

**Selective  
measurements of  
isoprene and  
2-methyl-3-buten-2-ol**

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# Selective measurements of isoprene and 2-methyl-3-buten-2-ol based on NO<sup>+</sup> ionization mass spectrometry

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## Abstract

Biogenic VOC emissions are often dominated by 2-methyl-1,3-butadiene (isoprene) and 2-methyl-3-buten-2-ol (232 MBO). Here we explore the possibility for selectively distinguishing these species using  $\text{NO}^+$  as primary ion based on PTR-MS technology. High purity of  $\text{NO}^+$  (> 90%) as a primary ion was achieved in laboratory and field experiments using a PTR-TOF-MS. Isoprene is ionized via charge transfer leading to the major product ion  $\text{C}_5\text{H}_8^+$  (> 99%) (e.g. Spanel and Smith, 1998). 232 MBO undergoes a hydroxide ion transfer reaction resulting in the major product ion channel  $\text{C}_5\text{H}_9^+$  (> 95%) (e.g. Amelynck et al., 2005). We show that both compounds are ionized with little fragmentation (< 5%) under standard PTR-MS operating conditions. Typical sensitivities of  $11.1 \pm 0.1$  (isoprene) and  $12.9 \pm 0.1$  (232 MBO)  $\text{ncpsppbv}^{-1}$  were achieved, which correspond to limit of detections of 18 and 15 pptv, respectively for a 10 s integration time. Sensitivities decreased at higher collisional energies. Calibration experiments showed little humidity dependence. We tested the setup at a field site in Colorado dominated by ponderosa pine, a 232 MBO emitting plant species. Our measurements confirm 232 MBO as the dominant biogenic VOC at this site, exhibiting typical average daytime concentrations between 0.2–1.4 ppbv. The method is able to detect the presence of trace levels of isoprene (90–250 ppt) without any interference from 232 MBO, which would not be feasible using  $\text{H}_3\text{O}^+$  ionization chemistry, and which currently also remains a challenge for other analytical techniques (e.g. gas chromatographic methods).

## 1 Introduction

Isoprene (2-methyl-1,3-butadiene) plays an important global and regional role in photochemistry and climate. It was first discovered by Rasmussen (1969) and Sanadze et al. (1976) that plants can synthesize and subsequently emit this chemical. Currently the global emission strength of isoprene is estimated to be  $560 \text{ Tgy}^{-1}$  (Guenther

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et al., 2006) (uncertainty range: 230–700 Tgy<sup>-1</sup>, e.g. Stevenson et al., 2006), which could exceed that of methane (IPCC, 2007). Many different VOCs are emitted into the atmosphere and together the global VOC emission source is currently estimated to be in the range of 1200–1350 Tgy<sup>-1</sup> (Goldstein and Galbally, 2007). Chameides et al. (1988) showed that isoprene was the single most important reactive VOC fueling ozone chemistry in the South Eastern US. Oxidation of isoprene leads to complex organic compounds, which will be oxidized further to CO<sub>2</sub>, or deposit in the form of highly soluble organic species or organic aerosol (e.g. Karl et al., 2010). It has recently been suggested that oxidation of isoprene is still poorly understood questioning our understanding of the oxidizing capacity of the atmosphere (Lelieveld et al., 2008; Hofzumahaus et al., 2009). Through these processes isoprene along with other VOCs exhibits a direct and indirect climate forcing on the Earth's atmosphere.

While isoprene is a dominant emission from many deciduous ecosystems, Goldan et al. (1993) reported the ubiquitous presence of 2-methyl-3-butene-2-ol (232 MBO) in a coniferous forest in the USA. Since then many studies (e.g. Harley et al., 1998; Schade and Goldstein, 2001; Baker et al., 2001; Kim et al., 2010) have confirmed the presence of this alcohol throughout coniferous ecosystems in the Western US. Due to the large emission source 232 MBO is sometimes also termed the “isoprene of the west”.

The ecological roles of isoprene and 232 MBO have not been entirely elucidated, but might reflect a plant's ability to protect against oxidative stress (Loreto and Schnitzler, 2010), act as a biochemical stat (Rosenstiel et al., 2004) or mitigate high temperature exposure (Sharkey et al., 2008).

With the emergence of fast online measurement techniques, ecosystem fluxes of both species are increasingly obtained by the eddy covariance technique. Proton-transfer-reaction mass spectrometry (PTR-MS) (Hansel et al., 1995; Lindinger et al., 1998; de Gouw and Warneke, 2007) has so far been the technique of choice (e.g. Karl et al., 2001; Warneke et al., 2002; Taipale et al., 2010; Müller et al., 2010). Previous studies (Fall et al., 2001) have identified the presence of a host of biogenic C5 alco-

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5 hols and aldehydes, which collisionally dissociate and could potentially interfere with the detection of isoprene using hydronium ion chemistry in PTR-MS. In many places isoprene dominates over most other BVOCs and these interferences are often shown to be minor (Karl et al., 2004; Warneke et al., 2010; Misztal et al., 2011); however mea-  
10 surements, particularly in coniferous ecosystems, can be more challenging due to the concomitant emission of isoprene and 232 MBO. Need for improved detection of these species is also corroborated by the fact that conventional GC (gas chromatographic) techniques can be prone to humidity and oxidant dependent detection uncertainties (Golden et al., 1995). Baker et al. (2001) have shown that anytime a sample treatment  
15 involves heating, 232 MBO can dehydrate (e.g. GC sample treatment). Here we test the feasibility of using  $\text{NO}^+$  ion chemistry to selectively distinguish isoprene and 232 MBO using PTR-MS technology.

## 2 Method and field site description

### 2.1 Field site and sampling inlet

15 The study was located at the Manitou Forest Observatory near Woodland Park, Colorado, USA (2290 m elev., lat.  $39^\circ 6' 0''$  N, long.  $105^\circ 5' 30''$  W) and took place in July 2011. The site has been described previously (e.g. Kim et al., 2010) and is representative of the montane ponderosa pine zone in the front range which extends from Southern Wyoming to Northern New Mexico. The canopy is open and of varying density, with  
20 mixed age ponderosa pine up to 100 yr old and a surface cover of grasses, sage, crocus, forbs and exposed cryptogammic soils. The average tree height surrounding the measurement tower was 18.5 m.

Measurements were taken from a 30 m tall tower. All instruments sampled off an approximately 35 m long Teflon line (OD:  $3/8''$ ), pumped at a speed of about  $30 \text{ l min}^{-1}$ ,  
25 so that overall delay times were measured between 3 and 5 s.

## 2.2 PTR-TOF-MS (H<sub>3</sub>O<sup>+</sup>)

A proton-transfer reaction time of flight mass spectrometer (PTR-TOF-MS) based on a high resolution time of flight mass spectrometer (HTOF-MS, Tofwerks, Switzerland) and developed at the University of Innsbruck (Graus et al., 2010) was operated using protonated water (H<sub>3</sub>O<sup>+</sup>) as reagent ion. De Gouw and Warneke (2007) reviewed the operational mode for H<sub>3</sub>O<sup>+</sup> chemistry using the PTR-MS technique in detail. Here we operated the instrument at 60 °C, a drift tube voltage of 580 V and a drift tube pressure of 2.3 mbar. These conditions resulted in an  $EN^{-1}$  ratio of about 125 Townsend (Td) ( $E$  being the electric field strength and  $N$  the gas number density; 1 Td =  $10^{-17}$  V cm<sup>2</sup>). 6 min average concentration measurements are used for the analysis presented in this manuscript. Details about TOF-MS data acquisition and data post processing can be found in Müller et al. (2010).

## 2.3 PTR-TOF-MS (NO<sup>+</sup>)

Measurements using NO<sup>+</sup> ionization were performed using a PTR-TOF-MS 8000 apparatus from Ionicon Analytik GmbH, Innsbruck (Austria) (Jordan et al., 2009a). The ionization conditions in the drift tube were controlled by drift voltage (530 V), drift temperature (60 °C) and drift pressure (2.3 mbar) resulting in an  $EN^{-1}$  of about 115 Td. In NO<sup>+</sup> mode the hollow cathode was supplied with dry, purified air entering the ionization region leading to the following ionization sequence:



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where rate coefficients  $k_2$  and  $k_3$  are much smaller than the collisional rate (i.e.  $k_3 \ll k_c$ ) and rate coefficients  $k_1$  and  $k_4$  proceed close to  $k_c$  (Federer et al., 1985).

The instrument utilized in this study is equipped with a dynamically adjustable source valve, which can be used to control the gas exchange rate in the ion-source via a differential pumping stage (e.g. Jordan et al., 2009b). The achieved purity of the  $\text{NO}^+$  signal was 93 % in the field and 95 % for laboratory calibration experiments. Knighton et al. (2009) have observed high purity of  $\text{NO}^+$  production and concluded that  $\text{NO}_2^+$  formation can be largely suppressed by adjusting the ion source extraction voltage. Here settings of 6–8 mA ion current, an extraction voltage of 120 V and a source valve setting of 35 % led to a fraction of about 1 %  $\text{NO}_2^+$  relative to  $\text{NO}^+$ .  $\text{O}_2^+$  and  $\text{H}_3\text{O}^+$  varied between 2–4 % and 1–3 %, respectively relative to the  $\text{NO}^+$  signal.

The sampling time per channel in the TOF was set to 0.2 ns, amounting to 174 499 channels for a mass spectrum up to about 428.5 Th. More detail on data acquisition and treatment can be found in Cappellin et al. (2012).

## 2.4 Calibration setup

A custom built calibration system was used to dilute gravimetrically prepared VOC standards including isoprene and 232 MBO. Gas standard 1 was gravimetrically prepared and provided by NOAA according to protocols published by Montzka et al. (1993). The standard contained methanol (1.89 ppmv), acetonitrile (2.00 ppmv), acetaldehyde (3.53 ppmv), acetone (1.99 ppmv), methylvinylketone (1.1 ppmv), limonene (2.1 ppmv), 2-methyl-3-buten-2-ol (2.2 ppmv), pyrrole (2.1 ppmv), benzene (1.49 ppmv), toluene (2.3 ppmv), methylethylketone (2.2 ppmv) with an uncertainty of  $\pm 5\%$ . Gas standards 2 and 3 were gravimetrically prepared in house and contained isoprene (gas standard 2: 7.25 ppmv; gas standard 3: 147.2 ppbv) and camphene (gas standard 2: 4.87 ppmv, gas standard 3: 96.6 ppbv). Both standards were cross-validated with GC-FID based on a NIST traceable hydrocarbon standard with an uncertainty of  $\pm 5\%$  (Greenberg and Zimmerman, 1984). Gas standard 4 was gravimetrically prepared by Apel-Riemer Environmental Inc (CO, USA) and contained isoprene (10 ppbv) and camphene (10 ppbv)

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with an uncertainty of  $\pm 5\%$  each. All VOC standards were prepared in ultrapure nitrogen.

Zero air was obtained by flowing ambient air through a small membrane pump (KNF, model MPU 2099-N8611.07, USA) pressurizing a flow controller (1 slm, Bronkhorst, model: F-201CV-K0ABD-22-V, Netherland), which was connected to a catalytic converter. Gas standards were selectively connected to a second flow controller (10 sccm, Bronkhorst, model: F-201CV-020-ABD-22-V, Netherland). The outflow from both flow controllers was connected via PFA Teflon fittings allowing a dynamic dilution range between 1/1000 and 1/10. Large flows were calibrated using a dry calibration system (Bios International, model DCL-MH, USA) and small flows ( $< 10$  sccm) were calibrated using the bubble meter technique. The uncertainty due to the dynamic dilution system is estimated to be  $\pm 10\%$ , leading to a combined uncertainty of  $\pm 15\%$ . This setup allowed performing calibration experiments at ambient humidity (30 % RH). Calibration experiments under dry conditions ( $< 1\%$  RH) were performed by passing dry zero air through the dilution flow controller.

### 3 Results

#### 3.1 Ion chemistry

Previous ion chemistry investigations (e.g. Spanel and Smith, 1998; Amelynck et al., 2005; Jordan et al., 2009b; Knighton et al., 2009) identified four dominant reaction pathways using  $\text{NO}^+$  as primary ion. These include charge transfer,



hydride ion transfer,



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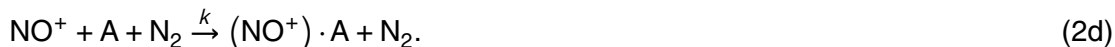
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hydroxide ion transfer,



and three body association reactions,



5 The ionization potential (IP) of NO (IP: 9.26 eV) is often much lower than for common VOCs detected in the atmosphere. Therefore Reaction (2a) only proceeds in selected cases. One such example is isoprene, exhibiting an IP of 8.84 eV. NO<sup>+</sup> ionization via charge transfer can typically be regarded as “soft”, leading to very little or no fragmentation (e.g. Spanel and Smith, 1998). Figure 1a depicts mass spectra for isoprene ionized by NO<sup>+</sup>. No significant fragmentation is observed and the major product ion appears on  $mz^{-1}$  680618<sup>+</sup> Th, corresponding to (C<sub>5</sub>H<sub>8</sub><sup>+</sup>):



15 Similarly, Knighton et al. (2009) have used NO<sup>+</sup> to selectively measure an anthropogenic pollutant (1,3 butadiene) and isoprene via charge transfer and reported negligible fragmentation for both compounds.

Due to the low IP of NO, many reactions will proceed via hydride ion transfer (Eq. 2b) or hydroxide ion transfer (Eq. 2c). Association (i.e. clustering) reactions (Eq. 2d) are largely suppressed under standard PTR-MS operating conditions (i.e. 115 Td) as a consequence of the high collisional energy ( $KE_{\text{cm}} = 0.16 \text{ eV}$ ). This is an important difference to other chemical ionization mass spectrometers, where collisional dissociation cells are often de-coupled from the reaction region, leading to potential nonlinear behavior masked by ligand switching reactions (Eisele et al., 1992).

The reaction between NO<sup>+</sup> and 232 MBO proceeds via hydroxide ion transfer according to



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Figure 1b shows mass spectra of 232 MBO ions measured during field and laboratory experiments. The major product ion (> 98 %) for 232 MBO is detected on molecular ion  $mz^{-1} 69\,0704^+$  Th corresponding to  $(C_5H_9^+)$ ; isoprene is observed on  $mz^{-1} 68\,0626^+$  Th. These measured signals are accurate to within  $7 \times 10^{-4}$  Th of the exact molecular ion. During field experiments a contamination peak at  $mz^{-1} 68\,995^+$  Th was present, which was absent during laboratory investigations. The nature of this peak remains unclear, but it was confirmed as internal contamination, when it remained high after passing ambient air through a catalytic converter. The peak did not interfere with any of the presented analysis.

### 3.2 Calibration

Figure 2 shows results from a typical calibration experiment performed for isoprene (black) and 232 MBO (red) at standard conditions (here defined as 115Td). For isoprene data from 3 different standards (gas standard 2, 3 and 4) were included. The 3 point calibration curve for 232 MBO was based on gas standard 1. Each set of calibrations included two repetitions. Table 1 summarizes results for isoprene and 232 MBO, which exhibit typical normalized sensitivities of  $11.2 \pm 0.1$  ncpsppbv $^{-1}$  and  $12.9 \pm 0.1$  ncpsppbv $^{-1}$ , respectively. For a primary ion count rate of  $4 \times 10^6$  cps, the corresponding actual sensitivities would be on the order of 44.8 cpsppbv $^{-1}$  and 51.6 cpsppbv $^{-1}$  for isoprene and 232 MBO. These values are comparable to sensitivities obtained with a similar PTR-TOF-MS instrument using  $H_3O^+$  ionization. Graus et al. (2010) for example reported sensitivities for isoprene on the order of 44.4 cpsppbv $^{-1}$ . Jordan et al. (2009a) reported typical normalized sensitivities for aromatic compounds (e.g. benzene and 1,3,5-trichlorobenzene) in the range of 11–13 ncpsppbv $^{-1}$ . Normalized sensitivities for isoprene reported here are about a factor of 2 lower than those reported by Knighton et al. (2009). The value presented here would fall close to the theoretically expected value assuming a rate coefficient of  $2.0 \times 10^{-9}$  cm $^3$  s $^{-1}$ . Similarly for 232 MBO, the calculated sensitivity would correspond to a reaction rate coefficient of  $2.3 \times 10^{-9}$  cm $^3$  s $^{-1}$ . At thermal energies ( $\sim 0.025$  eV)

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Spanel and Smith (1998) and Amelynck et al. (2005) reported rate constants for the {isoprene + NO<sup>+</sup>} and {232 MBO + NO<sup>+</sup>} reactions of  $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , respectively. The present data suggest that the reaction of NO<sup>+</sup> with these VOCs proceeds at the collisional limiting value under typical PTR-MS conditions, here characterized by a center of mass energy ( $KE_{\text{cm}}$ ) of  $\sim 0.16 \text{ eV}$ .

Figure 3 depicts the dependence of normalized sensitivities as a function of collisional energy ( $EN^{-1}$ ), expressed in units of Td. For this experiment the drift tube pressure was held constant at 2.3 mbar and the drift voltage was varied between 400 V and 600 V. Isoprene (black) closely follows a predicted slope based on the change in reaction time, while 232 MBO (red) exhibits a more pronounced change as a function of  $EN^{-1}$ . Regression lines fitted through the measured data are depicted by the solid lines with individual regression coefficients listed in the figure caption.

In order to probe any potential interference we performed a test where separate mixtures of 232 MBO and Isoprene were added to a sample flow of 1.5 lpm (Fig. 4). A 6.7 ppbv concentration of 232 MBO was added at measurement cycle 30. At cycle 67 an isoprene mixing ratio of 41.6 ppbv was added to this flow. Isotopic ratios of isoprene were subtracted from  $mz^{-1} 69$ . At cycle 150 the 232 MBO concentration was increased to 26.3 ppbv. The isoprene and 232 MBO standard addition was subsequently turned off as indicated on the graph. This test suggests that selective measurement of these chemical species can be performed interference free and could also potentially be used for conventional PTR-MS applications.

### 3.3 Field measurements

A field test was performed between 8 and 16 August 2011, when two PTR-TOF-MS instruments were deployed side by side. One instrument was operated in standard H<sub>3</sub>O<sup>+</sup> mode (Kaser et al., 2012) while the other instrument was operated in NO<sup>+</sup> mode. Figure 5 depicts diurnal cycles averaged over the entire 8 day period. The sum of isoprene and 232 MBO measured by both instruments agrees well (blue and green trace, upper panel). As confirmed before (Kim et al., 2010; Kaser et al., 2012) 232 MBO (red)

is the dominant biogenic VOC at this site. Isoprene is depicted in black and exhibits typical daytime concentrations of about 200–250 pptv. As expected for light dependent biogenic VOC (BVOC) emissions, the concentration of isoprene and 232 MBO rapidly declines after sunset. The lower panel shows the ratio between isoprene and 232 MBO with an average daytime value of about 0.2. The ratio increases to about 0.5 during night, which could be indicative of different emission patterns between these BVOCs or the influence of non-local isoprene sources. For the 2011 campaign the OH reactivity due to isoprene would amount to up to 40 % relative to that of 232 MBO for typical daytime conditions. Future eddy covariance measurements are needed to elucidate emission patterns of these two species in more detail at this site.

## 4 Conclusions

We have demonstrated that two dominant biogenic VOCs (isoprene and 232 MBO) can be selectively measured by chemical ionization mass spectrometry based on  $\text{NO}^+$  ionization. Our results confirm that isoprene is ionized via charge transfer, while 232 MBO undergoes a hydroxide transfer reaction. This allows the interference free detection of both species using PTR-MS technology, which is prone to collisional dissociation of 232 MBO interfering with the detection of isoprene using conventional  $\text{H}_3\text{O}^+$  ionization. The proposed method will also help assessing uncertainties of conventional gas-chromatography associated with the detection of isoprene in the presence of 232 MBO. Field measurements confirm 232 MBO as an important BVOC emitted from a coniferous ecosystem in Colorado. Our measurements also show the presence of trace amounts of isoprene. These findings will pave the way for more selective measurements of these compounds, which are often concomitantly emitted in semi-arid ecosystems throughout the Western United States.

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## 5 References

Amelynck, C., Schoon, N., Kuppens, T., Bultinck, P., and Arijs, E.: A selected ion flow tube study of the reactions of  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$  and  $\text{O}_2^+$  with some oxygenated biogenic volatile organic compounds, *Int. J. Mass Spectrom.*, 247, 1–9, 2005.

Baker, B., Guenther, A., Greenberg, J., and Fall, R.: Canopy level fluxes of 2-methyl-3-buten-2-ol, acetone, and methanol by a portable relaxed eddy accumulation system, *Environ. Sci. Technol.*, 35, 1701–1708, 2001.

Cappellin, L., Karl, T., Probst, M., Ismailova, O., Winkler, P. M., Soukoulis, C., Aprea, E., Maerk, T. D., Gasperi, F., and Biasioli, F.: On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry, *Environ. Sci. Technol.*, 46, 2283–2290, 2012.

Chameides, W. L., Lindsay, R. W., Richardson, J., and Kiang, C. S.: The role of biogenic hydrocarbons in urban photochemical smog – Atlanta as a case-study, *Science*, 241, 1473–1475, 1988.

deGouw, J. and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, 26, 223–257, 2007.

Eisele, F. L. and Berresheim, H.: High-pressure chemical ionization flow reactor for real-time mass-spectrometric detection of sulfur gases and unsaturated hydrocarbons in air, *Anal. Chem.*, 64, 283–288, 1992.

Fall, R., Karl, T., Jordan, A., and Lindinger, W.: Biogenic C5 VOCs: release from leaves after freeze-thaw wounding and occurrence in air at a high mountain observatory, *Atmos. Environ.*, 35, 3905–3916, 2001.

Federer, W., Dobler, W., Howorka, F., Lindinger, W., Durupferguson, M., and Ferguson, E. E.: Collisional relaxation of vibrationally excited  $\text{NO}^+$  (V) ions, *J. Chem. Phys.*, 83, 1032–1038, 1985.

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- Goldan, P. D., Kuster, W. C., Fehsenfeld, F. C., and Montzka, S. A.: The observation of a C5 alcohol emission in a North American pine forest, *Geophys. Res. Lett.*, 2, 1039–1042, 1993.
- Goldan, P. D., Kuster, W. C., and Fehsenfeld F. C.: Nonmethane hydrocarbon measurements during the tropospheric OH photochemistry Experiment, *J. Geophys. Res.*, 102, 6315–6324, 1997.
- 5 Graus, M., Müller, M., and Hansel, A.: High resolution PTR-TOF: quantification and formula confirmation of VOC in real time, *J. Am. Soc. Mass Spectr.*, 21, 1037–1044, doi:10.1016/j.jasms.2010.02.006, 2010.
- Greenberg, J. P. and Zimmerman, P. R.: Nonmethane hydrocarbons in remote tropical, continental, and marine atmospheres, *J. Geophys. Res.*, 89, 4767–4778, 1984.
- 10 Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature), *Atmos. Chem. Phys.*, 6, 3181–3210, doi:10.5194/acp-6-3181-2006, 2006.
- 15 Hansel, A., Jordan, A., Holzinger, R., Prazeller, P., Vogel, W., and Lindinger, W.: Proton transfer reaction mass spectrometry: online trace gas analysis at the ppb level, *Int. J. Mass Spectrom.*, 149, 609–619, 1995.
- Harley, P., Fridd-Stroud, V., Greenberg, J., Guenther, A., and Vasconcellos, P.: Emission of 2-methyl-3-buten-2-ol by pines: a potentially large natural source of reactive carbon to the atmosphere, *J. Geophys. Res.*, 103, 25479–25486, 1998.
- 20 Hofzumahaus, A., Rohrer, F., Lu, K. D., Bohn, B., Brauers, T., Chang, C. C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S. R., Shao, M., Zeng, L. M., Wahner, A., and Zhang, Y. H.: Amplified trace gas removal in the troposphere, *Science*, 324, 1702–1704, 2009.
- 25 IPCC: Climate change 2007 – synthesis report, Cambridge University Press, Cambridge, UK and New York, NY, USA, Geneva, Switzerland, 2007.
- Jordan, A., Haidacher, S., Hanel, G., Hartungen, E., Mark, L., Seehauser, H., Schottkowsky, R., Sulzer, P., and Mark, T. D.: A high resolution and high sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS), *Int. J. Mass Spectrom.*, 286, 122–128, 2009a.
- 30 Jordan, A., Haidacher, S., Hanel, G., Hartungen E., Hrbig, J., Maerk, L., Schottkowsky, R., Seehauser, H., Sulzer, P., and Maerk, T. D.: An online ultra-high sensitivity proton-transfer-reaction mass spectrometer combined with switchable reagent ion capability, *Int. J. Mass Spectrom.*, 286, 32–38, 2009b.

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Karl, T., Guenther, A., Jordan, A., Fall, R., and Lindinger, W.: Eddy covariance measurements of biogenic oxygenated VOC emissions from hay harvesting, *Atmos. Environ.*, 35, 491–495, 2001.

5 Karl, T., Potosnak, M., Guenther, A., Clark, D., Walker, J., Herrick, J. D., and Geron, C.: Exchange processes of volatile organic compounds above a tropical rain forest: implications for modeling tropospheric chemistry above dense vegetation, *J. Geophys. Res.*, 109, D18306, doi:10.1029/2004JD004738, 2004.

10 Karl, T., Harley, P., Emmons, L., Thornton, B., Guenther, A., Basu, C., Turnipseed, A., and Jardine, K.: Efficient atmospheric cleansing of oxidized organic trace gases by vegetation, *Science*, 330, 816–819, doi:10.1126/science.1192534, 2010.

Kaser, L., Karl, T., Schnitzhofer, R., Graus, M., Herdinger-Blatt, I. S., DiGangi, J. P., Hornbrook, R. S., Zheng, W., Flocke, F. M. Guenther, A., Keutsch, F. N., Apel, E., and Hansel, A.: Comparison of different real time VOC measurement techniques in a ponderosa pine forest, submitted, 2012.

15 Kim, S., Karl, T., Guenther, A., Tyndall, G., Orlando, J., Harley, P., Rasmussen, R., and Apel, E.: Emissions and ambient distributions of Biogenic Volatile Organic Compounds (BVOC) in a ponderosa pine ecosystem: interpretation of PTR-MS mass spectra, *Atmos. Chem. Phys.*, 10, 1759-1771, doi:10.5194/acp-10-1759-2010, 2010.

20 Knighton, W. B., Fornter, E. C., Herndon, S. C., Wood, E. C., and Miake-Lye, R. C.: Adaption of a proton transfer reaction mass spectrometer instrument to employ  $\text{NO}^+$  as reagent ion for the detection of 1,3 butadiene in the ambient atmosphere, *Rapid Commun. Mass Sp.*, 23, 3301–3308, 2009.

25 Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737–740, 2008.

Lindinger, W., Hansel, A., and Jordan, A.: On-line monitoring of volatile organic compounds at pptv levels by means of proton transfer- reaction mass spectrometry (PTR-MS) medical applications, food control and environmental research, *Int. J. Mass Spectrom.*, 173, 191–241, 1998.

30 Misztal, P. K., Nemitz, E., Langford, B., Di Marco, C. F., Phillips, G. J., Hewitt, C. N., MacKenzie, A. R., Owen, S. M., Fowler, D., Heal, M. R., Cape, J. N.: Direct ecosystem fluxes of volatile organic compounds from oil palms in South-East Asia, *Atmos. Chem. Phys.*, 11, 8995–9017, doi:10.5194/acp-11-8995-2011, 2011.

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Montzka, S. A., Trainer, M., Goldan, P. D., Kuster, W. C., and Fehsenfeld F. C.: Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere, *J. Geophys. Res.*, 98, 1101–1111, 1993.

Müller, M., Graus, M., Ruuskanen, T. M., Schnitzhofer, R., Bamberger, I., Kaser, L., Titzmann, T., Hoernagl, L., Wohlfahrt, T., Karl, T., and Hansel, A.: First eddy covariance flux measurements by PTR-TOF, *Atmos. Meas. Tech.*, 3, 387–395, doi:10.5194/amt-3-387-2010, 2010.

Loreto, F. and Schnitzler, J. P.: Abiotic stresses and induced BVOCs, *Trends Plant Sci.*, 15, 154–166, 2010.

Sanadze, G. A., Chiabrivili, N. G., and Kalandadze, A. N.: Identification of phytogetic isoprene by method of nuclear magnetic resonance spectroscopy, *Sov. Plant Physiol.*, 23, 898–900, 1976.

Schade, G. W. and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, *J. Geophys. Res.*, 106, 3111–3123, 2001.

Sharkey, T. D., Wieberley, A. E., and Donohye, A. R.: Isoprene emission from plants: why and how, *Ann. Bot.-London*, 101, 5–18, 2008.

Spanel, P. and Smith, D.: Selected ion flow tube studies of the reactions of  $\text{H}_3\text{O}^+$ ,  $\text{NO}^+$ , and  $\text{O}-2(+)$  with several aromatic and aliphatic hydrocarbons, *Int. J. Mass Spectrom.*, 181, 1–10, 1998.

Stevenson, D. S., Dentener, F. J., Schultz, M. G., Ellingsen, K., van Noije, T. P. C., Wild, O., Zeng, G., Amann, M., Atherton, C. S., Bell, N., Bergmann, D. J., Bey, I., Butler, T., Cofofa, J., Collins, W. J., Derwent, R. G., Doherty, R. M., Drevet, J., Eskes, H. J., Fiore, A. M., Gauss, M., Hauglustaine, D. A., Horowitz, L. W., Isaksen, I. S. A., Krol, M. C., Lamarque, J. F., Lawrence, M. G., Montanaro, V., Müller, J. F., Pitari, G., Prather, M. J., Pyle, J. A., Rast, S., Rodriguez, J. M., Sanderson, M. G., Savage, N. H., Shindell, D. T., Strahan, S. E., Sudo, K., and Szopa, S.: Multi-model ensemble simulations of present-day and near-future tropospheric ozone, *J. Geophys. Res.*, 111, D08301, doi:10.1029/2005JD006338, 2006.

Rasmussen, R. A.: Isoprene that missing link in terpene biosynthesis, identified as a foliage volatile, *Plant Physiol.*, S44, 40–42, 1969.

Rosenstiel, T. N., Ebbets, A. L., Khatri, W. C., Fall, R., and Monson, R. K.: Induction of poplar leaf nitrate reductase: a test of extrachloroplastic control of isoprene emission rate, *Plant Biol.*, 6, 12–21, 2004.



Taipale, R., Ruuskanen, T. M., and Rinne, J.: Lag time determination in DEC measurements with PTR-MS, *Atmos. Meas. Tech.*, 3, 853–862, doi:10.5194/amt-3-853-2010, 2010.

Warneke, C., Luxembourg, S. L., de Gouw, J. A., Rinne, H. J. I., Guenther, A. B., and Fall, R.: Disjunct eddy covariance measurements of oxygenated volatile organic compounds fluxes from an alfalfa field before and after cutting, *J. Geophys. Res.*, 107, 4067, doi:10.1029/2001JD000594, 2002.

Warneke, C., de Gouw, J. A., Del Negro, L., Grioude, J., McKeen, S., Stark, H., Kuster, W. C., Goldan, P. D., Trainer, M., Fehsenfeld, F. C., Wiedinmyer, C., Guenther, A. B., Hansel, A., Wisthaler, A., Atlas, E., Holloway, J. S., Ryerson, T. B., Peischl, J., Huey, L. G., Hanks, A. T. C.: Biogenic emission measurement and inventories determination of biogenic emissions in the Eastern United States and Texas and comparison with biogenic emission inventories, *J. Geophys. Res.*, 115, D00F18, doi:10.1029/2009JD012445, 2010.

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**Table 1.** Sensitivities in  $\text{ncps ppbv}^{-1}$  ( $=1 \times 10^6 \times \text{VOC}^+ [\text{cps}]/\text{NO}^+ [\text{cps}]/\text{ppbv}$ ) obtained for a drift pressure of 2.3 mbar, a drift voltage of 530 V and a drift tube temperature of 60 °C corresponding to  $EN^{-1} = 115\text{Td}$ .

Humidity	Isoprene	232 MBO
Humid 30 % RH	$11.1 \pm 0.1$	$12.9 \pm 0.1$
Dry < 1 % RH	$11.2 \pm 0.1$	$12.6 \pm 0.1$

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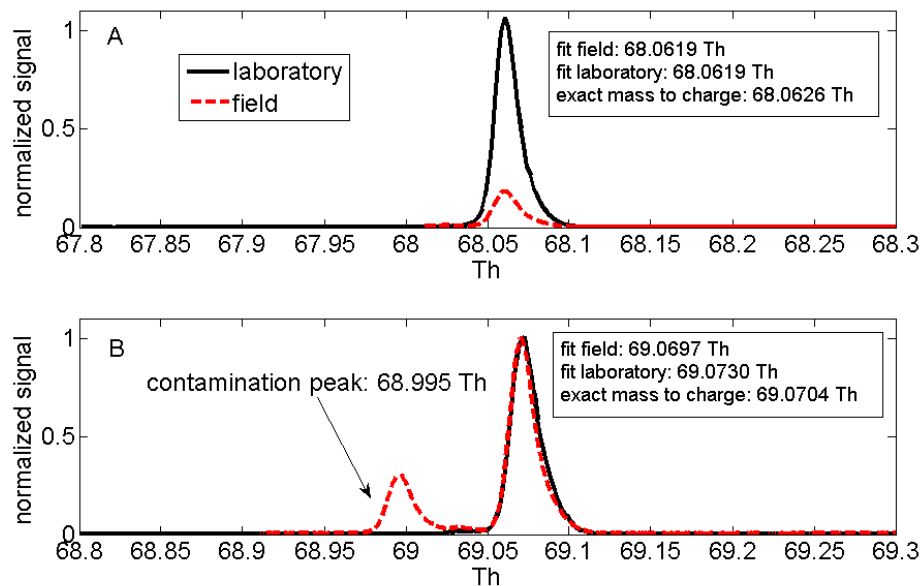
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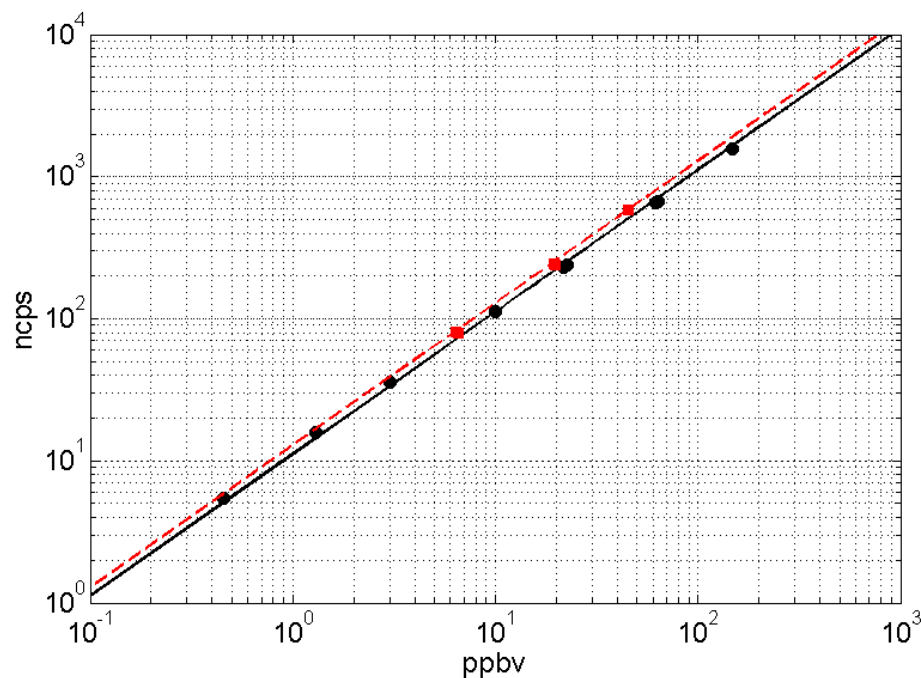


**Fig. 1.** Observed mass spectra for field and laboratory measurements depicting the molecular ion distribution on  $m/z^{-1}$  68<sup>+</sup> Th (A) and  $m/z^{-1}$  69<sup>+</sup> Th (B). Spectra are normalized by the 232 MBO count rate.

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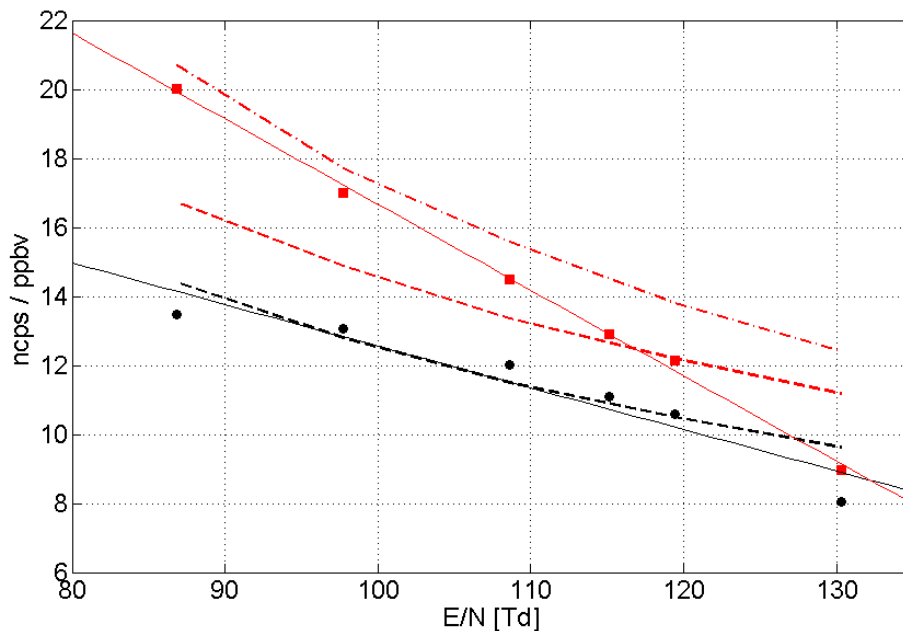


**Fig. 2.** Multipoint calibration curve for isoprene (black) and 232 MBO (red). Regression lines yield  $11.1 \pm 0.1$  ncps ppbv<sup>-1</sup> and  $12.9 \pm 0.1$  ncps ppbv<sup>-1</sup> for isoprene and 232 MBO, respectively.

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**Fig. 3.** Normalized sensitivities plotted as a function of  $E N^{-1}$ . Isoprene (black) and 232 MBO (red) exhibit higher sensitivities at lower collisional energies. The dashed lines indicate a theoretically calculated response curve based on a change in reaction time for a constant rate coefficient; the red dashed dotted line indicates the case using a varying rate coefficient for 232 MBO; the thin solid lines depict a linear fit ( $y = ax + b$ ) through measured data yielding the following fitting coefficients: isoprene:  $a = -0.12$ ,  $b = 24.6$  and 232 MBO  $a = -0.25$ ,  $b = 41.5$ .

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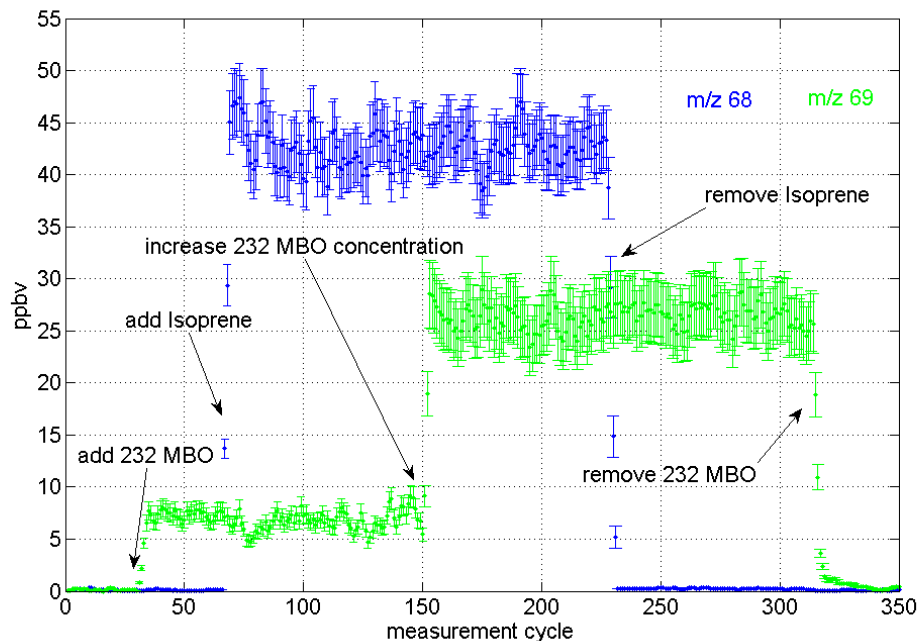
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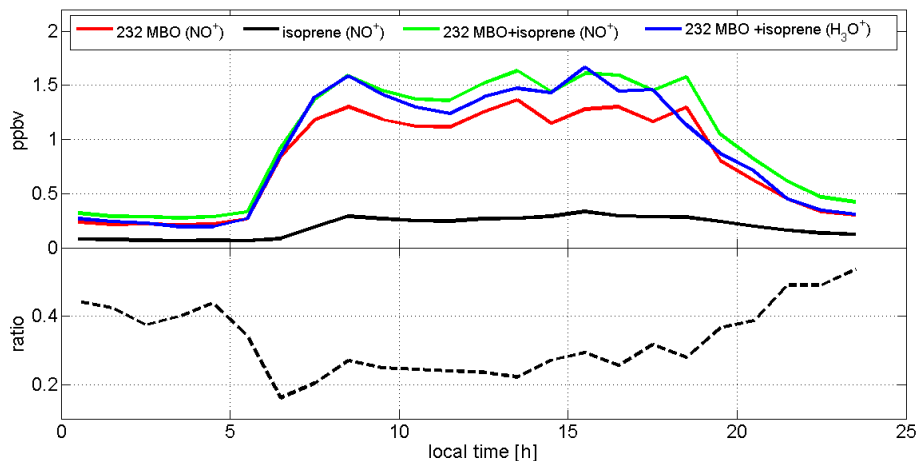


**Fig. 4.** Interference test: each measurement cycle represents a 1.5 s time interval; 232 MBO (green) and isoprene (blue) concentrations are varied as indicated in the graph. Error bars represent  $1 \sigma$ .

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**Fig. 5.** Diurnal concentrations of isoprene and 232 MBO using two PTR-TOF-MS instruments (upper panel); one instrument was operated in  $\text{H}_3\text{O}^+$  mode depicting 232 MBO + isoprene (blue trace); the other instrument was operated in  $\text{NO}^+$  mode separating 232 MBO (red) and isoprene (black). The sum of the two is also plotted for comparison (green trace). The lower panel depicts the ratio between isoprene and 232 MBO.

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