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*Supplement of*

## **Field observations of volatile organic compound (VOC) exchange in red oaks**

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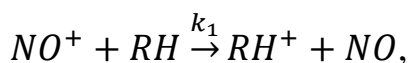
## S.1 PTR/SRI-ToF-MS operation and data analysis

VOC measurements were performed by a PTR/SRI-ToF-MS 8000 (Ionicon Analytik GmbH, Innsbruck Austria) equipped with a switchable reagent ion system (Jordan et al., 2009), allowing either  $\text{NO}^+$  or  $\text{H}_3\text{O}^+$  primary ion chemistry.

5 In  $\text{H}_3\text{O}^+$  mode the drift tube conditions were: 2.19 mbar drift pressure, 542 V drift voltage, and 60 °C drift tube temperature. The resulting  $E/N$  ratio was ca. 125 Townsend (Td) ( $N$  corresponding to the gas number density and  $E$  to the electric field strength; 1 Td= $10^{-17}$  Vcm<sup>2</sup>). The PTR-ToF-MS ion source produces  $\text{H}_3\text{O}^+$  primary ions at high purity, with a fraction of the spurious primary ions  $\text{NO}_+$  and  $\text{O}_2^+$  of 0.04-0.3% and 0.8-1.2%, respectively, with respect to the  $\text{H}_3\text{O}^+$  ion signal. The primary ion signal was  $1.1 \cdot 10^6$  cps and the percentage of first water clusters was about 19%. In  $\text{NO}^+$  mode the drift tube conditions were: 2.21 mbar drift pressure, 296 V drift voltage, 90 °C drift tube temperature. The resulting  $E/N$  ratio was ca. 74 Townsend (Td). The primary ion signal was  $1.2 \cdot 10^6$  cps. During the measurements the fraction of the spurious primary ions  $\text{NO}_2^+$ ,  $\text{O}_2^+$  and  $\text{H}_3\text{O}^+$  were 1.9-2.3 %, 0.1-0.5 % and 0.1-0.3 % respectively, relative to the  $\text{NO}^+$  signal. A time-of-flight (ToF) mass analyzer operated in its standard configuration (V mode) was used to separate and detect the ions exiting the drift region. The sampling time per bin of ToF acquisition was 0.1 ns, amounting to 350000 bins for a  $m/z$  spectrum ranging up to  $m/z = 400$ .

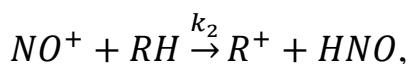
### 20 S.1.1 $\text{NO}^+$ chemistry in SRI-ToF-MS instrument

Previous ion chemistry investigations (Amelynck et al., 2005; Jordan et al., 2009; Knighton et al., 2009; Spanel and Smith, 1998) employing  $\text{NO}^+$  as primary ion have shown that four reaction pathways dominate. They feature charge transfer,



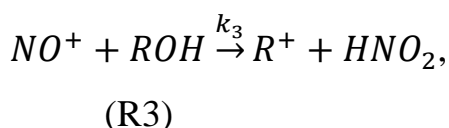
25 (R1)

hydride ion transfer,

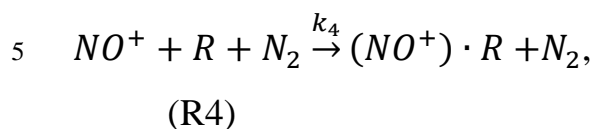


(R2)

hydroxide ion transfer,



and three body association reactions,



Isoprene and monoterpenes have ionization potentials lower than NO and charge transfer reactions with NO<sup>+</sup> ions (R1) occur at collision rates (Karl et al., 2012).

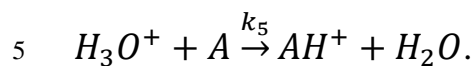
10 Reaction (R1) does not proceed for VOCs having ionization potentials higher than that of NO (9.26 eV) (Ebata et al., 1983).

The reaction of aldehydes with NO<sup>+</sup> typically proceeds mainly through hydride transfer (Eq. R2), whereas that of ketones is mainly through three body association (channel  
15 R4). As a result, in contrast to H<sub>3</sub>O<sup>+</sup>, NO<sup>+</sup> chemistry allows separation of isomeric ketones and aldehydes (Jordan et al., 2009). For example, in H<sub>3</sub>O<sup>+</sup> mode, MACR and MVK (C<sub>4</sub>H<sub>6</sub>O) are indistinguishable as both are detected in the protonated ion form at m/z 71.049 (C<sub>4</sub>H<sub>7</sub>O<sup>+</sup>). In NO<sup>+</sup> mode MACR yields m/z 69.033 (C<sub>4</sub>H<sub>5</sub>O<sup>+</sup>) from reaction R2 and, at a much reduced rate, m/z 100.039 (C<sub>4</sub>H<sub>6</sub>O·NO<sup>+</sup>) from reaction R4. MVK  
20 yields only m/z 100.039 from reaction R4 (Liu et al., 2013). Thus, concentrations of MVK and MACR can be independently determined (Liu et al., 2013). Acetone and MEK also proceed via three body association (R4) and yield ions at m/z 88.039 (C<sub>3</sub>H<sub>6</sub>O·NO<sup>+</sup>) and m/z 102.055 (C<sub>4</sub>H<sub>8</sub>O·NO<sup>+</sup>), respectively. Aldehydes such as acetaldehydes and benzaldehyde react at collision rate via mainly hydride ion transfer  
25 (R2). Methanol does not react with NO<sup>+</sup>.

### S.1.2 H<sub>3</sub>O<sup>+</sup> chemistry

The traditional operational mode of PTR/SRI-ToF-MS is H<sub>3</sub>O<sup>+</sup> ion chemistry, indicated as PTR-ToF-MS. We refer to the reviews on the subject for details (Blake et

al., 2009; de Gouw and Warneke, 2007). Briefly, the analyte gas mixture enters the drift tube, where molecules having a Gibbs energy of protonation (typically approximated with proton affinity) higher than water by more than 35 kJ·mol<sup>-1</sup> (Bouchoux et al., 1996) efficiently react with the H<sub>3</sub>O<sup>+</sup> primary ions by proton transfer



(R5)

Alkenes and oVOCs, including all of those in this study, typically exhibit proton affinities high enough for detection using H<sub>3</sub>O<sup>+</sup> ion chemistry.

### S.1.3 Spectral analysis

VOC concentrations were calculated from the ion signal at each corresponding mass-to-charge ratio. To correct for count losses due to the detector dead time, an off-line procedure based on Poisson statistics was applied (Cappellin et al., 2011a; Titzmann et al., 2010). An internal mass calibration procedure was used in order to achieve a mass accuracy better than 0.001 Th (Cappellin et al., 2010). Further processing included baseline removal and peak area extraction using the procedure described by (Cappellin et al., 2011b). An optimized peak shape determined from the measured spectra was used for fitting.

The instrument response to each VOC was calibrated using standard gas cylinders (Scott Specialty Gases/Air Liquide). Gas standard 1 contained isoprene (80.0 ± 5% ppm). Gas standard 2 contained isoprene (1.07 ± 5% ppm) and MACR (1.07 ± 5% ppm). Gas standard 3 contained MEK (1.09 ± 5% ppm), MVK (1.09 ± 5% ppm), acetone (1.09 ± 5% ppm), acetaldehyde (1.09 ± 5% ppm), and methanol (1.09 ± 5% ppm). The uncertainties of the calibration gases were ± 5%. Typical concentrations used for instrumental calibration were in the range 1-70 ppbv. For isoprene concentrations used for instrumental calibration were in the range 1 ppbv - 1 ppmv. Zero air generated as described previously was used for dilution. In the case of compounds for which gas standards were not available (benzaldehyde, 2-butanol, 3-buten-2-ol, monoterpenes), absolute concentrations were estimated with a theoretical approach (Cappellin et al., 2012) using reaction rates with the primary ion computed

at the set drift tube conditions (Su, 1994). Instrument sensitivities calculated with such method have been shown to agree with sensitivities determined experimentally within 10%, under certain instrumental conditions (Cappellin et al., 2012). In particular this is true when the identity of the compound and the fragmentation pattern are known. In some cases the chemical structure or fragmentation pattern is not known (e.g. monoterpenes) thus the expected uncertainty can increase. Moreover, some fragments can arise from multiple compounds (e.g.  $C_3H_5^+$ ). In  $H_3O^+$  mode the instrumental sensitivities were the following: 16.4 ncps/ppbv for isoprene, 27.1 ncps/ppbv for methacrolein, 28.7 ncps/ppbv for MVK, 28.0 ncps/ppbv for MEK, 40.0 ncps/ppbv for benzaldehyde, 21.4 ncps/ppbv for acetaldehyde, 25.8 ncps/ppbv for acetone, 13.2 ncps/ppbv for methanol, 28.5 ncps/ppbv for monoterpenes; where ncps are counts per second normalized to a primary ion signal of  $10^6$  cps. In  $NO^+$  mode the instrumental sensitivities were the following: 17.6 ncps/ppbv for isoprene, 16.4 ncps/ppbv for methacrolein, 21.0 ncps/ppbv for MVK, 26.5 ncps/ppbv for MEK, 43.7 ncps/ppbv for benzaldehyde, 13.3 ncps/ppbv for acetone, 29.9 ncps/ppbv for monoterpenes.

The spectral ion peaks employed to monitor the selected compounds are reported in Table S.1. Isoprene signal was monitored on the ion peaks 69.070 ( $C_5H_9^+$ ) for  $H_3O^+$  mode and 68.062 ( $C_5H_8^+$ ) for  $NO^+$  mode (Karl et al., 2012). At the site interferences from MBO in  $H_3O^+$  mode are negligible, given the species emitting the VOCs (Harley et al., 1998; McKinney et al., 2011). Methanol is detected at  $m/z$  33.033 in  $H_3O^+$  mode. Previous studies have established that it is free from contaminations (de Gouw et al., 2003; Warneke et al., 2003). In  $NO^+$  mode it was not possible to detect methanol as it does not react with the primary ion. MEK was monitored on the ion peaks 73.065 ( $C_4H_9O^+$ ) for  $H_3O^+$  mode and 102.055 ( $C_4H_8O \cdot NO^+$ ) for  $NO^+$  mode. Influence of butanal in  $H_3O^+$  mode might be present. However, no butanal has been found to be emitted by red oak branches (Helmig et al., 1999). Moreover, it has not been detected in past investigations using GC separation prior to PTR-MS analysis (de Gouw et al., 2003). Acetone was monitored on the ion peaks 59.049 ( $C_3H_7O^+$ ) for  $H_3O^+$  mode and

88.039 ( $C_3H_6O \cdot NO^+$ ) for  $NO^+$  mode. Influence from propanal in  $H_3O^+$  mode, although possible, is unlikely at the site (de Gouw et al., 2003; McKinney et al., 2011; Warneke et al., 2003), as it is a compound usually present in urban areas. Acetaldehyde is detected at  $m/z$  45.033 ( $C_2H_5O^+$ ) in  $H_3O^+$  mode. Acetaldehyde is not reported in  $NO^+$  mode as the main ion 43.018 ( $C_2H_3O^+$ ) is a common fragment, therefore not a reliable signal for acetaldehyde. The ion at  $m/z$  74.024 ( $C_2H_4O \cdot NO^+$ ), from the association reaction of acetaldehyde with  $NO^+$  had a weak signal and was discarded. Benzaldehyde was monitored on the ion peaks 107.049 ( $C_7H_7O^+$ ) for  $H_3O^+$  mode and 105.033 ( $C_7H_5O^+$ ) for  $NO^+$  mode. Given the relatively distinctive molecular formula of the aromatic benzaldehyde and the very good consistency between  $H_3O^+$  and  $NO^+$  data, influences on the signal from other compounds are not expected. Monoterpenes [generally constituted by numerous compounds sharing the same  $m/z$ , (Loreto et al., 1996)] were monitored on the ion peaks 137.132 ( $C_{10}H_{17}^+$ ) for  $H_3O^+$  mode and 136.125 ( $C_{10}H_{16}^+$ ) for  $NO^+$  mode. (de Gouw and Warneke, 2007) show that monoterpene measurements are free from interferences in  $H_3O^+$  mode. No contaminants are expected in  $NO^+$  mode.

In  $H_3O^+$  mode MACR and MVK lead to indistinguishable isomeric ions at  $m/z$  71.049 ( $C_4H_7O^+$ ). Moreover, isoprene hydroxy hydroperoxide isomers (ISOPOOH) decompose on instrument surfaces to form MVK or MACR, which is also detected at  $m/z$  71.049 (Liu, 2015; Liu et al., 2013; Rivera-Rios et al., 2014). As discussed in Section S.1.1, in  $NO^+$  mode MACR is detected mainly at  $m/z$  69.034 ( $C_4H_5O^+$ ) with a small contribution at  $m/z$  100.039 ( $C_4H_5O \cdot NO^+$ ) whereas MVK is detected only at  $m/z$  100.039. The isoprene hydroperoxide isomers 4,3-ISOPOOH (ISOPDOOH) and 3,4-ISOPOOH (ISOPCOOH) decompose to MACR and so can also produce a signal at  $m/z$  69.034 (Liu et al., 2016; Rivera-Rios et al., 2014). ISOPCOOH concentrations are, however, not relevant under atmospheric conditions and can be neglected. Therefore this peak corresponds to MACR + ISOPDOOH. Analogously, in  $NO^+$  mode 1,2-ISOPOOH (ISOPBOOH) produces MVK which yields product ions at  $m/z$  100.039

(Liu et al., 2016; Rivera-Rios et al., 2014). After correction for the contribution from MACR + ISOPDOOH, the peak at 100.039 thus corresponds to the sum MVK + ISOPBOOH.

5 In  $\text{H}_3\text{O}^+$  mode alcohols commonly undergo proton transfer reactions often followed by the elimination of a water molecule, while in  $\text{NO}^+$  mode alcohols typically react via hydride ion transfer (Spanel and Smith, 1997). In the ancillary fumigation experiments the alcohols 2-butanol and 3-buten-2-ol were monitored on 73.065 ( $\text{C}_4\text{H}_9\text{O}^+$ ) and  $m/z$  71.049 ( $\text{C}_4\text{H}_7\text{O}^+$ ), respectively, in  $\text{NO}^+$  mode. In  $\text{H}_3\text{O}^+$  mode they were monitored on  
10  $m/z$  57.070 ( $\text{C}_4\text{H}_9^+$ ) and 55.054 ( $\text{C}_4\text{H}_7^+$ ), respectively (Spanel and Smith, 1997).

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## 5 Supplementary tables

**Table S.1.** Ions employed to monitor the selected volatile compounds/species by means of SRI-ToF-MS in either  $\text{H}_3\text{O}^+$  or  $\text{NO}^+$  mode.

	$\text{H}_3\text{O}^+$ mode	$\text{NO}^+$ mode
Isoprene	$\text{C}_5\text{H}_9^+$	$\text{C}_5\text{H}_8^+$
MACR	$\text{C}_4\text{H}_7\text{O}^+$	$\text{C}_4\text{H}_5\text{O}^+$
MVK	$\text{C}_4\text{H}_7\text{O}^+$	$\text{C}_4\text{H}_5\text{O}\cdot\text{NO}^+$
MEK	$\text{C}_4\text{H}_9\text{O}^+$	$\text{C}_4\text{H}_8\text{O}\cdot\text{NO}^+$
Benzaldehyde	$\text{C}_7\text{H}_7\text{O}^+$	$\text{C}_7\text{H}_5\text{O}^+$
Acetaldehyde	$\text{C}_2\text{H}_5\text{O}^+$	
Acetone	$\text{C}_3\text{H}_7\text{O}^+$	$\text{C}_3\text{H}_6\text{O}\cdot\text{NO}^+$
Methanol	$\text{CH}_5\text{O}^+$	
Monoterpenes	$\text{C}_{10}\text{H}_{17}^+$	$\text{C}_{10}\text{H}_{16}^+$

## 10 Supplementary figure captions

**Figure S.1.** Picture of a (top of the canopy) branch enclosure employed in the experiments.



**Fig S.1**