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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compounds in the Western Mediterranean Basin: urban and rural winter measurements during the DAURE campaign" *by* R. Seco et al.

Anonymous Referee #1

Received and published: 24 January 2013

This is an excellent paper showing important measurements and analysis of VOC concentrations at two different locations differing in anthropogenic influences and with the focus on winter period. The story fits well with the other papers from the DAURE campaign. I would just have a few comments to be addressed and then I would like to recommend the article for publication in ACP.

1) Heights/elevations. Since the paper discusses the concentrations (rather than the fluxes), my suggestion is to be more clear about the heights and their possible effects on concentrations. For a constant flux (assuming there is no flux divergence), larger turbulent eddies at higher altitudes generally lead to lower concentrations. The sites

were located at different heights a.s.l., 80 and 720 m. Would different elevations have any impact on the observed differences in the concentrations? From p. 30915 l.12 it seems that the inlets were at 3 m at both sites. Please make it clear in the text above what (ground, vegetation, roof)?

2) Lifetimes. Although reactive compounds such as isoprene are characterized by a relatively small concentration footprint, methanol and compounds with long atmospheric life times may have remote sources. It might be worth discussing potential effects of the lifetimes on the interpretation of the results.

3) Acetic acid (MSY). This reviewer has a reservation to the quantification method of acetic acid from the PTR-ToF-MS. Table 1 footnote b: "These sensitivities were not measured in calibrations, and acetone sensitivity was used instead (divided by 2 in the case of acetic acid because of the fragmentation on m/z 43.02, see Langebner et al., 2012)." The approach taken from the cited paper in preparation might be of concern. I refer the authors to Haase et al., 2012 who reviewed and showed that the sensitivity ratios of the parent ion (m/z+ 61) and dehydrated CH3CO+ (m/z+ 43) in acetic acid calibrations ranged from 0.04 to 7.6 in various studies. Does the factor 2 come from the calibration on the same instrument? Therefore, I guess the reported concentrations at the MSY site may have been different at the two sites. Given such a high uncertainty, it is suggested to either conduct a lab calibration at the same drift-tube conditions and humidity, or omit acetic acid results from the MSY site .

4) Ethanol (BCN). This reviewer is surprised with the high sensitivity for ethanol (10.9 ncps/ppbv) and low detection limit (79 ppt) for such a high E/N ratio (140 Td). Lab studies suggest optimal sensitivity for ethanol at 90 Td (e.g., slide 8 in Galbally et al., 2010). At 140 Td the sensitivity can be one order of magnitude lower possibly due to fragmentation into H3O+. Therefore, the sensitivities closer to those reported for the PTR-ToF instrument at the MSY site would be expected. For the sake of data quality, it is strongly recommended to either use the calibrated sensitivity from this instrument at the same E/N ratio or to use another approach which accounts for fragmentation.

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Otherwise, quantification of ethanol should be omitted from the BCN site.

5) Uncertainties. Please either add a note or reference on estimated uncertainties, or/and add error bars to the figures. Concentrations of compounds derived from calibration and transmission may have different uncertainties.

6) Scenarios. This reviewer likes the identified atmospheric scenarios and their discussions. Please revise acetic acid and ethanol though, with respect to 3) and 4).

technical:

7) p.30914 l.2 change “measuring” to “measurements”

8) P.30914 l.15 replace “We here” with “Here, we”

Literature:

Galbally et al., A re-analysis of the capacity of PTR-MS to uniquely identify and quantify VOCs in global background air. GAW Reactive Gases Workshop Helsinki, June 2010. http://www.wmo.int/pages/prog/arep/gaw/documents/Galbally_GAW_VOC_2010.pdf accessed January 2013.

Haase, K. B., Keene, W. C., Pszenny, A. A. P., Mayne, H. R., Talbot, R. W., and Sive, B. C.: Calibration and intercomparison of acetic acid measurements using proton-transfer-reaction mass spectrometry (PTR-MS), Atmos. Meas. Tech., 5, 2739-2750, doi:10.5194/amt-5-2739-2012, 2012

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 30909, 2012.