Author´s response to AMT review - first stage (Response to reviewer #2) Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-412, 2017

"Preparation and analysis of zero gases for the measurement of trace VOCs in air monitoring"

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The authors are grateful to referee#2 for his time and effort in evaluating this manuscript and for his constructive suggestions for improvements. All points made by the reviewer are addressed on the following pages. Concerning the proposal to publish this work as a technical note, we do no oppose but would like to leave this decision to the editor.

Referee #2

Comment 1:

In summary, the results presented are suitable to be published in AMT but as a Technical Note after streamlining the results presented together with an Electronic Supplement. The experiments conducted are tests with already available techniques for purifying air and thus no clear innovative approach is presented which may merit a publication as a full paper. The "introduction" should be condensed with finally leading to the research questions. The author team should justify their selection of the used purifying techniques.

Response:

We now provide a supplement and the introduction was condensed. We removed the part describing several methods for generating hydrocarbon free air. Instead we just listed the different principles with some references for the interested reader.

p.2 lines 8ff:"Commonly used purification technologies in atmospheric monitoring include but are not limited to gas purifiers based on inorganic media (e.g. Conte et al., 2008) or activated carbon (Van Osdell et al., 1996; Sircar et al., 1996), metal catalysts (Liotta, 2010; Heck et al., 2009) andphotocatalytical techniques (Debono et al, 2013; Huang et al., 2016) ."

The research question we address is the application of suitable gas purifiers for ambient VOCs monitoring stations – a respective line was added into the last paragraph of the introduction, where the selection of purifying techniques was justified:

p.3 lines 1-3:

" In this study, three purifiers were selected to test their removal efficiency of a defined amount of VOCs to be applicable for ambient air monitoring stations. An adsorption cartridge with an inorganic media was selected for low-cost zero gas production without the need of electricity. In addition, the commonly used catalytic technique with an infinite lifespan has been tested for two types of catalyst."

Comment 2:

In the "experimental" part all commercial suppliers of materials should be listed.

Response:

The supplier of the adsorption cartridge did not agree to have the trademark published. We added a remark referring to this in p.3 line 6-7:

"…specified by the manufacturer (it was agreed not to publish the name and trademark)."

Comment 3:

Details of the analytical systems used in the experiments should be reported in the supplement, likely in a Table.

Response:

We provided the requested table with information on the used gas chromatography instruments in the supplement (Table S1).

Comment 4:

The "data analytical details" chapter should be moved to the supplement as well as Table 1 and Table 2. A summary of the applied techniques is sufficient as part of the experimental/method section.

Response:

We moved chapter 3 together with Table1 1and 2 to the supplement. In section 2, p.4, lines 1-2 we added the applied method how detection limits were derived:

"Detection limits for all systems were determined using IUPACs method based on the Neyman–Pearson theory of hypothesis testing (IUPAC, 1995, Section S2 in the supplement)."

Comment 5:

The "results and discussion" part should focus on the performance of the purifying systems only. Additional information should be moved to the supplement. Figures 2 and 3 can be skipped. Figures 4, 5 and 6 may also be skipped or moved to the supplement, Figure 7 should be moved to the supplement.

Response:

We condensed the chapter and moved Figures 2 to 7 to the supplement.

Comment 6:

In the "conclusion" part of the paper please avoid duplication of the abstract and focus on aspects users of air purification systems should consider.

Response:

We shortened the conclusion and focused on the main points of the paper:

p.10, line 1ff:

"Two tested catalysts in this study were able to remove a large range of different VOCs. High mole fractions up to 50 nmol/mol were purified and residual concentrations were below the detection limits of the systems going down to less than 1 pmol/mol for NMHCs.

The tested adsorption cartridge was not suitable to remove light NMHCs (C_2 to C_4). There was a breakthrough behaviour of these compounds which was not constant. Also, VOC memory effects were observed. To characterise these effects repetition of measurements (> 5) would be of an advantage. However, it removed heavier VOCs, OVOCs and monoterpenes. An advantage of the adsorption cartridge is the lack of electricity. It could be a good alternative for applications where the breakthrough of light VOCs is of no relevance. A big disadvantage is the high influence of humidity on the lifetime of this kind of purifier. The tested model in this study was only adequate for use with very dry air up to maximum 1 µmol/mol water content. With this awareness it is highly recommended to enquire the maximum applicable water content of the used gas from the manufacturer of a purifier.

Finally, zero gas is often produced by compression of ambient air which constitutes a complex matrix with residual humidity. The cleaning process to receive high purity zero gases is a challenge to any purifying system. It is highly important to explicitly examine a gas purifier for its intended application. Tests should be done at the given conditions, e.g. the same flow rates and the same gas matrix with special focus on given target component concentrations and humidity. For the tests, measurement systems with adequate detection limits are essential. Potential internal blanks have to be detected and well characterised. Their long-term behaviour has to be controlled, especially for the enduring use in air quality monitoring stations".