HOCH_2CHO$, MW =60), and ethylene glycol ($HOCH_2CH_2OH$, MW = 62) were also detected as the M•H^+ ion at *m/z* 79, *m/z* 61, and *m/z* 63, respectively. However, signals of fragment ions which are formed by the H_2O elimination from M•H^+ at *m/z* 61, *m/z* 43, and *m/z* 45, respectively, might be more intense than that of M•H^+, because they have an OH group. At present, ion signals at m/z 73 and 89 cannot be assigned. By PTR-MS, it was not successful to detect oligomeric hydroperoxides involving a Criegee intermediate as a chain unit. Probably, such oligomeric hydroperoxides are decomposed in the drift tube.

This study demonstrated the successful detection of not only organic acids but also organic hydroperoxides produced via ethylene ozonolysis using chemical ionization with acetic acid-acetate as the reagent ion. Although we did not estimate the detection limits in the present work, the intensity of the present reagent ion, AcOH•AcO^-, was similar to that of SO_2•$^{35}Cl^-$, by which HONO was measured. With further optimization of the operational conditions (flow system, etc.) and calibration of the performance parameters (linearity, humidity dependence of detection sensitivity, etc.), the acetic acid-acetate CIMS is expected to be a useful technique for the detection of various organic hydroperoxides as well as organic and inorganic acids in the atmosphere.

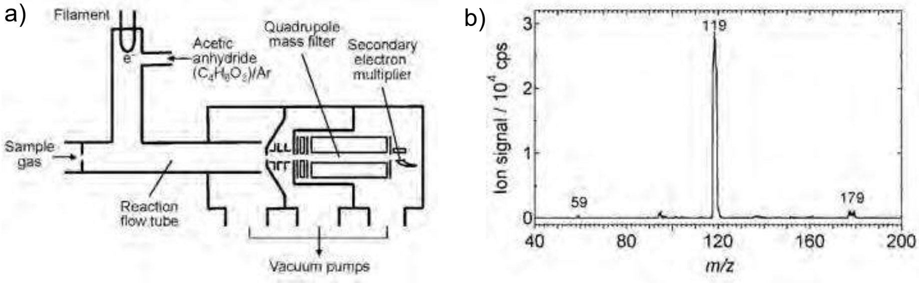

Figure 1: (a) A schematic diagram of the AcOH•AcO^- CIMS instrument [1]. (b) A mass spectrum of the reagent ion, AcOH•AcO^- (m/z 119) [1].

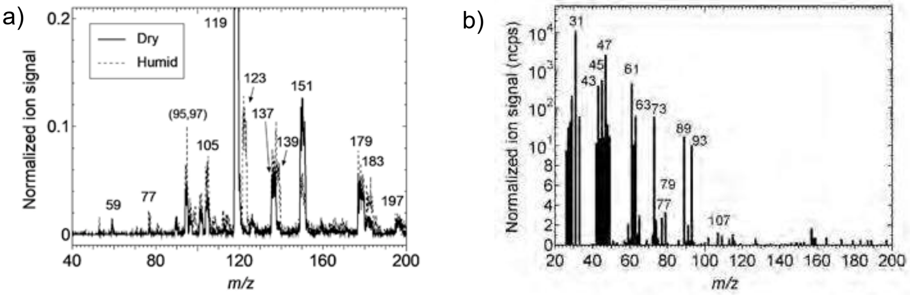

Figure 2: (a) AcOH•AcO^- CI mass spectra obtained under dry and humid (RH ≈ 25 %) conditions [1]. Signal intensities are normalized to the reagent ion intensity (AcOH•AcO^-) at m/z 119. (b) A PTR mass spectrum obtained under dry conditions.

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High temperature PTR-TOF-MS for EC flux measurements of VOCs

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Abstract

The performance of the PTR-TOF-MS 4000 with high temperature inlet and reaction chamber is investigated for the feasibility to conduction eddy covariance (EC) flux measurements of volatile organic compounds (VOCs). The tubing is made of glass or Sulfinert® coated copper tubing to prevent reactions with sulfur compounds. Optimization regarding inlet flow and drift tube pressure will be investigated further.

Introduction

Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) is a highly sensitive analytical technique capable of measuring volatile organic compounds (VOCs) in the air developed about 20 years ago [1]. Later developments use a time-of-flight (TOF) mass spectrometer to measure VOCs at ultra-low concentrations under high mass resolution [2]. An advantage of the PTR-TOF-MS is the capability to make a full spectrum of complex air mixtures in less than 100 ms [2]. Measurements on 10 Hz timescale can be used for Eddy Covariance (EC) flux measurements of any compound [3]. Sticky compounds as NH_3 and semi-volatile organic compounds (SVOC) have a long response time and have a large spillover effect when concentrations changes [4,5]. The High-Temperature PTR-MS (HT-PTR-MS) is intended to measure sticky compounds or SVOCs [6]. Sintermann et al., [7] used a high temperature inlet and drift tube for fast measurements of ammonia with chemical ionization mass spectrometry (CIMS). We aim for a similar approach with a combination of HT-PTR-MS and PTR-TOF-MS would give the advantages of fast measurements of sticky polar compounds. Our goal is to measure fluxes of compounds as phenols, carboxylic acids and ammonia with EC by using the fast measurements of a custom built high resolution and high sensitivity PTR-TOF-MS 4000 with high temperature and a hexapole ion guide.

Experimental Methods

The PTR-TOF-MS 4000 has a mass resolution higher than 4000 for m/z above 147 and higher than 3500 for m/z above 79. The inlet tube and reaction chamber can be heated up to 180°C. The detection limit is below 5 pptv and the sensitivity is above 200 cps per ppbv. A hexapole ion guide focus the ion beam with limited losses of ions, thus is a factor for the overall sensitivity and mass resolution. Sulfinert® coated cupper tubes and glass capillaries are used as inert materials to avoid sulfur and other compounds to react. See Figure 1 for the configuration of the inlet and used materials.

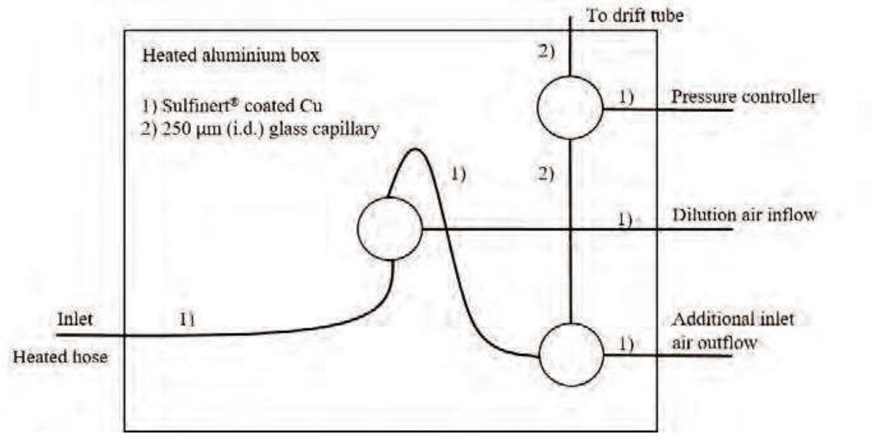

Figure 1: Schematics of the inlet configuration that is connected in a heated aluminum box. It is possible to pull more air through the inlet tube with the additional air inlet flow. Furthermore, the inlet air can be diluted with an external pressurized gas.

Results

The setup with non-coated copper tubing connected to the T-pieces for the pressure controller and additional inlet air was tested with a sulfur mix standard gas containing methanethiol (MT), dimethyl sulfide (DMS) and hydrogen sulfide (H_2S). Despite minimum contact with between the gas and the copper tubing in the T-piece connection, it was clear from the tests that MT and H_2S was lost giving a low sensitivity of these two compounds, whereas less reactive DMS was recovered. After the change to Sulfinert® tubing, the sensitivity of MT and H_2S was increased.

In order to keep the lag time low we intend to have an inlet flow of 1000 sccm, which is the maximum for the configuration. However, as the pressure controller and inlet flow controller is connected to the same pump, we experience problems obtaining stable pressure in the drift tube when we use a high inlet flow. This is seen in Table 1, where we cannot get an inlet flow higher than 200 sccm with a stable drift tube pressure.

Table 1: Settings and values for flow controller for inlet flow, pressure controller and pressure in drift tube.

FC Inlet [sccm]		*Pressure controller [mbar]*		*Pressure drift tube [mbar]*	
Set point	*Value*	*Set point*	*Value*	*Set point*	*Value*
0	*0*	*489*	*489*	*2.20*	*2.19*
50	*50*	*489*	*489*	*2.20*	*2.19*
100	*100*	*491*	*491*	*2.20*	*2.19*
150	*150*	*492*	*492*	*2.20*	*2.19*
200	*200*	*1000*	*328*	*2.20*	*1.57*
250	*244*	*1000*	*169*	*2.20*	*1.09*
500	*237*	*1000*	*161*	*2.20*	*1.06*
1000	*232*	*1000*	*159*	*2.20*	*1.06*

Discussion

The problems concerning the unstable pressure in the drift tube when using high inlet flow are essential to solve. We plan to use glass capillaries of different inner diameter. If this is not enough, it might be necessary to separate the PC and inlet flow so they do not use the same pump. This would require an installation of a second pump to make to two systems work independent of each other.

Our plans involve tests with a range of VOCs, e.g. acetic acid and butanoic acid along with ammonia and sticky compounds as trimethylamine. We wish to determine the response times for the feasibility to measure EC fluxes with PTR-TOF-MS. This will be conducted under different temperatures, relative humidity, inlet flows and ionization energies. Furthermore, it is interesting to test the performance with O_2^+ as primary ion for ammonia.

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PTR-ToF-MS VOC profiling of raw and cooked gilthead sea bream (Sparus aurata) from different geographical origin

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Abstract

Fish volatile compounds provide information both on quality and freshness of fish. In this study, proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) equipped with a multipurpose head-space automated sampler was successfully used to investigate the VOC profiles of raw and cooked gilthead sea bream (*Sparus aurata*) from different geographical origins and farming methods.

Introduction

Fish aroma is a leading consumers' criterion to evaluate its freshness and quality [1]. Volatile organic compounds (VOCs) released from fish depend not only on freshness of the product, but also dietary treatment and some other factors of fish husbandry [2]. GC-MS is typically used to evaluate aroma profiles of wild and reared gilthead sea bream (*Sparus aurata*) [2-4]. Proton Transfer Reaction-Mass Spectrometry with Time-of-Flight analyser (PTR-ToF-MS) should be the valuable alternative for analysis of fish samples in a rapid and non-invasive way. Coupling PTR-ToF-MS to a multipurpose head-space automated sampler should give the possibility to perform analysis of raw and cooked fish in an automated way with a precise control of experimental conditions and increase the analytical throughput

Experimental Methods

Wild and reared gilthead sea bream (*Sparus aurata*) were selected for studying their VOCs profiles by a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) coupled to a multipurpose head-space automated sampler (Gerstel GmbH, Mulheim am Ruhr, Germany). Reared fish was originated from two different farms: one in Adriatic Sea and another in Tyrrhenian Sea. From five fishes of each category, 3 g of a dorsal part of fish fillet were sampled in triplicate and put in 20 mL glass vials at 10°C. Prior to measurements samples were stored at -80°C. Before analysis the samples were thawed at 4°C, then each vial was incubated at 25°C for 25 min and measured for 1 min. Cooking was simulated by incubating each vial at 70°C for 25 min and cooling down at 25°C for 25 min. Measurements follow as for the raw samples. To increase sensitivity, an ion funnel was operated at the end of the drift tube.

Data processing of PTR-ToF-MS spectra consisted of dead time correction, external calibration and peak extraction [5] followed by descriptive statistics and multivariate analysis.

Results and discussion

Two hundred fifty nine out of 429 mass peaks were selected for the further analysis eliminating mass peak of impurities, isotopes, and water clusters. Many of them can be tentatively identified based on sum formula, isotopic pattern and literature. Principal component analysis (PCA) was performed on the selected mass peak of all samples showed the clear separation between raw and cooked fish. The aroma profile of raw fish was not as intense as the cooked one. From the score plot of PCA of raw fish samples, a clear separation between three types of fish samples was observed. According to the score plot of PCA of cooked fish the differences between raw and reared fish remained but the differences between two farming systems became less evident.

According to the level of Trimethylamine and S-containing compounds fish samples were equally fresh. No significant differences in main lipid oxidation aldehydes and alcohols were observed which can be explained by a freshness of both types of fish samples [2]. The wild fish samples were richer in butanal, butanone, butanol, acetone, methanol and some other compounds. The concentration of these compounds augmented significantly with cooking.

The reared fish from Adriatic Sea was richer in monoterpene compounds from the essential oils [3] and aromatic compounds which are usually associated with the metabolism of carotenoids or thermal degradation of sugars and amino acids [3]. For these compounds it was observed a negligible effect of cooking.

In this work, for the first time PTR-ToF-MS coupled both to a multipurpose headspace automated sampler was applied for a rapid and non-invasive screening of aroma profile of raw and cooked gilthead sea bream. The technique was successful in characterizing wild and reared fish.

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Characterization of extra virgin olive oils by PTR-ToF-MS

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Abstract

In this study, for the first time proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS) equipped with a prototype fast-GC system and a multipurpose head-space automated sampler was used to investigate the volatilome of extra virgin olive oils (EVOO) in a rapid and non-invasive way. The technique was successful in finding clusters of EVOO sharing similar characteristics.

Introduction

Extravirgin olive oil (EVOO) aroma, the first to be perceived attribute of high-quality olive oil [1] and taste contribute to drive consumer preferences. Volatile organic compounds (VOCs) release from EVOO are influenced by different factors such as olive variety, geographical region, harvesting period, fruits ripening, processing methods, and storage conditions [2]. Proton Transfer Reaction-Mass Spectrometry with Time-of-Flight analyser (PTR-ToF-MS) was already successfully applied for screening of olive oils [3], apples [4], and other food products. Coupling PTR-ToF-MS to a multipurpose head-space automated sampler and a fastGC add-on gave the possibility to perform analysis in an automated way with a precise control of experimental conditions, increase the analytical throughput, add a chromatographic dimension to PTR-ToF-MS data [5].

Experimental Methods

Two hundred EVOO (monovarietals and blends) from 12 Italian regions and three other countries producers of EVOO harvested in 2 different years were selected for studying their VOCs profiles by a commercial PTR-ToF-MS 8000 instrument (Ionicon Analytik GmbH, Innsbruck, Austria) coupled both to a multipurpose head-space automated sampler (Gerstel GmbH, Mulheim am Ruhr, Germany) and a prototype fastGC system (Ionicon Analytik GmbH, Innsbruck, Austria) with a short polar GC column (MXT-WAX Cap. Column 6m, 0.25mm ID, 0.25um, Restek, Bellefonte, PA). For each sample, prepared in triplicate, 1mL of unfrozen EVOO was transferred into 20 mL glass vial and capped. Immediately after preparation the vial was flushed for 90 sec with pure N_2 in automatic way by a multipurpose head-space automated sampler. Prior to measurements samples were stored at 15°C in dark. Immediately before the analysis each vial was incubated at 37°C for 30 min and then measured for 30 sec in a direct mode and then the fastGC was sampling a headspace for 30 sec. The fastGC temperature ramp was from 40°C till 220°C and lasted 130 seconds, which was optimal for the separation of the investigated VOCs.

Data processing of both direct and fastGC PTR-ToF-MS spectra consisted of dead time correction, external calibration and peak extraction [6].

Results and discussion

One hundred sixty eight out of the 429 mass peaks detected from direct PTR-ToF-MS data were selected for the further analysis eliminating mass peaks related to impurities, isotopes, and those not having significantly higher concentration in oil samples than in blank samples. Principal component analysis (PCA) was performed on the selected dataset for the general overview paying attention to the differences in geographical region, olive variety, and harvesting year. The grouping based on a geographical region was observed especially for well-presented geographical regions such as Apulia, Sicily, and Tuscany. The influence of the year of harvest was negligible. EVOO from the same olive variety differed according to geographical regions.

Partial least squares discriminant analysis (PLS-DA) was performed on the reduced dataset of direct PTR-ToF-MS contained only four most abundant regions such as Apulia, Sicily, Lazio, and Tuscany. The model of four components showed the best results. The test set contained 40 samples: 10 samples randomly selected from each region. Error rate of classification was 25±5% with the main confusion between Apulia and Lazio EVOO. According to non-parametric ANOVA ($p<0.001$) 131 out of 168 selected mass peaks were significantly different among the samples from these four regions.

The differences in some important VOCs found in PTR-ToF-MS data were supported by chromatographic data from a fastGC add-on.

In this work, for the first time PTR-ToF-MS coupled both to a multipurpose headspace automated sampler and a fastGC add-on was applied for a rapid and non-invasive screening of EVOO. The technique was successful in characterizing different EVOO according to the geographical region and variety, identifying differences in the release of important classes of compounds.

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Fluxes of biogenic volatile organic compounds in a green oak forest

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Abstract

Volatile organic compounds (VOCs) play a key role in atmospheric chemistry. 90% of them are of biogenic origin and, more specifically, forests represent a large source of monoterpenes and isoprene [1]. Thanks to the use of a high-precision PTR-Qi-TOF-MS, this work aimed at identifying less known VOCs emitted by forests, and characterize their vertical and temporal dynamics in a mixed green oak (*Quercus ilex*) forest at the ICOS site of Puechabon in the South of France.

The field campaign was carried out from 20 June until 10 July 2018. The experimental set-up combined eddy-covariance flux measurements at the stand level, VOC concentration measurements at different heights in the canopy (vertical profile) and flux measurements in dynamic chambers over several compartments of the ecosystem.

At the canopy level, results from the analysis of eddy-covariance fluxes showed that monoterpenes and isoprene were the main VOCs emitted by the forest. Apart from these main VOCs, smaller emissions of methanol, acetaldehyde and acetic acid were observed. Many other VOCs were also detected and contributed to a much lesser extent to the total VOC emissions.

At the plant level, about 15 compounds contributed up to 60 - 90% of total emissions depending on the species and on the oak chemotype. Oaks mainly emitted monoterpenes but also methanol. Boxwood, present in the undergrowth, mainly emitted isoprene. Surprisingly, one oak had a distinct emission profile, with lower monoterpene emissions and larger emissions from other masses.

Part of this work is still ongoing and further data analyses have to be performed but these first results provide interesting insights to better characterize VOC emissions in mixed forest ecosystems.

Introduction

Volatile organic compounds (VOCs) are an essential component of atmospheric chemistry that contributes to the production of pollutants that are harmful to human health and the environment: ozone (O_3) and secondary organic aerosols ([2], [3]). Fluxes of most VOCs, 90% of which are of biological origin [1], are not quantified and not exhaustive. Managed ecosystems, which represent about 50% of the land area in Europe, constitute the most important potential for VOC emissions (55% forests; 27% agriculture; 18% rest - grasslands, wetlands, shrubs, [4]).

In this context, the COV3ER project (funded by the ADEME-CORTEA French research program) aimed at bringing new references of VOC fluxes on such types of ecosystems, and namely on a forest ecosystem. The main aim of the present work was to identify potentially unknown VOCs emitted by forests, besides monoterpenes and isoprene – the most reported forest emitted VOC in the literature, and to study their temporal and vertical emission dynamics.

Experimental Methods

The present study was carried out at the ICOS forest site of Puechabon (FR-Pue), which is located 35 km northwest of Montpellier (Herault, France) and benefits from a typical Mediterranean climate. The vegetation is largely dominated (80%) by holm oak (*Quercus ilex*). The undergrowth consists of bushes whose main species are boxwood, filaria, pistachio terebinth and juniper (*Buxus sempervirens*, *Phyllirea latifolia*, *Pistacia terebinthus* and *Juniperus oxycedrus*).

A field campaign was carried out at this site from 20 June until 10 July, 2018. The experimental set-up dedicated to study VOC exchanges dynamics at different spatial and temporal scales consisted in (i) a mast for eddy-covariance fluxes exchanged at the forest stand level, (ii) a separate mast for VOC concentrations measurements at various heights in the vegetation (vertical profile), and (iii) home-made (CEFE, CNRS) dynamic chamber systems. Additionally, CO_2/H_2O fluxes and meteorological information were continuously recorded at the site together with O3 fluxes and O_3/NO_x profiles in the forest. VOC concentrations were monitored with a PTR-Qi-TOF-MS (Ionicon, Austria, National instrument within the ANAEE-France framework). VOC data acquisition was performed using a home-made program developed under LabView®.

VOC fluxes at the stand scale were measured at a height of 10 m by the eddy-covariance technique (e.g. [5]), which required a 3-D sonic anemometer (R3-50 model, Gill, USA). A 30 m, 3/8 inner diameter, 50°C heated Teflon PFA tube was used to sample the air at 50 NL min^{-1} for VOC analysis. Data were recorded at a frequency of 20 Hz and post-processed following the usual requirements of the eddy-covariance procedure.

Measurements in dynamic chambers to isolate a plant part of the ecosystem were carried out on 5 species, among the most common in the undergrowth of the Puechabon forest. Branch-scale VOC emissions were monitored for 1 to 3 days on each species. For this purpose, the VOC concentrations at the inlet and outlet channels were measured for 2 to 4 minutes per hour, the VOC emissions were then calculated by difference in concentration between the 2 channels. Oak trunks were also monitored, as well as the soils.

Results and Discussion

VOC fluxes at the stand scale

The analysis of BVOC fluxes measured by the eddy-covariance method showed that the monoterpenes (m/z 137.13) and their fragments (hexene, m/z 81.06) dominated the flux exchanges in this forest ecosystem. The second most emitted VOC was the isoprene (m/z 69.07). These three compounds are typically found in VOC emissions from forest sites. The holm oak (*Quercus ilex*), is a strong emitter of monoterpenes [6] unlike the sessile oak (*Quercus petraea*), which is an isoprene emitter [7]. At the Puechabon site, boxwood, present throughout the undergrowth environment, is the main emitter of isoprene, as it was shown by the chamber measurements (see further). Methanol emissions have also been observed by [6] on holm oak at a rate about 10 times lower than monoterpenes, in good agreement with our results. Other compounds such as acetaldehyde (m/z 45.03) and acetic acid (m/z 61.02) were also found to be emitted from the Puechabon site, in lesser quantities. The fluxes of monoterpenes, hexene and isoprene showed very clear daily emission cycles throughout the period.

VOC emissions at the plant scale

The measurements showed that about 15 compounds contributed up to 60 - 90% of total emissions depending on the species and on oak chemotype. The main compounds emitted by oaks are monoterpenes, contributing 60 to 80% of total emissions, followed closely by isoprene (only 2 to 6%). Similarly, pistachio trees mainly emitted monoterpenes but also methanol. On the other hand, the profile of boxwood differed completely with isoprene as the main emitted compound.

Among the 4 oak trees sampled using the dynamic chambers, one appeared to have a distinct emission profile. Indeed, lower emissions of monoterpenes and higher emissions of m/z 47.01 (formic acid), m/z 61.03 (acetic acid), m/z 159.14 (potentially nonanoic acid) and m/z 201.04 were observed. It was also distinguished by a higher proportion of m/z 101.06 that may correspond to pentenoic acid or an isoprene oxidation product (ISOPOOH). The same behavior was observed for methanol as it was emitted only by one oak sample while it was deposited in the 3 others. Since it was the third most emitted compound according to eddy-covariance measurements, it can be deduced that the contribution of other species or even soil was preponderant for the ecosystem. In addition, it can be noted that the sesquiterpenes mixing rations were very low in the 3 studied species (<1%).

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Biogenic Volatile Organic Compounds (BVOCs) composition and biosphere-atmosphere exchange over a Sorghum bicolor crop during a whole growing season in Southern Europe

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Abstract

Biogenic Volatile Organic Compounds (BVOCs) emitted from plants can be very reactive thus playing an important role in atmospheric chemistry, being able to affect air quality and climate at regional level. BVOCs composition and exchange dynamics are related to plant species and environmental factors such as temperature, solar radiation and soil water availability. Up to now only few studies have focused on BVOCs exchanged in croplands; indeed measurements over an entire growing season have been reported rarely and mostly regarded maize and switchgrass cultivated in USA and Northern European regions. Grain Sorghum bicolor is a species very resistant to drought and heat, hence it is a common and valid alternative crop to maize in Southern European regions, as well as in any non-irrigated area characterized by very limited precipitation, especially in summertime. In this work, we monitored a multitude of BVOCs exchanged over a sorghum crop cultivated in Southern Italy by Proton Transfer Reaction 'Time-of Flight' Mass Spectrometer (PTR-TOF-MS), providing composition and dynamics during an entire growing season, from germination to mowing at grain emergence. Due to the real-time detection made possible by PTR-TOF 1000 we recorded BVOCs concentrations at a frequency response of 10 Hz without losing sensitivity. As a result, from 1 June to 4 October 2018, we successfully measured highly reactive hydrocarbons as monoterpenes and isoprene, as well as oxygenated compounds as methanol, acetaldehyde, acetone and acetic acid. Furthermore, we will couple the recorded BVOCs concentrations to ultrasonic anemometer measurements of wind speed to calculate the eddy covariance (EC) emission and deposition fluxes which will allow a direct and accurate estimation of the total amount of BVOCs exchanged between the sorghum crop and the atmosphere.

Self and Cross Reactions of Atmospherically Relevant Peroxy Radicals

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Abstract

Volatile organic compounds (VOCs) are trace gases in the atmosphere. Globally, there are anthropogenic as well as natural sources of VOCs. Once these trace gases are emitted, they react in the atmosphere forming peroxy radicals (RO_2 radicals) as reactive intermediates. The atmospheric fate of RO_2 radicals is still not completely understood. Here, we show that the rate coefficients for self – and cross reactions of peroxy radicals bearing functional groups are fast enough to compete with corresponding reactions with NO and HO_2. The accretion products have low vapor pressures. Hence, they play an important role for new particle formation and particle growth.

Introduction

The global emission rate of volatile organic compounds (VOCs) from natural and anthropogenic sources into the atmosphere is about 1.3×10^9 metric tons of carbon per year [1]. VOCs mainly react with atmospheric radicals like the hydroxyl radical (OH) or ozone (O_3) to peroxy radicals (RO_2 radicals) [2]. The lifetime of peroxy radicals is very short considering the reactions of RO_2 radicals with NO, HO_2 or other RO_2 radicals. In the literature, reaction pathway (1) is dominant in comparison to reaction pathway (2) but only self and cross reactions of ethylperoxy radicals and acetyl radicals were analyzed [3], [4], [5].

(1a) $RO_2 + R`O_2 \rightarrow RO + R`O + O_2$

(1b) $\rightarrow ROH + R´(-H{=}O) + O_2$

(2) $RO_2 + RO_2 \rightarrow ROOR` + O_2$

In flow reactor experiments we show that accretion product formation from self and cross reactions of peroxy radicals get more important with higher functionalization of the reacting RO_2 radicals. These ROOR` products have a very low vapor pressure. Consequently, the accretion products can contribute to secondary organic aerosol (SOA) production.

Experimental Methods

Flow reactor

In all our experiments we used the flow reactor from TROPOS to produce RO_2 radicals. The flow reactor consists of two glass tubes. Synthetic air with ozone flows through an inner tube into the flow reactor tube where the reactant is diluted in synthetic air. The extremely clean and nearly wall-free flow system had a pressure of 1 bar and a temperature of 297 K. Ozone concentrations were monitored by an ozone analyzer. VOC concentrations were measured with a PTR-MS (Ionicon Analytik). More details of this setup are described in [6], [7], [8].

Mass spectrometers

The NH_4+-CI3-ToF-MS is a chemical ionization time of flight mass spectrometer and it is based on the recently developed PTR3-TOF-MS [9]. We use ammonia as reagent ion which allows very soft ionization of the analyte compounds at a pressure of 80 mbar. Three metal rods in the drift tube produce an electric radio frequency (RF) field. By adjusting the RF voltage, we can change the energy per collision and as a result the primary ion distribution. For this study we performed daily calibrations of a trace gas standard including hexanone. We calculated the concentrations of the measured oxidized compounds from the sensitivity of hexanone. The CI-APi-ToF-MS (Airmodus, Tofwerk) ionizes with acetate or protonated n-propylamine. The reagent ions in the sheath air flow are mixed with the sample air flow at atmospheric pressure. The concentration determination is described in [6].

Results and discussion

Our goal is to analyze chemical properties and further reactions, especially accretion product formation reactions of atmospherically relevant peroxy radicals. In figure 1 we show the results of a flow reactor study with 1,3,5-trimethylbenzene (TMB) as precursor VOC. TMB is emitted in urban areas. It primarily reacts with the hydroxy radical (OH). In this experiment we injected tetra methyl ethylene (TME) and ozone as an OH radical source [6]. The hydroxyl radical is a major product of TME ozonolysis. The measured RO_2 radical from the TME ozonolysis, $CH_3C(O)CH_2O_2$, is shown in figure 1A and it perfectly fits with the calculated yield. $HO\text{-}C_9H_{12}(O_2)O_2$ is the first RO_2 radical from TMB reaction with OH. Autoxidation leads to $HO\text{-}C_9H_{12}(O_2)_2O_2$ and $HO\text{-}C_9H_{12}(O_2)_3O_2$. The agreement of the measured concentrations with different instruments and reagent ions is remarkable. The accretion products of the RO_2 radicals are shown in figure 1B. $C_{12}H_{18}O_6$ and $C_{18}H_{26}O_8$, the ROOR` products with the highest concentrations, are results from cross reaction of $CH_3C(O)CH_2O_2$ with $HO\text{-}C_9H_{12}(O_2)O_2$ and self reactions of $HO\text{-}C_9H_{12}(O_2)O_2$ radicals. The k-rates of the two accretion reactions are respectively 3.2×10^{-11} and 1.7×10^{-10} cm^3 $molecule^{-1}$ s^{-1}.

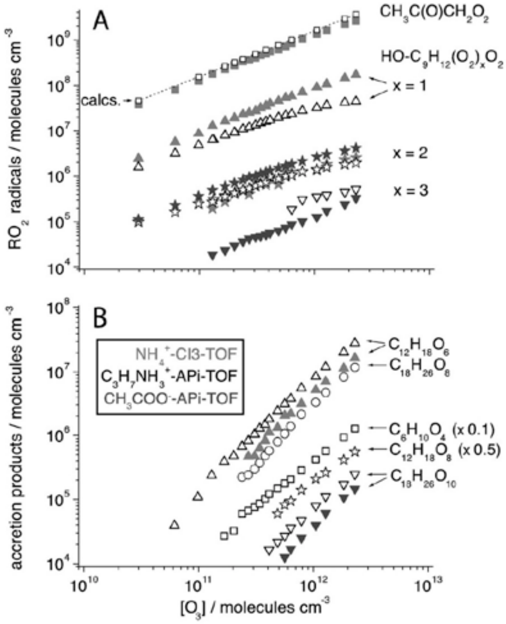

Figure 1: A) RO_2 radicals and B) ROOR` products of 1,3,5-trimethylbenzene (TMB) oxidation. OH is generated by tetra methyl ethylene (TME) ozonolysis. [TMB]=2 x10^{11} molecules cm^{-3} and [TMB]=4 x 10^{12} molecules cm^{-3}. Reaction time was 7.9 s.

The rate coefficients of the accretion formation reactions for different systems are higher than expected. These ROOR` products could play an important role for new particle formation and particle growth because they have low vapor pressures. These previously underestimated reactions can help to understand SOA production in the atmosphere in more detail.

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Bidirectional Ecosystem−Atmosphere Fluxes of Volatile Organic Compounds Across the Mass Spectrum: How Many Matter?

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Abstract

Terrestrial ecosystems are simultaneously the largest source and a major sink of volatile organic compounds (VOCs) to the global atmosphere, and these two-way fluxes are an important source of uncertainty in current models. Here, we apply high-resolution mass spectrometry (proton transfer reaction-quadrupole interface time-of-flight; PTRQiTOF) to measure ecosystem−atmosphere VOC fluxes across the entire detected mass range (m/z 0−335) over a mixed temperate forest and use the results to test how well a state-of-science chemical transport model (GEOS-Chem CTM) is able to represent the observed reactive carbon exchange. We show that ambient humidity fluctuations can give rise to spurious VOC fluxes with PTR-based techniques and present a method to screen for such effects. After doing so, 377 of the 636 detected ions exhibited detectable gross fluxes during the study, implying a large number of species with active ecosystem−atmosphere exchange. We introduce the reactivity flux as a measure of how Earth−atmosphere fluxes influence ambient OH reactivity and show that the upward total VOC (ΣVOC) carbon and reactivity fluxes are carried by a far smaller number of species than the downward fluxes. The model underpredicts the ΣVOC carbon and reactivity fluxes by 40−60% on average. However, the observed net fluxes are dominated (90% on a carbon basis, 95% on a reactivity basis) by known VOCs explicitly included in the CTM. As a result, the largest CTM uncertainties in simulating VOC carbon and reactivity exchange for this environment are associated with known rather than unrepresented species. This conclusion pertains to the set of species detectable by PTR-TOF techniques, which likely represents the majority in terms of carbon mass and OH reactivity, but not necessarily in terms of aerosol formation potential. In the case of oxygenated VOCs, the model severely underpredicts the gross fluxes and the net exchange. Here, unrepresented VOCs play a larger role, accounting for ~30% of the carbon flux and ~50% of the reactivity flux. The resulting CTM biases, however, are still smaller than those that arise from uncertainties for known and represented compounds.

Spatial Distribution of Vehicle Combustion Related Nanoparticles in the Urban Area of Innsbruck

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Introduction & Background

Air pollution is traditionally measured at a few localized stations equipped with a suit of sophisticated sensors. This approach gives a very accurate but only locally valid air pollution level depending on the pollutant such as ozone, NOx, or particulate matter (PM). While single point measurements of PM10 (particulate matter smaller 10 micrometer) give a good pollution estimate that is valid for a larger area such as an entire city, particle number (PN) or particle surface area are dominated by local sources that are mostly traffic related. Modern vehicle combustion engines that are not equipped with special particle filters emit ultrafine particles (UFP) (particles smaller 100 nanometer [3]) coated with unhealthy compounds in high numbers. At present, there is a broad discussion related to the health impacts caused by UFP in cities. Ultrafine particles penetrate alveoli and are deposited in humans [4]. Human exposure to ultrafine particles in an urban area can be assessed by monitoring the lung deposition surface area (LDSA). Here we present how LDSA values are distributed over the city of Innsbruck. We monitored LDSA with a diffusion charger [1] mounted on to a bicycle. We present results obtained during one year of measurements starting in December 2017 resulting in LDSA values covering a total distance of more than 2000 km of the road net of Innsbruck. The same roads were measured multiple times during different meteorological conditions throughout the year. During a few days in August, September and December 2018, we measured additionally the particle number concentration (PNC) and the particle size distribution (PSD) in the range from 10 to 1000 nm at several different locations close to a busy high way in summer and in winter.

Methodology

We mounted a Partector (NANEOS, Switzerland), a GPS and a GoPro camera on to a bicycle and monitored the personal exposure of the bicycle rider. Due to the small size, low weight and long battery lifetime, the Partector is well suited for mobile measurements. The Partector with its high time resolution of seconds is an ideal tool to map out the spatial distribution of Lung deposition surface area (LDSA) in the urban environment of Innsbruck with a bike at different seasons. PNC were monitored with a Scanning Mobility Spectrometer (GRIMM Aerosol Technik, Germany, SMPS +C model 5416). This model features the Vienna-type DMA (differential mobility analyzer) design, well known for highest size resolution and lowest diffusional particle losses – even for smallest particles. With this setup it was possible to measure PNC and PSD in the size range from 10 - 1000 nm with a sampling rate of about 4 minutes [2]. The GRIMM SMPS and the NANEOS Partector were mounted on a bicycle trailer equipped with a car battery power supply offering several hours of operation (see figure 1).

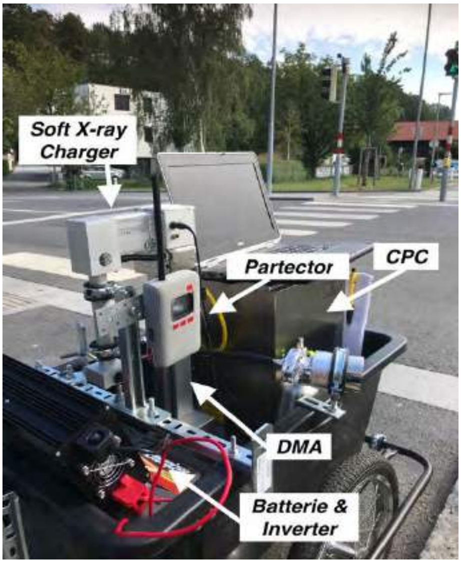

Figure 1: Experimental setup of the mobile particle measuring station.

Results & Conclusion

We found highest LDSA values close to high ways, busy streets and street crossings. Diesel and petrol engines under high load during steep uphill climbs or speeding up from street crossings cause largest emissions. In addition, some kind of local traffic busses and two stroke engines show very high emissions. Weather conditions impact the base level and the distribution of LDSA (see figure 2). During enhanced wind "Föhn" conditions LDSA-background show an all-time low and LDSA- "hot spots" are strongly localized at emission sources.

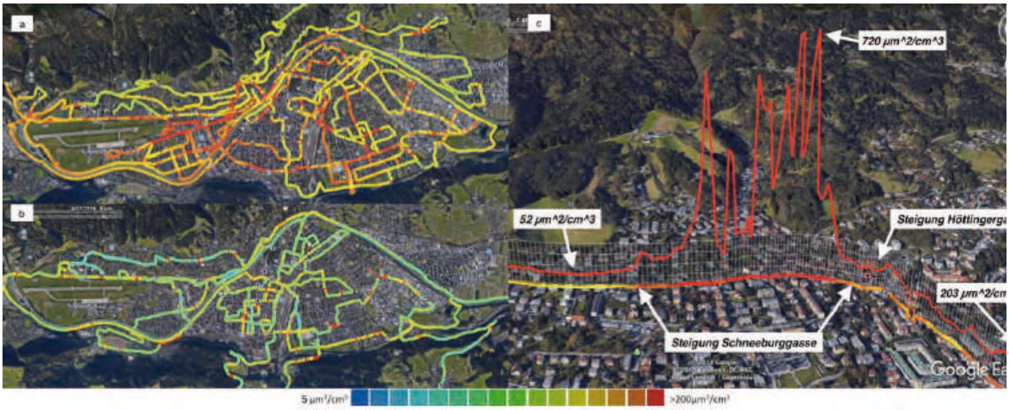

Figure 2: LDSA-Concentration during different Conditions. (a) shows the morning distribution of a summer day. (b) illustrates the nanoparticle ''hot-spots'' of a summer day afternoon. (c) is an example of vehicle plumes caused maxima on an uphill street

Acknowledgement

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Functional Nanomaterials for Electrochemical CO2 Reduction Investigated using PTR-TOF MS for Real Time Product Identification

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Abstract

The utilisation of CO2 as a chemical feedstock for value added products can pave the path for mitigating greenhouse gas emissions. Electrochemical CO2 reduction (ECO2R) has the potential to be an efficient way for producing industrial feedstock.[1] However, producing multi-carbon (≥C2) gaseous and liquid products with high selectivity, high faradaic efficiency, and low activation over potential is still a challenge. An appropriate design of catalysts with suitable morphology can address these challenges by producing ≥C2 products. Once the products are formed they are measured both quantitatively and qualitatively using online gas chromatography (for gaseous products), high performance liquid chromatography, or nuclear magnetic resonance (for liquid products). In these cases of product identification, the analysis is done only periodically. Typically, in GC the cycle time varies between 10 - 15 mins per data point and for HPLC it varies between 1 - 2 hours. Though these traditional analytical techniques are very reliable in for quantitative analysis, they fail to give real-time data. Hence in many cases the possible reaction pathway for desired product remains unidentified. Thus it is very important to study the real time dynamics of the products obtained from ECO2R. Though there have been reports on real time analysis of gaseous products they have been mostly qualitative.[2] Moreover, there are very few demonstrations of real-time liquid product analysis either quantitative or qualitative. The recent report of using selective-ion flow tube mass spectrometry (SIFT-MS) for real time analysis of both liquid and gaseous products is still mostly qualitative.[3] Thus an analytical tool that would both qualify and quantify simultaneously all gaseous and liquid products with high precision and resolution is needed. Here-in we report the use of PTR-TOF MS for real time study of the products obtained from ECO2R. The advantages of identifying VOC's and hydrocarbon products at a very low integration time of 100 ms with greater temporal resolution provides real insight into the reaction mechanisms and also quantitatively explain the reaction dynamics of both liquid and gaseous products.

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Sparkling Science CHAMPIONS - Chemical defense mechanisms of plants in oxidative stress situations

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Abstract

Within the Sparkling Science project CHAMPIONS (**Ch**emic**a**l defense **M**echanisms of **p**lants **i**n **o**xidative stress situatio**ns**) students from two high schools located in Salzburg, Austria are taking part in answering the science question - Can we detect oxidative stress of plants? The focus of the project lays on monitoring abiotic stress of plants caused by elevated ozone concentrations during spring and summer. Using small, mobile research stations, based on low-cost, semi-conductive sensors and bio-indicator plants, young students were measuring ozone volume mixing ratios and meteorological parameters at 15 different locations from May to August 2018. Additionally, they monitored the development and growth of the bio-indicator plants as well as the temporal progressions of ozone damage to bio-indicator plants on the basis of weekly reports.

Introduction

Tropospheric ozone represents a relevant atmospheric pollutant, because of its strong oxidizing potential. Depending on the ozone dose plants will be damaged at molecular and cellular level caused by the oxidative damage to lipids, proteins and nucleic acids [1]. If the ozone flux into the plant exceeds a certain amount, discolorations and necrosis of isolated spots on the plant leaves are formed and can further lead to vegetation and crop loss. Ozone is not emitted directly into the atmosphere but formed from photochemical reactions of nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOC) [2].

To measure the direct impact of ozone on plants two campaigns in spring and summer 2018 and 2019 are carried out by the young students from the BORG Mittersill and BG/BRG Zell am See. Therefore, small, mobile, citizen science capable measurement devices (CHAMP) were developed [3]. These measurement devices contain semi-conductive sensors for measuring temperature, humidity, solar radiation and ozone. The students were involved in building and calibrating the sensors as well as taking care of the research stations during the campaign. The sensors were cross calibrated by the students in our lab with a Ozone Analyzer Model 49i from Thermo Fisher Scientific, to reduce humidity dependent sensitivities [3].

In addition to the measurements of environmental parameters with the CHAMPs the observed bio-indicator plants (provided by the Institute of Soil Ecology, German Research Center for Environment and Health, Neuherberg, Germany) are an essential part of the campaign. Therefore, each measurement location contained a CHAMP, as well as two different varieties of bean plants (*Phaseolus vulgaris*), one ozone-tolerant (*Wade* variety) and one ozone-sensitive bean plant (*Cannelino* variety). In total 15 research stations with both ozone, sensitive and tolerant bean plants were set up at the student's home (Figure 1).

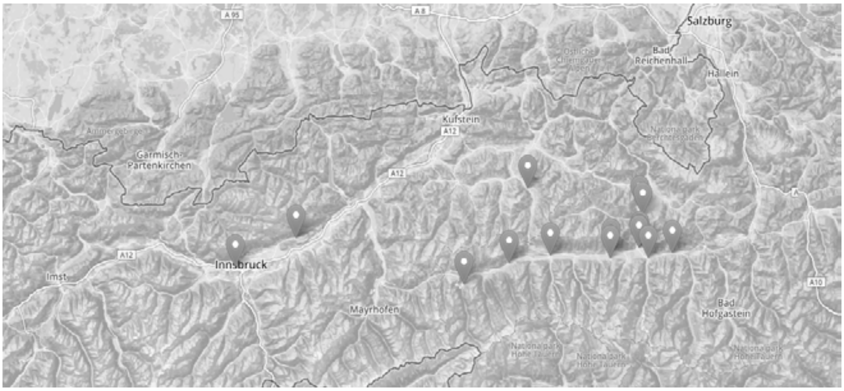

Figure 1: Positions of the measurements in Tirol and Salzburg (Austria) at the student's home.

Results and Discussion

In May 2018 the first measurement campaign started. With the support of the students from BORG Mittersill and BG/BRG Zell am See it was possible to measure ozone, temperature, humidity and solar radiation, over a period of more than three months at 15 different locations and monitor the damages of bean plants caused by ozone.

Figure 2 depicts an average diurnal cycle of ozone volume-mixing ratios (VMR) obtained from May to September 2018. Ozone volume-mixing ratios measured by two CHAMPs are compared to ozone VMR measured by the Umweltbundesamt (Ozone Analyzer Model TEI 49i, Thermo Fisher Scintific). The location of the CHAMP-08 research station is in Bramberg, close to Mittersill, while the CHAMP-11 and Umweltbundesamt data are obtained at different places in Zell am See 25 km from Mittersill. All three averages show a similar diurnal pattern with a maximum ozone VMR in the afternoon between 3 and 5pm. The maximum value of this data is between 25 and 40 ppbv, while the Umweltbundesamt data shows the highest VMR of the three compared stations.

All three measurement devices, the two CHAMPs and the Ozone Analyzer from the Umweltbundesamt, are located at different locations. Depending on altitude, NO_x concentration, VOC concentration, sunlight etc. the ozone VMR is different at any location.

Additionally, the ozone sensor in the developed sensing system are semi-conductor sensors. Sensitivity, selectivity and stability of semi-conductor sensors are generally problematic. Although a humidity dependent calibration was performed, the accuracy of the ozone sensors may still suffer from temperature effects, cross-sensitivities to other gases and long term stability. However the data analyzed so far looks promising.

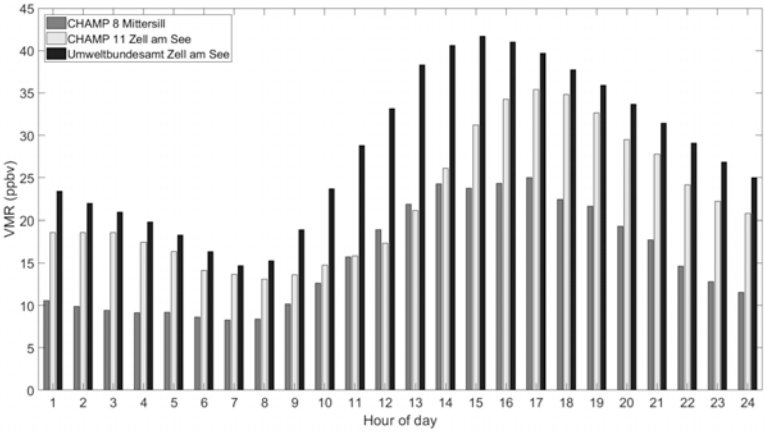

Figure 2: Average diurnal cycle of ozone volume-mixing ratios measured by two home-built devices.

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Development of a Sensing System and Measurement Network for Monitoring the Spatial Distribution of Ozone in an Alpine Valley

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Abstract

Air quality monitoring is extremely important as air pollution (e.g. ozone) has a direct impact on human and plants health. Therefore, we want to introduce a low-cost, mobile and citizen science capable sensing system for participatory air quality monitoring. The complete measurement system (called CHAMP) includes sensors for measuring ozone, temperature, humidity and solar radiation. A first representation of the data is provided by an integrated display, which also serves to output error messages. An integrated real time clock is used to keep time, and data points regularly stored to a memory card. To display and compare the data, a public web site has been set up, which represents current measurements [1].

Introduction

The ongoing Sparkling-Science project *CHAMPIONS* focuses on the determination of the spatial distribution of ozone and the effective ozone dose for plants in an alpine valley (Pinzgau, Salzburg). Ozone is produced through a series of reactions involving nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) in the presence of sunlight. Owing to its adverse health effects to humans, animals and plants, tropospheric ozone has become one of the most studied topics in recent decades [2] [3]. Studies have clearly demonstrated that elevated ground-level ozone concentrations lead to eye irritation and severe respiratory distress in humans, but also to crop and forestry losses [4].

The students from two schools from Salzburg (BG/BRG Zell am See, BORG Mittersill) are the essentials for a successful outcome of the project. The students are involved in building the sensing systems, doing calibrations to quantify the results and monitoring the measurements.

Results

The developed measurement device consists of a semiconductor gas sensor for measuring ozone (MiCS 2614, SGX Sensortech) in a range of 10 - 1000 ppbv. In order to measure the temperature and humidity a sensor module, called DHT22 is used. According to the manufacturer, the temperature is being measured in a range of -40°C to 80°C with an accuracy of 0,1°C. The output value for the humidity is the relative value in a range of 0-100% with an accuracy of 5%. The solar radiation is measured with a sensor called BH1750. Employing a photodiode the incident light can be detected by measuring the photocurrent. This analog signal is converted within the chip, to a digital signal that corresponds to the illuminance in Lux. For controlling theses sensors, a microcontroller (Arduino Uno) is used. By means of an integrated real-time clock and a memory card module, the data is stored with time stamp on a memory card. To represent the measured values an integrated display is included, which also serves to output error messages. In figure 1, the final measurement device is shown, located next to two test plants.

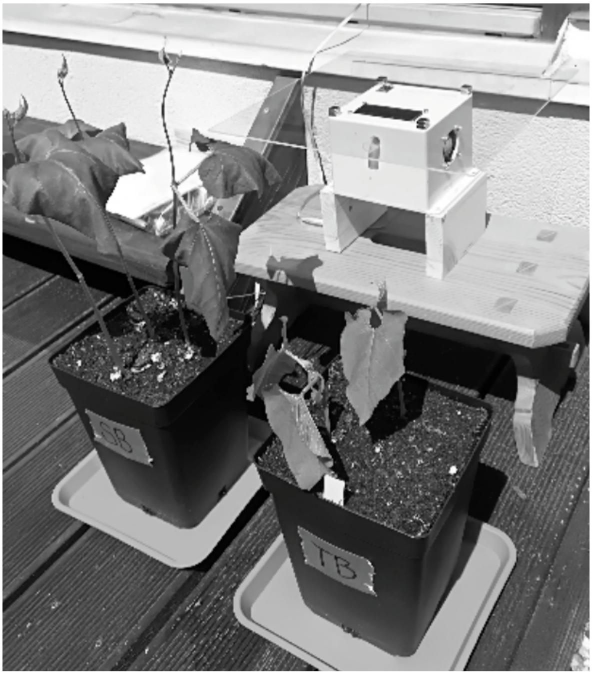

Figure 1: Set up of the developed sensing system (CHAMP).

Challenges

The calibration of the low-cost ozone sensor remains a challenge. The sensitivity, selectivity and stability of such a semi-conductive gas sensors are generally problematic. Therefore, we performed an extensive calibration procedure. Air flows with different humidities and different ozone concentrations are measured simultaneously with a “standard” ozone analyzer (Model 49i, Thermo Fisher Scientific) and the low-cost ozone sensor. Depending on the humidity, the measured analog signal of the ozone sensor can be assigned to the correct ozone concentration. In order to receive the ozone values in our CHAMP from sensor raw data and humidity a third order polynomial function is fitted to the calibration data.

First use of the developed sensing system

The first monitoring mission of the developed sensing system was during the campaign in the Sparkling Science project CHAMPIONS. In total 15 devices built up a measurement network for monitoring ozone, temperature, humidity and solar radiation in the alpine valley Pinzgau (Salzburg). During this campaign the students from the BG/BRG Zell am See and BORG Mittersill are responsible for their own sensing system. Once every week they used the SD card to upload the measured data on a public website [1]. On this website the project CHAMPIONS is described to address the public, especially the families of the students involved in the project. Another feature of the website is that by uploading the data the students get instantaneously a plot of the uploaded data. Furthermore all students have the possibility to create own plots, where they can compare data from each sensing system. Through this website, it is thus possible that the students can intensively deal with the topic.

In figure 2, one example of the measured data of one sensing system is shown over a period of more than 3 months.

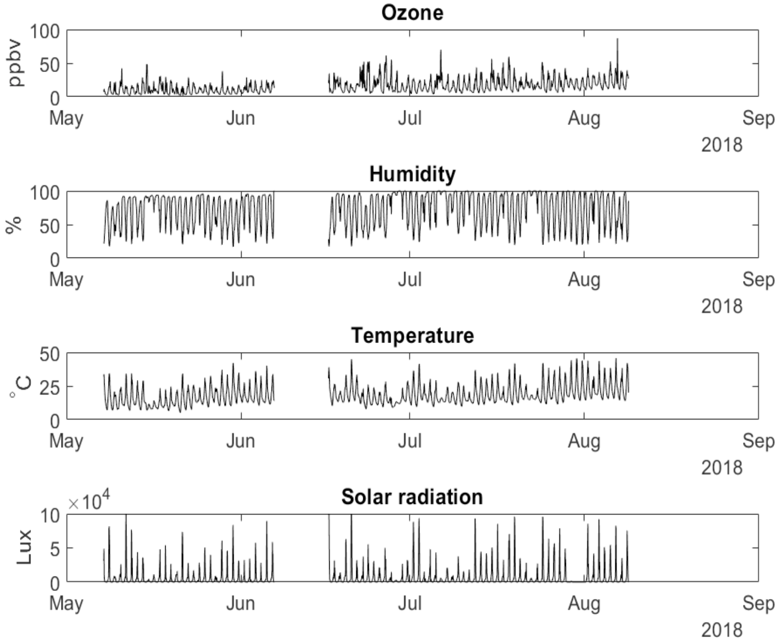

Figure 2: Example of the measured parameters of one sensing system during the first measurement campaign in spring and summer 2018.

Conclusion and Outlook

Without the energetic support of the students from the BG/BRG Zell am See and BORG Mittersill it is not possible to carry out the project CHAMPIONS. The students are included in building and calibrating the sensing system and doing the measurements.

The sensing system, as presented here, is promising but some improvements are already planned. The data of the low-cost ozone sensor showed a cross-sensitivity to temperature and according to the manufacturer with NO_x. With an improved calibration setup, it is possible to calibrate also the temperature dependency. Furthermore, another gas sensor for measuring nitrogen oxides is planned to be part of the sensing system. Besides the improvement of the CHAMP sensors, it is planned to upload the measured data automatically via Wi-Fi. With this upgrade, it is possible to monitor the air quality on-line.

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Application of PTR-TOF-MS for measurement of odor release from slurry application in field trials using dynamic chambers

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Abstract

This study investigates the emissions of volatile organic compounds and sulfuric compounds from field applied slurry. The measurements are performed online in real-time with a Proton-Transfer-Reaction Mass-Spectroscopy (PTR-MS) connected to nine dynamic chambers, allowing for experiments with three variables in triplicates. Four different experiments were conducted. Between 67 and 120 hours of continuous measurements were collected from each experiment. It is demonstrated that PTR-MS is suitable for measuring VOC and sulfur compounds in field conditions. The results shows that it is possible to get accurate results with low variance under different combinations of weather, soil and slurry. The key features of the setup is the flexibility that allows for experiments under different conditions and long measurement periods.

Introduction

Emissions from field applied slurry is a large contributor to air pollution and often a great nuisance of residents living in areas with agriculture [1-5]. Being able to accurately quantify these is important in order to evaluate which abatement techniques is most efficient. PTR-MS has successfully been used to measure and quantify volatile organic compounds (VOCs) and sulfuric compounds from livestock production with high accuracy [2, 5]. Feilberg et al [3] showed that PTR-MS gave the most comprehensive results in terms of quantitative odorant measurements from field applied slurry using static chambers. Laboratory test of PTR-MS measurements on dynamic chambers has shown good results [4].

Based on the previous work a flexible setup combining dynamic chambers and PTR-MS for odor measurements has been designed. The system can be transported and set up relatively fast, making it possible to measure at different sites. Being able to perform experiments under different conditions (soil, slurry, application technique, weather etc.) can give a more comprehensive knowledge about the compounds emitted during slurry application, which is an important step towards selecting the most suitable techniques.

Experimental Methods

Experimental setup

Emissions were measured during four different experiments testing three different application techniques (trailing hose, Bomech trailing shoe and Vogelsang trailing shoe). One experiment on a coarse sandy soil and one on a loamy sand soil, both with winter wheat crops fertilized with pig slurry, and two experiments on a loamy sand soil with clover grass crops fertilized with cattle slurry. All experiments varied the application techniques in triplicates.

The experimental setup consisted of nine wind tunnels operated as dynamic chambers with a continuous and constant airflow. The wind tunnels consisted of a rectangular open-bottomed stainless steel chamber (80x40x25 cm). For each tunnel, a frame was mounted in the soil. Within the frame a pre-measured amount of slurry was poured mimicking different application techniques. Right after slurry application the tunnels were placed on the frame and measurements started. Air was drawn continuously through the tunnels with an air exchange rate of 25 times per minutes. From the tunnels air was drawn through PTFE tubing heated to 41°C to a valve block that ensured measurements for eight minutes from each tubing. Three tubes for background measurements were evenly distributed between the tunnel measurements. The air from the valve block was analyzed in real-time by a Proton-Transfer-Reaction Time-of-Flight Mass-Spectroscopy (PTR-TOF 400, Trace VOC Analyzer, IONICON, Analytik, Innsbruck, Austria) for measurements of odorous compounds (Figure 1).

The instrument was operated with H_3O^+ as the primary ion at 140 Td E/N (drift tube settings: 120 V, 2.4 mbar and 80°C) in full scan mode. Airflow was 400 mL min^{-1} and measurements were recorded every 10 seconds.

A weather station was used to log air and soil temperature every 10 minutes.

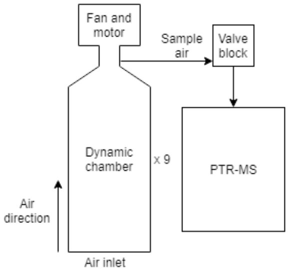

Figure 1: Simplified sketch of experimental setup.

Data treatment

For each detected compound a mean of the last 30 seconds of measurements per measurement cycle (8 minutes) was used for further calculations.

An average of the background measurements (n = 3) were calculated for each compound and measuring cycle. The 30 second mean measurement of each compound and each tunnel in a cycle was subtracted the background measurements. The concentration values were multiplied with the rate constant. The air temperature data and air flow through the tunnels was used to convert the concentrations from ppb to mol min^{-1} m^{-2}. For each compound the accumulated emissions in a tunnel were calculated, and the total mean emissions for each compound per application technique.

Due to software failure and temporary power cuts to the system sections of data is missing during some of the experiments. These data are estimated in order to calculate a total emission during the experiment.

Results

Several compounds were detected for both pig and cattle slurry. The ones deemed most interesting in respect to odor are Hydrogen sulfide, Methanthiol, Acetic acid, Propanoric acid, Butanoic acid, Pentanoic acid, 4-Methylphenol and 4-Ethylphenol.

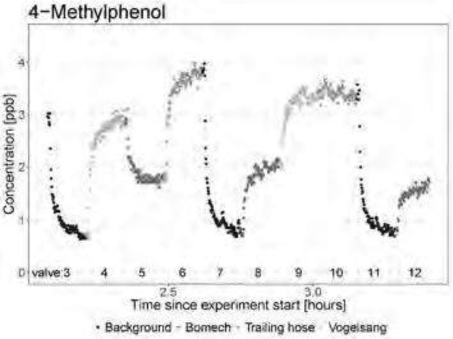

Figure 2: Selection of raw data for 4-Methylphenol (pig slurry, coarse sand).

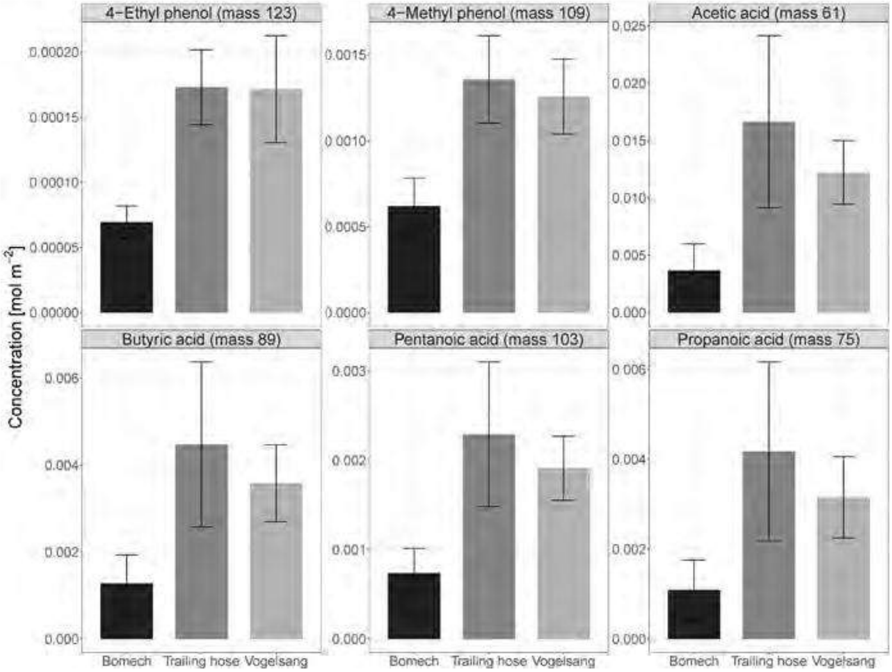

Figure 3: Accumulated emissions of selected compounds (pig slurry, coarse sand).

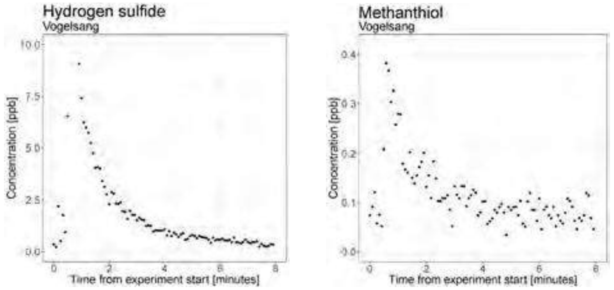

Figure 4: Examples of measurements of Hydrogen sulfide and Methanthiol during the first measurement cycle (pig slurry, loamy sand). Hydrogen sulfide has not been calibrated for the humidity-dependent sensitivity.

The intervals of 8 minutes seemed to be sufficient to reach a stable reading (Figure 2). An emission pattern is observed for the three different methods that is consistent throughout the different compounds (Figure 3). When the chambers were closed rapidly after slurry application it was possible to detect both Hydrogen sulfide and Methanthiol during the first measurement (Figure 4).

Discussion

VOC measurements in real time from field applied slurry was successfully obtained with PTR-MS and dynamic chambers. It was possible to detect a difference in application techniques with relatively low standard variation. The setup takes advantage of the low detection limit and the full scan option of the PTR-MS, thereby enhancing the likelihood of detecting all compounds of interest from complex matrix', like animal slurry. Hydrogen sulfide and Methanthiol was detected right after slurry application. The pattern of the rapid decay due to the high instability of the compounds fits with literature.

The environment inside the dynamic chamber is different from real field conditions, but the low variation indicates that the method gives reliable quantitative data, which can be used to compare different application techniques, slurry types or soil types. The setup allows for experiments under real-like agricultural conditions, which is an improvement, compared to laboratory setups. The system allows for continuous measurements over long periods, giving complete datasets.

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Pilot studies for the identification of mushroom species by PTR-MS rapid and non-invasive analysis: Cortinarius spp. and Fomes spp.

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Abstract

Given their economic, ecologic and sanitary relevance, the development of rapid and non-invasive methods for the assessment of mushroom species is a relevant technological task. Usually, the taxonomy and systematic classification within a genus is based on macro-, micro-morphological, macrochemical, and ecological characters. However, odor and taste of the fresh fruiting bodies can also contribute to the recognition of different species [1]. Our previous investigation on yeasts indicates the interest of a PTR-MS analysis of the volatile organic compounds (VOCs) of fungi [2]. Therefore, we underwent two different pilot studies to verify the possibility to use PTR-MS as a fast tool to support species identification of mushroom fruit bodies aiming (i) at a better comprehension of their physiology and ecologic role and (ii) at supporting the development of practical tools for the mushroom industry. Here we present preliminary data on a two basidiomycete genera forming different types of fungal fruiting bodies, annual agaricoid fruiting bodies of *Cortinarius* spp. and pluriennual polyporoid fruiting bodies of *Fomes* spp..

Cortinarius

The *Cortinarius* is one of the largest mushroom genus of the family *Agaricaceae* with over 2,000 different species [3]. While detecting this as genus on the basis of macroscopic traits is usually easy because they have specific morphological characteristics like the presence of a cortina, a fragile partial veil, covering their gills when young and the rusty brown color of the spores, detecting the species of *Cortinarius* without microscopic or molecular analysis is nearly impossible [4].

Several species and species groups in *Cortinarius* genus have distinctive odors. For example, *C. odorifer* possess a typical anise-like odor [5], while *C. traganus* has a fruity odor usually associated to over-ripe pears [6]. Volatile organic compounds (VOCs) emissions may be helpful in adding relevant information for the species detection of *Cortinarius* which is particularly important due to the occurrence of deadly poisonous species in the genus.

In particular, the VOC emissions of eighteen *Cortinarius* species from the Alps, identified by morphological and macrochemical traits, were analyzed in triplicates with a commercial PTR-MS system (Ionicon GmbH, Innsbruck, Austria) equipped with a quadrupole detector. The VOC fingerprints that were obtained allows the separation of the species and for 10 out of 18 of them it was possible to find single features that separate one species from all the others.

Fomes

Fomes fomentarius is a widespread polypore known as the “tinder fungus”. Recently it has also been named “iceman’s fungus” after Peintner *et al.* [7] studied it in the remains of the famous Ötzi who probably used it to preserve fire and for medication. Despite its use as medicinal polypore since long time, fomitin being the active compound, there are still open questions on the presence of cryptic species [8].

In the second pilot study, two *Fomes* species, previously identified as *F. fomentarius* (L.) Fr., and *F. cornocchiae* at int., where evaluated by the direct PTR-ToF-MS analysis of their head-space composition both from ambient dried fruit bodies and *in vitro* pure cultures. It was indeed possible to identify significant differences in the volatile compound profiles of these two *Fomes* species, with many similarities between the pure culture and fruit body samples. This confirms that also polypore species have a species-specific VOC production. However, a few molecules (terpenes in particular) seem to be influenced by the growing substrate and environment.

Our analytical approach based on a fast and non-invasive analysis of the headspace of mushrooms could be used to detect and discriminate different species of *Cortinarius* and *Fomes* and indicates the possibility of the rapid determination of mushrooms species with possible application in mycology and industrial quality control.

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Total OH reactivity around the Arabian Peninsula from ship-based measurements

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Abstract

The Arabian Peninsula is a global change hotspot where an increase in heat extremes and photochemical pollution is expected in the future. The region is a worldwide hub of oil and gas production, accommodates densely populated urban (350 million people) and industrialized areas, and its surrounding waters include key trading routes and bottlenecks for marine traffic. Due to the high solar irradiation, ambient humidity and intense pollution sources in the region, photochemical processes in the atmosphere are expected to be highly active. However, very few observational atmospheric data exist for this region. Therefore a first comprehensive measurement campaign, termed the AQABA (Air Quality and Climate Change in the Arabian Basin) Campaign, was conducted in summer 2017. Measurements were made from on-board the vessel *Kommandor Iona*, which sailed around the Arabian Peninsula via the Mediterranean, the Suez Canal, the Red Sea, the Indian Ocean, the Arabian Gulf and back along the same route. The vessel hosted a broad range of instrumentation for observation of gas and particle species, amongst which there was a CRM-PTRMS to make the first ship-borne direct measurements of total OH reactivity. Total OH reactivity is the combined loss rate of all compounds that can react with the OH radical, the most important oxidant in the troposphere. The reaction of primary pollutants (e.g. CO), greenhouse gases (e.g. CH_4) and VOCs with OH affects both ambient ozone and particle concentrations. Here we show the combined influence of photochemically aged air and fresh emissions, e.g. from petrochemical industry or marine traffic, in the Suez Canal and Arabian Gulf. These two areas display contrasting relationships between OH reactivity and ozone. Taking into account the OH reactivity contributed by 100 species measured individually by PTR-ToF-MS and other instruments, the measured total OH reactivity can be accounted for within its measurement uncertainty both in the Arabian Gulf and the Suez region.

Fast airborne chemical analysis of biomass burning organic aerosol by CHARON PTR-ToF-MS

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Abstract

We herein report on the first successful airborne deployment of a CHARON-PTR-ToF-MS instrument onboard the NASA DC-8 Airborne Science Laboratory. Exemplary data obtained during the interception of a wildfire plume demonstrate that the chemical particle analyzer responds sufficiently fast (< 10s) and delivers an elementally resolved analysis of a large fraction (> 80%) of the total sub-micrometer particulate organic mass.

Introduction

Biomass burning (BB) emissions contain a myriad of organic compounds in the gas and the particulate phase. Many of the emitted compounds undergo rapid photochemical transformations after their release into the atmosphere. A detailed chemical characterization of organic aerosol that is primarily emitted or secondarily formed from BB is an important but challenging analytical task. This task becomes even more difficult if sampling takes place from a rapidly moving platform such as an aircraft. Over the past decade, the aerosol mass spectrometer (AMS) has been deployed on many research aircraft for chemical particle measurements. In the AMS, most organic analytes do, however, decompose prior to their mass spectrometric detection. In the newly developed CHARON-PTR-ToF-MS instrument, vaporization and ionization of organic analytes occurs under much softer energetic conditions. The technique has been successfully deployed on the ground, but no airborne measurements have hitherto been reported. Herein, we present the first exemplary results from airborne CHARON PTR-ToF-MS measurements conducted in summer 2018 as part of NASA's Student Airborne Research Program (SARP).

Experimental Methods

The PTR-ToF-MS instrument used in this study has been described in detail previously [1]. The instrument has recently been upgraded with a longer ToF flight tube and RF ion optics for improving mass resolution and sensitivity. The CHARON particle inlet has also been described in detail elsewhere [2][3]. A pressure-controlled inlet was added to keep the CHARON inlet at a constant sampling pressure. The pressure-controlled inlet was connected to the University of Hawaii shrouded diffuser type inlet on the NASA DC-8.

Results & Discussion

On the 25th of June 2018, the DC-8 intercepted the plume emanating from the Lions Fire in the Sierra National Forest. The time evolution of the total particulate organic mass concentration is shown in Figure 1. The 1/e- and 1/e²-decay times of the total organic signal after leaving the plume are 6.3 s and 25 s, respectively, proving the real-time measurement capability of the analyzer. The insert shows the average mass spectrum recorded during the plume transect. 230 peaks were resolved: 65% of the detected organic mass was associated with $C_xH_yO_z^+$ ions, 7% with $C_xH_y^+$ ions and 9% with $C_xH_yN_z^+$ ions. The remaining peaks were not elementally resolved.

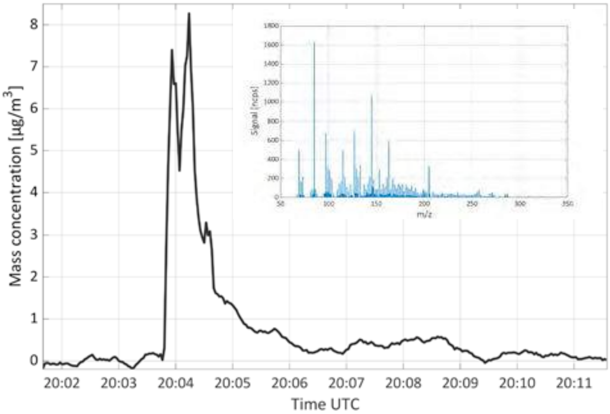

Figure 1: Time trace of the total particulate organic mass concentration as recorded by CHARON-PTR-ToF-MS. Insert: Average mass spectrum recorded during the Lion's Fire plume transect.

We were able to assign the 20 highest peaks to compounds that are commonly found in fire-emitted particles (*e.g.*, vanillin, vanillic acid, and levoglucosan). Levoglucosan was the most abundant organic species (~17% of the total organic mass). The small peaks in the mass spectrum derive from unidentified organic compounds in the single digit ng/m³ concentration range.

Acknowledgements

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PTR-ToF-MS/QMB-Electronic-Nose synergies explorations: a case study

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Abstract

In this work we show a case study exploring the potentialities of connecting a PTR-ToF-MS and an electronic nose can in series to measure the same samples at the same time.

The hyphenated instruments have shown interesting potential synergies in the specific task of discriminating a commercial tomato sauces after different storage procedures, suggesting specific improvements to the development of a dedicated electronic nose.

Introduction

The analysis of volatile organic compounds (VOCs) is of paramount importance for the characterization of diverse kinds of samples. A wide range of analytical instruments and techniques have been developed in order to gain more information compatibly with the limitations imposed by the specific application.

Monitoring of food products in terms of quality, control of production processes and storage, has shown to be a very challenging task for any kind of instrument or combination of techniques already explored in the literature. We have already proposed to use PTR-MS in combination with different types of electronic noses in order to help designing a specific electronic nose for any application [1].

Electronic nose is potentially the most interesting instrument in various areas of food safety assessment for rapid early detection of contamination and defects in food production or storage chains. However, in spite of several positive achieved results [2], their intrinsic lack of selectivity makes the interpretation of the results rather difficult.

On the other side, between the analytical instruments, PTR-ToF-MS is one of the most promising techniques that allows direct, fast, sensitive monitoring of VOCs [3].

We have also already shown [4] that the two instruments can operate simultaneously on the same sample sharing the sampling system. This feature allows to measure the exact composition of the sample analyzed by the electronic nose.

Experimental Methods

An electronic nose made of 12 porphyrinoids coated Quartz Microbalances [5] has been connected in series to a PTR-TOF-MS, sharing its automated sampling system, as schematically shown in Figure 1.

The hyphenated instruments have been tested in an experiment aimed at the identification of commercial tomato sauces after different storage procedures. Three sets of 10 replicas have been measured to evaluate the tomato sauce headspace: a) after one week storage at 8°C once inoculated with Penicilium spp. Fungi; b) after one week storage at 8°C and treated with a natural antifungine (thyme vapors) once inoculated with Penicilium spp.; c) fresh tomato sauce.

Samples have been placed in an automated sampler, in order to condition the samples to a standard temperature and perform the measurement with the same carrier flow.

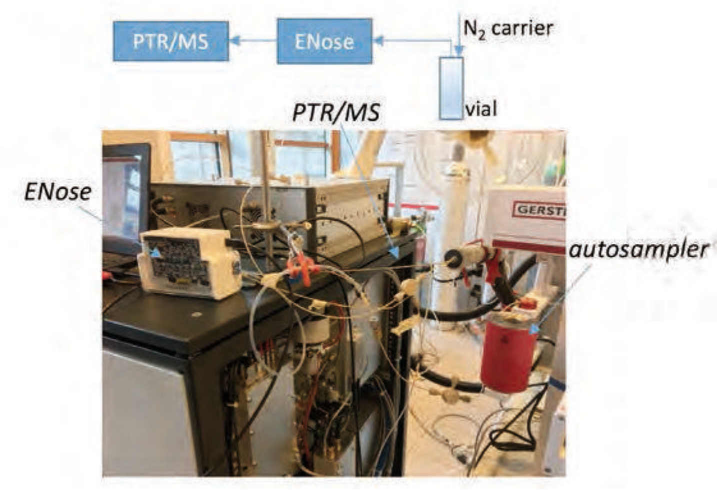

Figure 1. Sketch of the experimental setup and picture of the instruments arrangement

Results

A preliminary analysis of the dataset, has already shown promising result in spite of the very limited statistics available up to now. Two of the three type of samples measured with the hyphenated instruments have been previously sampled many times only with electronic noses, but the dispersion of samples in the same class has always covered potential discrimination especially between the fresh tomato samples and the inoculated ones.

The first evidence is the paramount importance of using a common automated sampling system improving dramatically at least the apparent discriminant power of the electronic nose. Furthermore having the two instruments on the same samples it is possible to choose in the mass spectra the peaks more meaningful (see Table 1) for the optimal discrimination obtained by PTR-ToF-MS data (see Figure 2).

The ion masses pointed out in Table 1 have been selected for a further investigation to check if could have been produced by the Penicillium spp. Fungi inoculated in the contaminated samples.

Table 2 instead report the main volatile metabolites produced by Penicillium spp. as resulting by a literature through scrutiny. In the last column of Table 2 are reported the more intense mass peaks following the National Institute of Standards and Technology.

All these data suggest many possible direction for further investigation and exploitation of the hyphenated instruments data.

m/e (a.m.u.)	p value	Fresh Tomato Sauce	Inoculated Tomato Sauce	Inoculated Sauce stored under Thyme vapors
29.0390	0.0054	22±2	178±62	286±82
41.0386	0.00036	75±7	104±17	148±22
43.0542	0.00044	26±4	80±18	115±17
46.0369	0.00031	4.5±0.2	22±4	35±0.8
48.0525	0.0046	6.8±0.5	48±16	75±20
57.0699	0.039	16±2	108±25	135±28
69.0698	4.9E-09	19±2	6±1	29±6

Table 1: Main peaks discriminating fresh and inoculated tomato sauce.

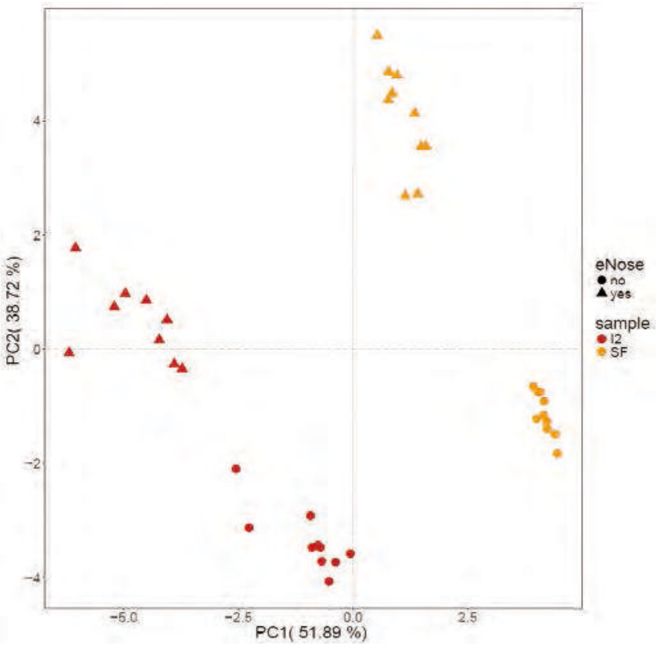

Figure 2: PCA analysis discriminating fresh samples from inoculated ones.

IUPAC Name	Empirical formula	Exact Mass	M1,M2,M3
Heptadec-1-ene	$C_{17}H_{34}$	237,258	41,43,55
Oct-1-en-3-ol	$C_8H_{16}O$	128,12	57,43,72
2-methylpropanoic acid	$(CH_3)_2$-CHCOOH	88,052	43,41,73
2-methylbutanoic acid	$C_5H_{10}O_2$	102,068	74,57,29
3-methylbutanoic acid	$C_5H_{10}O_2$	102,068	60,43,41
Undecan-2-one	$C_{11}H_{22}O$	170,167	58,43,59

Table2: Tentative attribution of main peaks to Penicillium spp volatile metabolites.

Discussion

Results show that the two instruments can operate simultaneously on the same sample. This feature allows to measure the exact composition of the sample analyzed by the electronic nose.

This preliminary results remove the serendipitous character of electronic nose applications providing an optimum tool for a more accurate and effective design and test of sensors for selected applications.

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Long term BVOC measurements with PTR-MS from a 325m tower in the Amazon rainforest

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Abstract

Biogenic Volatile Organic Compounds (BVOC) are copiously emitted by terrestrial vegetation and are of great interest because of their ability to regulate the oxidative capacity of the atmosphere. Their emissions are driven primarily by light and temperature, so Tropical forests are the strongest global source of BVOC. We have initiated a long-term project to characterize ambient BVOC concentrations at three heights over the pristine rainforest, at the Amazonian Tall Tower Observatory (ATTO; 02.14°S, 58.99°W). The aim of the project is to evaluate source flux and atmospheric oxidation variations on timescales beyond those of our previous short term intensive campaigns (2-3 weeks). A new PTR-Tof 4000 (IONICON Analytik GmbH) was installed in a laboratory container at the foot of the 325m tower with sampling inlets at 80, 150 and 325 meters. After installation, it was operated remotely from February 2018, covering both wet and dry seasons. Here we present the first results from this ongoing project as a function of time-of-day, height and season.

Quantitative detection of RO2 radicals and other products from cyclohexene ozonolysis with NH4+ and acetate Chemical Ionization Mass Spectrometry

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Abstract

The performance of the novel ammonium-CI3–TOF, based on the design of the PTR3-TOF and utilizing NH_4^+ adduct ion chemistry was investigated for the first time. It is able to quantitatively measure first generation oxidized product molecules (OMs) as well as highly oxidized organic molecules (HOMs). The gas-phase ozonolysis of cyclohexene served as a test system in order to evaluate the capability of the detection system. Experiments have been carried out in the TROPOS free-jet flow system at close to atmospheric conditions. Product ion signals were simultaneously observed by the ammonium-CI3-TOF and an acetate-CI-API-TOF. Both instruments are in remarkable good agreement within a factor of two for HOMs. For OMs not containing an OOH group the acetate technique can considerably underestimate concentrations. First steps of cyclohexene ozonolysis generate ten different (m/z product peaks) main products comprising 92% of observed OMs. The remaining 8% are distributed over several minor products (m/z peaks) that can be attributed to HOMs, mainly to highly oxidized RO_2 radicals. Dimers, formed via the pathway $RO_2 + R'O_2 \rightarrow ROOR'$, have been observed by both instruments as well. Summing up, observed ammonium-CI3-TOF products yield 4.9×10^9 molecules cm^{-3} in excellent agreement with the amount of reacted cyclohexene of 4.5×10^9 molecules cm^{-3} for reactant concentrations of $[O_3] = 2.25 \times 10^{12}$ molecules cm^{-3} and [cyclohexene] = 2.0×10^{12} molecules cm^{-3} and a reaction time of 7.9 s. NH_4^+ adduct ion chemistry based CIMS techniques offer a unique opportunity for complete detection of the whole product distribution, and consequently, for a much better understanding of atmospheric oxidation processes.

Introduction

Organic peroxy radicals (RO_2) are key intermediates of hydrocarbon degradation that are emitted in large amounts into the atmosphere by biogenic and in lesser amount by anthropogenic sources. As the organic structure (R) strongly affects their reactivity, it is important to quantify RO_2 radicals individually. Recently Noziére and Hanson (2017) reported the “speciated” detection of RO_2 radicals with detection limits of $1 - 10 \times 10^8$ molecules cm^{-3}. Here we demonstrate that the ammonium-CI3-TOF using NH_4^+ adduct ion chemistry can quantitatively measure all RO_2 radicals and oxidized product molecules (OMs) from cyclohexene ozonolysis simultaneously, that has been chosen as a first test reaction system, reaching limit of detections of $2 \times 1\ 0^5$ molecules cm^{-3}. For the first-time carbon closure was achieved with a single instrument. The versatility and sensitivity of the NH_4^+-CI3-TOF technique is high enough to apply this technique not only for laboratory based studies but also for environmental measurements in real-time.

Experimental Methods

The gas-phase reaction of ozone with cyclohexene was studied in the TROPOS free-jet flow system (scheme 2) that is designed in a way, that wall losses of reaction products are negligible during the 7.9 seconds reaction time. The reaction was varied by varying cyclohexene, keeping ozone constant at $[O3] = 2.3 \times 10^{12}$ cm^{-3}. Products were quantified by an ammonium-CI3-TOF utilizing NH_4^+ ion chemistry and an acetate-CI-APi-TOF using CH_3COO^- ion chemistry.

The ammonium-CI3-TOF

We modified the recently developed PTR3-TOF (Breitenlechner et al., 2017) using $NH_4^+(X)_n$ clusters as adduct ions, which exchange the ligand X being mainly NH_3 (and also H_2O; n=1, 2) at every collision with an oxygenated molecule (OM) according to equation (1).

$$NH_4^+(X)_n + OM \rightarrow OM\text{-}NH_4^+ + nX \quad (1)$$

The ammonium-CI3-TOF (chemical-ionization-time-of-flight) mass spectrometer (Fig. 1) was calibrated with a gas standard containing 3-hexanone in nitrogen. We obtained a sensitivity of 28 Hz / pptv (ion count rates were duty cycle corrected as described in Breitenlechner et al., 2017). RO_2 radicals were corrected by a factor of 2 due to calculated diffusion controlled inlet wall losses.

Results

Carbon Closure

93.5 % of found products are low oxidized molecules ($C_{5\text{-}6}H_{8\text{-}10}O_{1\text{-}4}$). The further 6.5% contain at least 5 oxygen atoms and could be identified as radicals and – in smaller concentrations – their hydroperoxids. A product spectrum with and without OH scavenger is shown in fig.1.

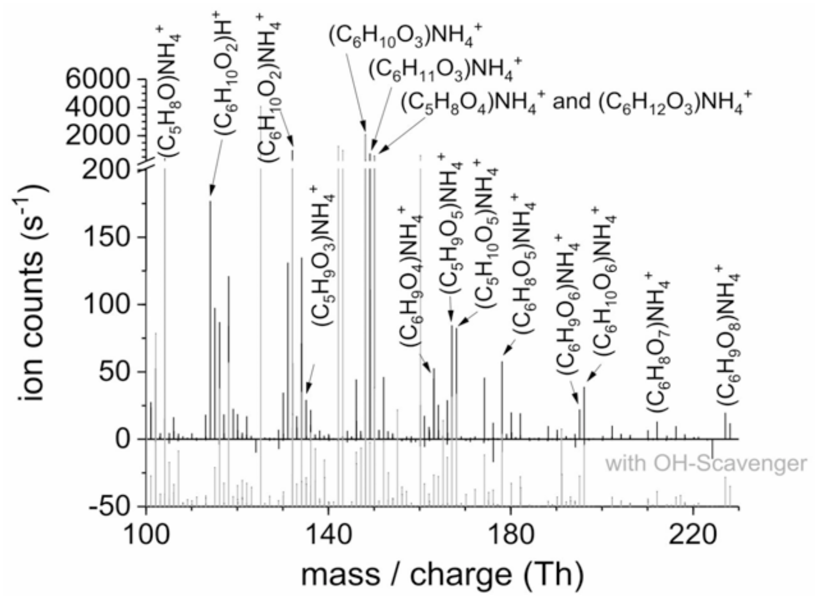

Figure 1: NH_4^+-CI3-ToF mass spectra from cyclohexene ozonolysis without (black) or with (grey) propane as OH-Scavenger.. $[O_3]= 2.25x10^{12}$ cm^{-3}, $[C_6H_{10}] = 2.0x10^{12}$ cm^{-3} , $[C_3H_8]=1.23x10^{16}$ cm^{-3}

RO_2 radicals

The found RO_2 radicals behave as first-order products from cyclohexene ozonolysis, increasing linearly with increasing reactant, as can be seen in fig. 2. The radicals from ozonolysis can be sorted into two groups: O,O-$C_6H_{9-x}(OOH)_xO_2$ with x={0,1,2,…} and O-$C_5H_{9-\alpha}(OOH)_\alpha O_2$ with α={1,2,…}. Additionally, OH radicals created as a side product of the ozonolysis can react with cyclohexene to form the radical OH-$C_6H_{10}O_2$. The amount of measured HO-$C_6H_{10}O_2$ is in good agreement with its calculated concentration from known cyclohexene reaction rates and OH production. Both instruments are within a factor of two for HOMs, an example is the radical O,O-$C_6H_{9-x}(OOH)_xO_2$ with x=2. For OMs not containing an OOH group as e.g. the HO-$C_6H_{10}O_2$ radical, the acetate technique can underestimate concentrations by 2-3 orders of magnitude.

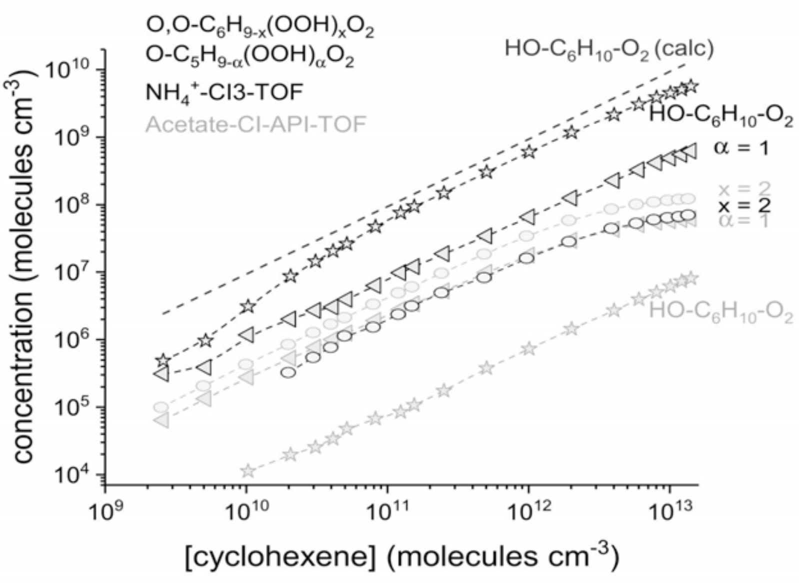

Figure 2: Concentrations of chosen low-oxidized RO_2-radicals and $OH-C_6H_{10}-O_2$. Calculated $OH-C_6H_{10}-O_2$ (reaction time 7.9 s) shown as dashed line.

Dimer formation of RO_2 radicals

All measured dimers - with sum formulas $C_{11-12}H_{18-20}O_x$ and quadratic dependency on cyclohexene - can be formed via the pathway $RO_2 + R'O_2 \rightarrow ROOR'$ as shown for selected ones in fig. 3.

Their 2nd order reaction rates range from $2x10^{-12}$ molecules cm^{-3} s^{-1} for the reaction of $OH-C_6H_{10}-O_2$ with $O-C_5H_8(OOH)_1O_2$ to $9x10^{-11}$ molecules cm^{-3} s^{-1} for the reaction of $O,O-C_6H_7(OOH)_2-O_2$ with $O-C_5H_8(OOH)_1O_2$.

Discussion

This study, showing the stands in line with studies by Berndt et al., 2018, showing that the self and cross accretion product formation of peroxy radicals is a very fast process for functionalized RO_2-radicals, which can be a competing process even under atmospheric conditions, when NO is present. The excellent agreement of measured products with reacted cyclohexene enhances credibility in the quantification of OMs, RO_2 radicals and dimers by the ammonium-CI3-TOF. Thus we can conclude, that the ammonium ionization technique is a very promising way to study the chemical processes of VOCs in the gas phase.

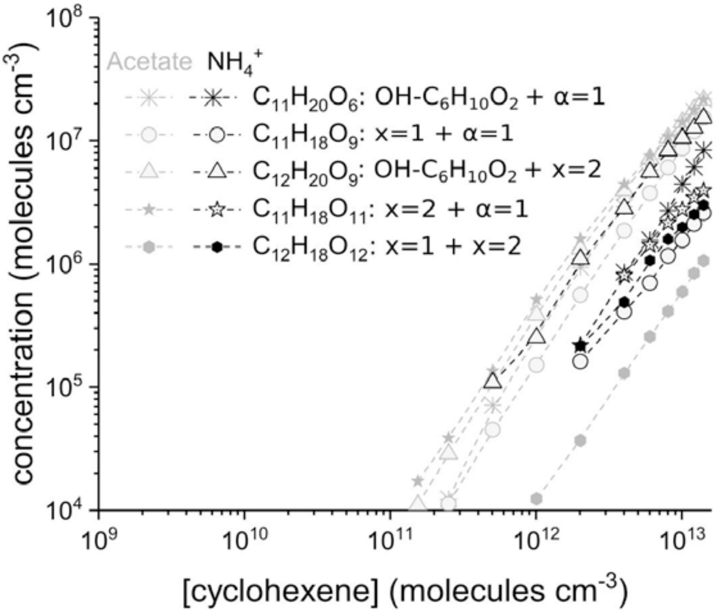

Figure 3: selected C_{11}- and C_{12}- dimer concentrations from cyclohexene ozonolysis.

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Explainable machine learning prediction of VOC in an university building microenvironment

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Abstract

In this study we applied a novel SHapley Additive exPlanations feature attribution framework to examine the relevance of meteorological parameters and identify key factors that govern indoor and outdoor isoprene concentrations obtained by PTR-MS measurements in an university environment. According to the results, ambient temperature appeared to be far the most important predictor of isoprene levels, followed by relative humidity and air pressure.

Introduction

Spatial evolution of isoprene concentrations in different environments depends on biogenic and anthropogenic emission sources and ambient conditions. Even the past environmental conditions experienced by the leaves, the soil moisture stress, and the age of leaves, have shown to affect isoprene fluxes (Müller et al., 2008). Once emitted in the air, isoprene fate is also dependent on meteorological conditions – it is dispersed under the influence of wind, subjected to photochemical reactions being predominantly enhanced by solar radiation (Cheng et al., 2018), or it acts as a precursor in the reactions of secondary organic aerosol formation under low relative humidity conditions (Zhang et al., 2011). In this study, we used the SHapley Additive exPlanations (SHAP) framework to obtain a more detailed insight into the meteorological factors that govern isoprene concentrations in indoor and outdoor environment.

Experimental Methods

Isoprene concentrations were measured in real time using proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria) in the period from March to July 2016. The measurement site was located at Singidunum University, Belgrade, Serbia (44°78' N, 20°48' E). Drift tube parameters included: pressure, ranging from 2.04 to 2.14 mbar; temperature 60^0C; E/N parameter, 145 Td providing reaction time of 90 µs. The count rate of $H_3O^+H_2O$ was 3 to 8% of the $9.2 \cdot 10^6$ counts s^{-1} count rate of primary H_3O^+ ions.

Regression analysis by means of eXtreme Gradient Boosting (XGBoost Python Package) was implemented for estimating the relationships between isoprene indoor/outdoor concentrations and meteorological parameters, including outdoor temperature, pressure, relative humidity and wind speed and direction, as well as the indoor temperature, pressure and relative humidity.

Accurate interpretation a model's prediction supports deeper understanding of the process being modeled. The SHAP method (Lundberg and Lee, 2017), based on unification and additive attribution algorithms, offers uniquely consistent, locally accurate attribution values attributing to each feature the change in the expected model prediction when conditioning on that feature.

Results and Discussion

The SHAP analysis (Stojić et al., 2019) was successfully applied to reveal in which respect the ambient conditions affected indoor and outdoor concentrations of isoprene as confirmed by the XGBoost predicted/observed relative errors of 18% and 25%, and the correlation coefficients of 0.88 and 0.91, respectively. The SHAP summary plot and the magnitude of mean SHAP values, as a measure of feature importance (Figure 1), suggest that ambient temperature appeared to be far the most important predictor of isoprene outdoor levels, followed by relative humidity and pressure, whereas the impact of wind speed and direction could be considered negligible.

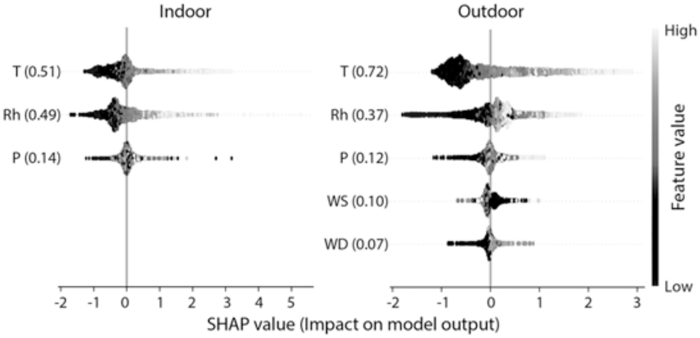

Figure 1: SHAP summary plot and mean SHAP value magnitude (values in brackets).

The dot density, in which each dot represents a particular measurement, show that lower temperatures were the most common in the dataset. However, a smooth increase in the model's output and long-tailed distribution reaching to the right suggest that increased temperature and its extreme values could significantly affect outdoor isoprene distribution. Similar results were registered for indoor isoprene (Figure 1). Furthermore, the SHAP analysis allowed for distinguishing between main (Figure 2) and interaction effects (Figure 3, right) of the most influential predictors of indoor and outdoor isoprene levels.

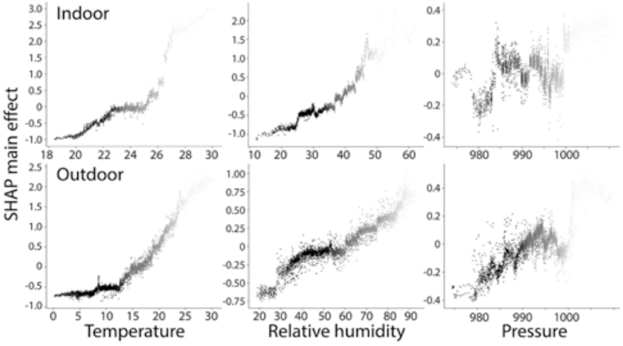

Figure 2: SHAP main effects.

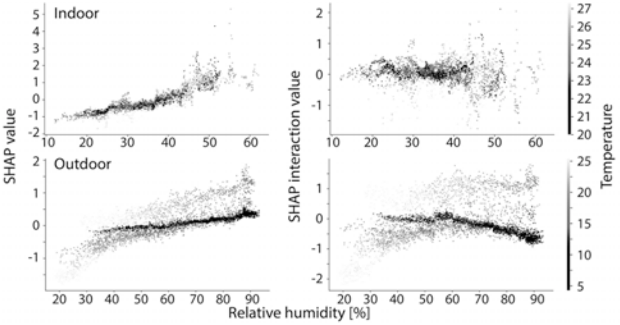

Figure 3: SHAP dependence (left) and interaction plots (right).

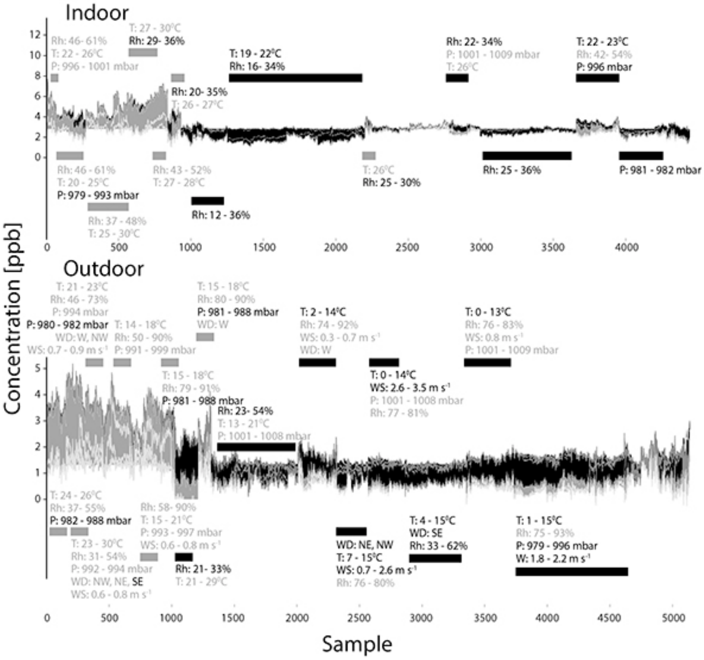

Figure 4: SHAP supervised clustering (contributors which push the model output from the base value `higher/lower are presented in grey/black`*).*

As showed by SHAP dependence plot (Figure 3, left), relative humidity has a stronger influence on isoprene concentrations in indoor than outdoor environment. Additionally, the same Figure reveals that higher indoor air temperatures were accompanied by increased relative humidity. For outdoor, the opposite tendency was observed, but with lower SHAP values and related impact on the model's output. Interactions among temperature and relative humidity caused most of the variance in the isoprene concentrations, as can be seen in Figure 3 (right). Supervised SHAP clustering classified indoor and outdoor isoprene level of pollutants into several subgroups, annotated by features which define them (Figure 4). As can be noted, the relationships between indoor/outdoor isoprene concentrations and ambient conditions were particularly evident for the temperatures above 15°C and relative humidity exceeding 40%.

As can be concluded, our knowledge of isoprene/volatile organic compound behavior and environmental fate could benefit from further investigation of interrelationships between major air pollutants and meteorological features.

Acknowledgments

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Multifractality of isoprene temporal dynamics in outdoor and indoor university environment

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Abstract

In this study the multiscale multifractal method was used with the aim to capture the fractal behaviour of indoor and outdoor isoprene time series obtained by PTR-MS measurements in an university environment (Belgrade, Serbia), as well as to investigate to what extent variations in isoprene levels can be considered random or persistent. As shown, isoprene time series exhibited persistency, slightly affected by the concentrations occurring randomly only at the level of small fluctuations and small scales within the time frame of 20 hours. The results herein presented contribute to better understanding of isoprene temporal evolution and provide theoretical background for enhanced forecasting of volatile organic compound concentrations in general.

Introduction

A number of literature sources have demonstrated that the behavior of heterogeneous and dynamic environmental systems or nonlinear processes, such as temporal and spatial evolution of isoprene, can be described by multifractal formalism. In this study we used multiscale multifractal method (MMA) for capturing the fractal behavior of isoprene outdoor and indoor concentration time series in an university environment and to investigate to what extent variations in isoprene levels can be considered random or persistent.

Experimental Methods

Isoprene concentrations were measured in real time using proton transfer reaction mass spectrometer (Standard PTR-quad-MS, Ionicon Analytik, GmbH, Austria) in the period from March to July 2016. The measurement site was located at Singidunum University, Belgrade, Serbia (44°78' N, 20°48' E). Drift tube parameters included: pressure, ranging from 2.04 to 2.14 mbar; temperature, 60 0C; voltage, 600 V; E/N parameter, 145 Td providing reaction time of 90 µs. The count rate of H3O+H2O was 3 to 8% of the 9.2·106 counts s−1 count rate of primary H3O+ ions. The measurements were performed continuously, except for brief interruptions for background level determination (10 min, 4 times per day) and calibration (5 times for the entire period).

Data Analysis

MMA is a generalization of the standard multifractal detrended fluctuation analysis (MF-DFA) (Stojić et al, 2016), which adds the dependence on scale, providing a broader analysis of the fluctuation properties, as well as more general and stable results (Stojić et al, 2017, Gierałtowski et al, 2012). For imputing missing data we employed *missForest,* a random forest based non-parametric algorithm available in R package and capable to deal with high dimensions, complex interactions and nonlinear data structure. The algorithm uses bootstrap aggregation of multiple regression trees and continues repeating the imputation procedure until a pre-defined stopping criterion is met, *i.e.* until the difference between the newly imputed data matrix and the previous one increases for the first time with respect to both variable types.

Results and Discussion

The complete indoor and outdoor isoprene time series obtained by missing value imputations are presented in Figure 1. The correlation between indoor and outdoor pollutant concentrations was 0.74. The *missForest* algorithm performed well, with predicted/observed out-of-bag normalized root mean squared error (NRMSE) of 0.009/0.011, and 0.078/0.083; and imputation out-of-bag NRMSE of 0.009 and 0.075, for indoor and outdoor isoprene concentrations, respectively.

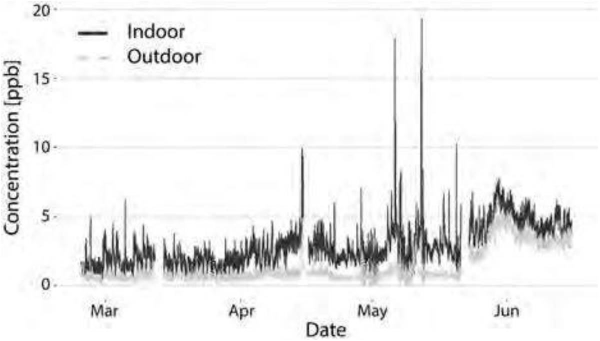

Figure 1: Isoprene indoor/outdoor time series.

The density of Miss Forest predicted and observed isoprene concentrations are in good agreement (Figure 2). Both indoor and outdoor isoprene concentrations fluctuated randomly over time (Hurst exponent, H=0.7–1.35), and their variation patterns were characterized by long-range correlated and persistent structure (Figure 3). Furthermore, the investigation of randomized isoprene time-series (Figure 4) revealed that the multifractality of the compound's indoor and outdoor concentration originates from both nonlinear correlations and a fat-tailed probability distribution.

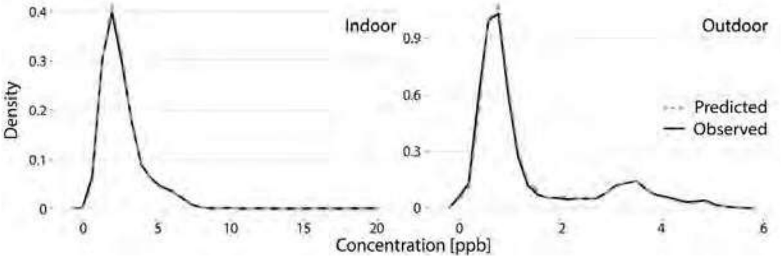

Figure 2: The density of predicted and observed isoprene concentrations.

As indicated by the minima and maxima of Hurst exponent and multifractal parameter (Figure 3), the indoor isoprene time-series were more influenced by small fluctuations compared to outdoor isoprene time-series, which mainly approached the most recognized fractal phenomena with long memory known as "pink noise". The variations could be explored with respect to different emission sources of isoprene that dominate over indoor and outdoor environment. Current knowledge suggests that three main sources of outdoor isoprene refer to vehicle emissions, evaporative emissions from petroleum products and plant emissions, although at temperatures exceeding 25°C dominant part of outdoor isoprene might be assigned to biogenic sources (Bari et al., 2015). On the other hand, the indoor isoprene levels are mostly affected by adhesives, coatings and the occupant's breath (Huang et al., 2016). In addition, non negligible factors are distinguishing features of interior spaces and occasional contributions of outdoor air through air-conditioning and building openings.

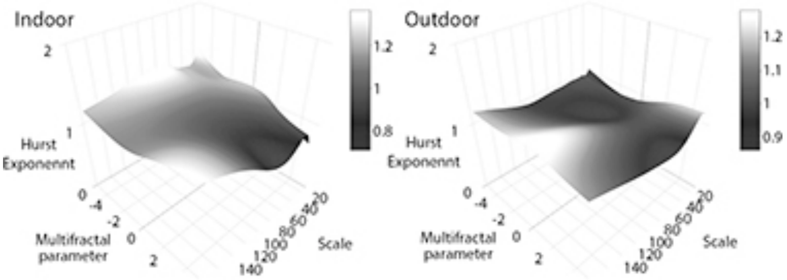

Figure 3: Isoprene indoor/outdoor time series Hurst surfaces.

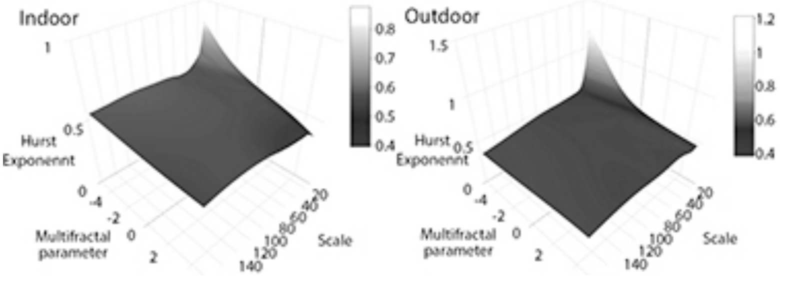

Figure 4: Isoprene randomized indoor/outdoor time series Hurst surfaces.

Indoor and outdoor isoprene time-series could be considered statistically different as indicated by the values of generalized distance Hurst coefficient (Figure 5) which highly exceeded the threshold value (0.065). The differences are primarily caused by strong fluctuations in both domains (negative and positive) of the multifractality parameter's interval at temporal scales between 60 and 160.

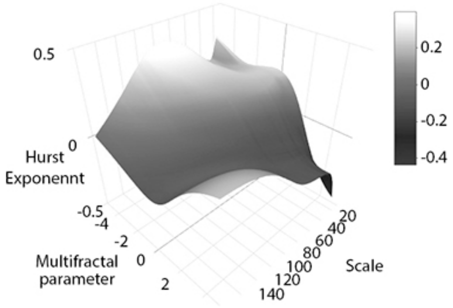

Figure 5: The difference between isoprene indoor and outdoor time series Hurst surfaces

Acknowledgments

This paper was realized as part of projects No III43007 and No III41011, which were financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia for the period 2011-19.

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Overview of Volatile Organic Compounds (VOCs) measured by PTR-ToF-MS around the Arabian Peninsula

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Abstract

From June to August 2017, a proton transfer reaction time-of-flight mass spectrometry (PTR-ToF-MS) was operated on board research vessel Kommandor Iona during the AQABA (Air Quality and Climate Change in the Arabian Basin) ship campaign to measure volatile organic compounds (VOCs) continuously in marine atmospheric boundary layer around Arabian Peninsula. Air quality in this region is heavily influenced by dust events, emissions from marine transportation and the oil/petroleum industry. In this study, the highest mixing ratios of most oxygenated VOCs (OVOCs, e.g. methanol, acetaldehyde, acetone etc.) and aromatics (e.g. benzene toluene etc.) were observed in the Arabian Gulf, varying from tens of ppt to several ppb (e.g. acetaldehyde up to 8.35 ppb, acetone up to12.9 ppb, and toluene up to 2.86 ppb). Photochemical OVOC production is strong in the region due to the co-location of high primary emissions (from the petroleum industry and marine transportation) with high OH radical abundance (due to high sunlight and moisture levels). The OVOCs were found to correlate relatively well with ozone (r2 >0.5), indicating that the high ozone mixing ratios (83.6±38.2 ppb) observed in Arabian Gulf are driven by local photochemistry. Similar high mixing ratios of aromatics (900±334 ppt) but lower OVOC mixing ratios were measured in the Suez region (Gulf of Suez and Suez Canal), one of the busiest marine trading route among the world. A short duration correlation between acetonitrile and CO (r2=0.85) indicates that biomass burning, from north Egypt (possibly from crop residues), can affect the air chemistry in Suez area. In contrast, OVOCs and aromatics were low in Arabian Sea region, where the air is mainly influenced by clean marine air from Indian Ocean. This unique dataset obtained from the campaign can provide new insights into the atmospheric processes in the Middle East, to assess the impact of the oil industry related emissions and improve the model predictions related to air quality among the area.

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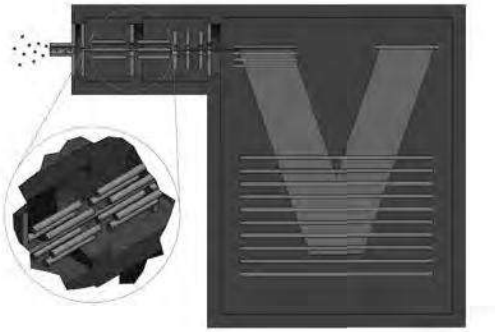

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