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Atmospheric Measurement Techniques Discussions

Interactive comment on "A method for real-time profiling of organic trace gases in the planetary boundary layer" *by* R. Schnitzhofer et al.

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The authors want to thank the anonymous reviewers for their good comments and suggestions that helped to improve the quality of the manuscript.

Anonymous Referee #1

I think this is an important piece of work that shows it is possible to make accurate profiles of various atmospheric compounds in the lower part of the boundary layer. It

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Interactive Discussion

Discussion Paper

would greatly increase our understanding of processes in the (polluted) boundary layer if these experiments could be repeated at other sites. However, there are probably legal limitations on how high you can fly a tethered balloon (or parafoil kite) at most sites, and specifically on sites in an industrial (and thus polluted) environment. Also prior permission from air traffic control could be required. In my opinion the authors should put a word of warning about this in the paper.

REPLY: The legal limitations concerning air traffic control are mentioned in section 3.2.

Specific comments ==========

In section 1, an example of a small sensor is given. Another example is of course the widely used ECC ozone sensor used in ozonesondes.

REPLY: This instrument is mentioned in the revised version of the manuscript. “Examples are the miniature aerosol spectrometer (GRIMM 1.108 “Dustcheck”, 2.4 kg, GRIMM Labortechnik, 1996), which determines the aerosol mass for 15 different size bins (compare Malletto et al., 2003) or the wildly used ozonesonde “ECC ozone sensor” developed by Kohmyr (Kohmyr 1971).”

In section 2.2 the 200 meter Teflon tube is discussed. I assume all experiments were done with a brand new tube. I wonder how this tube will behave after some time, when dust (from aerosols) starts to accumulate in the tube. Have the laboratory experiments been repeated after the field campaign?

REPLY: The Teflon tube was not brand new, as it was already used by for the proof of principle during the Arctic Ocean Experiment in 2001 (AOE-2001). After some years carefully stored it was flushed with purified and humidified air for several days. The line tests were performed during and after the INNOX-2006 field campaign, where no aging effect was realised.

In section 3.1 the unit "m/z" is used without an explanation. I understand that this is completely trivial to the authors, but even so, "m/z" must be properly introduced.

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REPLY: In the revised version of the manuscript m/z is explained in detail. “The signal at m/z 59 showed a slight increase (+7%) when the line was connected indicating that acetone (or propanal/glyoxal which are also detected at m/z 59) is produced in the line (line contamination, formation due to chemical reactions, permeation through the Teflon line). Hereby m/z denotes the dimensionless quantity formed by dividing the mass of an ion (m) in unified atomic mass units by its charge number (z).” Farther in the text m/z is written in italic letters as proposed by the International Union of Pure and Applied Chemistry (IUPAC; Murray, et al. 2006).

Later on in paragraph 3.1 it is suggested that toluene might condense in the Teflon line (tube?). Although toluene can condense at 0 °C, it will not do so under normal atmospheric conditions. I think the correct verb here is "to adsorb". It should be noted that the system is used at a much lower temperature than the 0 °C by which is was tested.

REPLY: In the revised version of the manuscript this part is adjusted. “. . .indicating that toluene partly adsorbs on the wall at 0°C. Note that the system was in use at even lower temperatures (-12°C) during the INNOX-2006 field campaign described in Section 3.2.”

In table 1, a list is made of the 50% rise and fall times of the relevant compounds. I think this should be compared to the theoretical value, for compounds that do not adsorb to Teflon. From the data in the paper I conclude that the volume of the inlet system is 3.7 liters, at a flow of 7 l/s this would result in a 50% rise time of 31.4 seconds. Can the authors give a more accurate value? If this value is correct, 3 compounds in table 1 have a shorter rise time. Can this be explained?

REPLY: Due to the pressure drop along the line the flow-velocity increases towards the end. The calculated residence time in the 200 m long tube is 23.2 s. In addition to the 200 m line, there is a shorter inlet system with smaller flows into the PTR-MS, which has to be accounted as well. In section 2.2 we added the sentence: “The calculated residence time in the 200 m long Teflon tube, including the effect of the pressure drop

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that increases the flow velocity towards the end, is 23.2 s."

In Figure 2, it is unclear which of the lines represent ascending, resp. descending measurements. For some -but not all- this can be found in the text. I would like to see this made clear in the graphs (either in the legend, or with an arrow near the lines).

REPLY: Which of the lines represent ascends and descends is explained in the legend of Fig. 2 in the revised version of the manuscript.

Technical corrections ==========

(please note that I am not a native English speaker) Consider the following changes: teflon -> Teflon ; radiotransmitted -> radio transmitted ; vaccuubrand -> vacuubrand ; sentitive -> sensitive ; implicantions -> implications ;

REPLY: The typos have been corrected in the revised version of the manuscript.

Anonymous Referee #2

Schnitzhofer et al. describe a tethered balloon sampling method adjunct with PTR-MS, an useful and economical vertical profiling method in the very bottom of the planetary boundary layer. Technical descriptions along with laboratory explorations on possible artefacts from the long sampling line are the main highlights of this paper and the authors show some air pollutant profiles during the wintertime inversion event. As PTR-MS has been utilized ax a standard analytical tool to measure VOC distributions in the atmosphere, the contents of this research article can provide useful information to expand research horizon of the PTR-MS user community. However, authors tend to provide incomplete information for their data analysis. This could potentially cause confusions of readers, who have intention to apply the method in their research. I, therefore recommend authors to provide more details to the points, described below.

Page 1771 The title is not informative to grasp ideas what the research paper is about. At least, "tethered balloon" and "PTR-MS", two important words in this paper are desirable to be included in the title of this paper.

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REPLY: The title has been complemented in the revised version of the manuscript. “Real-time profiling of organic trace gases in the planetary boundary layer by PTR-MS using a tethered balloon”

Affiliation: Institut ->Institute

REPLY: The typo has been corrected in the revised version of the manuscript.

Page 1722 Abstract: It is desirable to include quantitative information in the abstract for the readers, who cannot make an extra time to read the whole paper. In the context, I recommend to add more information such as tested compounds, possible positive and negative artefacts, and caution for the readers, who plan to apply the method for their research.

REPLY: The abstract has been adapted in the revised version of the manuscript. “Positive and negative artefacts of the inlet line were characterised in the laboratory and in the field with a set of 11 different VOCs including both pure and oxygenated hydrocarbons. The only two compounds that showed a significant effect during this test were acetone (+7%) and xylene (-6%).”

Line 13 add previous publications that applied the tether balloon method the end of the first sentence.

REPLY: References were added in the revised version of the manuscript. Stull, R.B.; An Introduction to Boundary Layer Meteorology; Kluwer Academics Publishers; 1988

Line 19-21 an important role: Please briefly describe roles of VOC in the atmosphere such as ozone and aerosol formation in terms of local air quality to global climate implications. Line 21 Although Fehsenfeld et al (1992) could be one of the good references for VOC research in the atmosphere, there are a number of up-to-date references for the topic. Please list recent studies and summarize what we have learned from the studies.

REPLY: More information on the role of VOCs is added in the revised version of the

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manuscript. “They play a crucial role in the tropospheric ozone production (e.g. Monks et al. 2009) and in the formation of secondary organic aerosol (e.g. Monks et al. 2009, Hallquist et al. 2009). Some VOCs were recognized to have severe health effects (WHO 2000).”

Line 25-26 a helicopter observation platform (http://hop.pratt.duke.edu/publications_and_presentations) could fill the gap between fixed wing platform and ground born measurements.

REPLY: A sentence has been added in the revised version of the manuscript. “In principle this gap could be filled by helicopter-borne measurements, which are rather expensive as well, and expected to influence small scale gradients by artificially increasing the turbulence.”

Line 15. Although authors can direct readers to other references for further information, a research paper should contain all the core information, which is necessary to understand the framework of the research. Since “proof-of-principle” of the previous study (Jensen et al) can enhance reader’s understanding on the analytical method of this research, I recommend to summarize what “proof-of-principle” is at least briefly.

REPLY: More information has been added in the revised version of the manuscript. “. . .the proof-of-principle, by measuring acetone profiles in the arctic environment, we have. . .”

Line 25 (i.e. most VOCs) -> (most VOCs except alkane compounds) could be more specific. Add proton affinity of water.

REPLY: This information has been added in the revised version of the manuscript. “. . .that have a higher proton affinity than water (691 kJ mol-1; i.e. most VOCs except alkanes).”

Line 26 a quadrupole mass spectrometer-a quadrupole mass filter-SEM detector system.

REPLY: In the revised version of the manuscript this part has been changed to:

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"...analysed and detected by a quadrupol mass filter secondary-electron-multiplier (SEM) detector system."

Page 1774 Add a figure, schematically describe the system in the section 2.2. That can be much effective way to illustrate the method.

REPLY: A schematic drawing of the experimental setup is now shown in Fig. 1. The text in section 2.2 has been changed accordingly.

Line 25 Add information on the residence time of the sampled air in the Teflon tube.

REPLY: In the revised version of the manuscript we added the sentence: "The calculated residence time, including the effect of the pressure drop, in the 200 m long Teflon tube alone is 23.2 s."

Page 1775 Line 1-10 Describe more thoroughly how you "spiked" the gas standard and maintained the concentration levels of 4 to 12 ppbv. What was the duration of the standard addition?

REPLY: More information has been added in the revised version of the manuscript. "...VOCs (including both pure and oxygenated hydrocarbons) was spiked with 50 sccm into about 7 SLPM of air. The volume mixing ratios (VMR) of the VOCs diluted in pure nitrogen in the standard were a few ppmv (depending on the compound), resulting in VOC levels in the rage of 4 to 12 ppbv."

Line 10-15 What are the uncertainties in measurements of xylene and acetone? Some portions of the "+7%" and "-6%" of artefacts may be explained by the uncertainties?

REPLY: The precisions (1 Sigma) of the measurements are 0.6% at a count rate of 1000 cps (acetone) and 0.7% at a count-rate of 700 cps (xylene).

Line 13 Discuss plausible mixing ration ranges of glyoxal and propanal at the study site in the winter time. Further discussion on possible interference estimations based on the proton transfer reaction constants of the compounds can provide more solid proof

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for the assumption of interferences.

REPLY: The ambient mixing ratios of glyoxal and propanal during this study are expected to be very low, as both compounds were not detected by GC measurements during the INNOX-2006 campaign.

Line 16-22 What were the ozone levels during the experiments?

REPLY: The ozone levels during the INNOX-2006 were usually very low, typically 5 ppbv.

Line 23 to the end of the section: readers could have better understanding about the discussion by adding a figure, showing temporal variations of counts from analytes for the experiments

REPLY: We feel that the paper would not significantly benefit from an additional figure showing the time series of the line characterisation. An example of the line tests to analyse the response time of certain VOCs is now plotted in Fig. 3.

Page 1776 Describe notable characteristics of the research region. Is it industrialized area or suburb or rural area? What are the dominant VOC emissions around the area?

REPLY: More information has been added in the revised version of the manuscript. “Beside, residential heating during wintertime the A-12 motorway is the main pollution source in the region.”

Table 1. As pointed out above, at least one example of the temporal variation of counts during the experiments is desirable to understand what the numbers in the table mean.

REPLY: A figure has been added in the revised version of the manuscript. The text in section 3.1 has been changed accordingly.

Fig 1. It is hard to read the differences due to the relatively wider range of mixing ratios. I would suggest changing y-axis as ratios of with/without 200 m Teflon line.

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REPLY: WE adjusted the figure in the proposed way and looking at it we had the impression that it is more complicated. Therefore we did not change this figure.

References:

Murray, K.K., Boyd, R.K., Eberlin, M.N., Langley, J.G., Li, L., Naito, Y.; Standard definitions of terms relating to mass spectrometry, IUPAC Recommendatios 2006 (available at: http://www.iupac.org/reports/provisional/abstract06/murray_prs.pdf)

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