

Field observations of Volatile Organic Compound (VOC) exchange in red oaks

General comments:

Cappellin and coauthors present 42 days of VOC measurements above a mixed red oak forest in central Massachusetts. The measurements consisted of 22 days of concentration profile, followed by 20 days of branch chamber measurements, where the last day was used for fumigation. In the results 6 different VOCs and 2 VOC groups are presented. The manuscript meets the scope of the journal and can be accepted for publication after addressing following comments:

Specific comments:

Did the authors present all VOCs that showed exchange? If not, how many were measured and what was the selection criteria?

P6 L14: as it is a mixed forest: what are the major tree species? This information can be helpful for the interpretation of the concentration profiles and the flux upscaling.

P7 L21 & P9 L9: randomly cycle between the inlets -> what are the benefits of randomly cycling? Isn't it disadvantageous, that e.g. the highest inlet could be measured for 1 h in a row, while a lower inlet would be measured with a 1:40 h gap? Please rephrase so it is more clear that random cycling means that all four heights were sampled in a random order during 1 h of measurements (and not, that random means that e.g. one height could be measured multiple times during 1 h).

P9 L24 – P10 L5: The fumigation experiments are not well described here, please specify:

- in which mode was the instrument used (according to P15 L20 it was NO^+ , but it is not clear if also H_3O^+ was used),
- the used concentrations (in the gas cylinders)
- the target VOCs
- what was the final concentration or dilution which was delivered to the branch enclosure?
- how long did it take (in average) until the signal was stable?

This information is important for the reader.

P10 L7: 2.4 PTR/SRI-ToF-MS operation and data analysis: Please state typical primary ion counts for H_3O^+ and NO^+ mode and add the percentage of the first water cluster (in the H_3O^+ mode).

P13 L9-13: What were the uncertainties of the calibration gas? What were typical concentrations/dilution used for calibrations and could the authors state the used sensitivities (measured and calculated)?

P13 L18: Please reformat this sentence, as the reader could get the impression that the uncertainty of the calculated sensitivity is 10%. While I guess the author means that the calculated sensitivity is within 10% of the experimental estimated sensitivity (which has a 15% uncertainty). Otherwise the reader could believe that calculating a sensitivity is actually better (less uncertainty) then getting it via calibration. Please also state that the cited study was measured in a laboratory with known compounds and known fragmentation patterns. Whereas here the chemical structure is not known (e.g. monoterpenes) and fragmentation patterns vary. Additionally fragments cannot be assigned to one compound, as many compounds fragment to the same masses (e.g. C_3H_5^+ ; $\text{C}_2\text{H}_3\text{O}^+$; C_6H_9^+). Please remove the "Mueller et al., 2014" reference, as it just very briefly names the theoretical approach, but doesn't compare calculated with theoretical sensitivities.

P15 L19: It is true that 2-butanol is measured in the H_3O^+ mode at M 57.070 (C_4H_9^+). But there could be a potential influence from protonated butene, which is known to be emitted from trees (e.g. Hakola et al., 1998). Was this considered (and dismissed by comparison with the NO^+ measurements)? Were there any interferences from the water cluster (H_7O_3^+) when measuring 3-buten-2-ol in the H_3O^+ mode?

P17 L13: Have there been more studies which showed ecosystem MVK + MACR emissions from oak forests since 2005?

Technical corrections:

P3 L3 & following: order of references: chronological; here: (Guenther et al., 1995; Benkovitz et al., 2004). (The references at the end of the manuscript are sorted alphabetically).

P3 L8: forming -> to the formation of

P4 L21: quite toxic -> toxic

P7 L3: NO_y -> NO_y (y subscript)

P7 L14 & following: inch -> metric units (SI units), please change all imperial units to SI units.

Please have a look at: http://www.atmospheric-chemistry-and-physics.net/for_authors/manuscript_preparation.html at the “Mathematical notation and terminology”

P7 L18 & following: slm -> L min⁻¹

P8 L3-4: remove bold format

P8 L8: (See Section 2.4 for details) -> (see Sect. 2.4)

P8 L9: Palladium -> palladium

P8 L18: [version 1.47, (Schneider et al., 2012)] -> (version 1.47; Schneider et al., 2012)

P8 L18: A fourth bag not containing a branch was -> A fourth, empty enclosure was

P8 L24: Bios DryCal Flow Calibrators -> please specify the used type

P9 L4: to achieve residence times of 38s -> please specify that the residence time belongs to the enclosure

P9 L17: in the empty bag -> empty enclosure

P9 L21: (See Section 2.4 for details) -> (see Sect. 2.4)

P10 L1: flow controllers (MKS instruments) -> please do not state just a company, always add the used type of instrument

P10 L20-21: ...per channel350,000 channels -> “bin” is a more common used word (e.g. Graus et al., 2010) as channels could be confused with the channels in the MCP; -> 350 000 in the remaining manuscript not thousand-separator was used (see Table 1 & 2; Fig 01)

P11 L5 & following: (5a), (5b),... please start with 1 (not 5) and proceed from there. For chemical reactions (R1), (R2),... is used.

P11 L24 & following: (channel 5b) -> (Eq. R2)

P16 L4 & following: Figure 1 -> Fig. 1 (Figure X is just used when starting a sentence, otherwise Fig. X is used)

P28 L23-24: [see e.g. (Omasa et al., 2002)] -> (e.g. Omasa et al., 2002)

P32 L11: stages, In -> stages. In

Table 1 & 2: [nmol/m²/s¹] -> [nmol m⁻² s⁻¹]

please change the average daytime emission of ISOP to 2±1 x10⁴ (same for average 24h emission)

if there was no isoprene flux during night, please change 0.0 ± 0.0 x10⁵ to 0; if there was a flux then please give proper values (same goes for maximum deposition rate)

Table 3: [mol / (m³·Pa)] -> [mol m⁻³ Pa⁻¹]

Fig03 & Fig07: please use same notation for axis label units []

Fig 03,04,06: state the fit parameters in the figure (legend)

References:

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, 2010.

Hakola, H., Rinne, J. and Laurila, T.: The hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*), *Atmos. Environ.*, 32(10), 1825–1833, doi:10.1016/S1352-2310(97)00482-2, 1998.

Müller, M., Mikoviny, T. and Wisthaler, A.: Detector aging induced mass discrimination and non-linearity effects in PTRToF-MS, *Int. J. Mass Spectrom.*, 365–366, 93–97, doi:10.1016/j.ijms.2013.12.008, 2014.