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Comment

Interactive comment on “Diffusion of volatile organics through porous snow: impact of surface adsorption and grain boundaries” by T. Bartels-Rausch et al.

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We'd like to thank the referee for the valuable suggestions and critical comments. We have rewritten the parts of the manuscript that must have been misleading. Please find our detailed responses below.

1) In the abstract the authors stated that the structure of snow was analyzed by means of X-ray computed micro-tomography. Why later in the experimental method section 2.1 a polarized microscope was used and what is the role of diethyl phthalate?

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The porosity and the tortuosity of both snow samples were derived based on X-ray computed micro-tomography reconstructions. This analysis needed no preparation of the sample. From these images the contact area of individual snow spheres can in principle also be deduced, but this was not done in this work. Rather, thin sections were analysed under a polarized microscope to quantify the grain boundary area. The advantage is that with this method grain boundaries within the individual snow spheres can also be analysed. To reveal the total grain boundary content of the sample with this method, the porous snow sample was stabilized for cutting thin sections. This is done using diethyl phthalate that fills the pores and solidifies so that thin sections can be cut.

We have clarified this both in the abstract and in the experimental section. We added additional references referring to the method.

6) Section 3.3, p 6146 lines 25 -28, since the authors did not characterize the total grain boundary of the snow-maker snow samples then how valid is the comparison between snow-maker snow and shock frozen snow?

We agree that experimental data to support the stated grain boundary content of the snow-maker snow would be mandatory to derive a quantitative correlation of grain boundary content with diffusivity. And we can assure that this was planned, but not done due to technical difficulties (The snow samples accidentally melted before the analysis was done).

Further, as no difference in the diffusivity between the two samples was observed we concluded that variations in grain boundary content are irrelevant for the diffusion behaviour of gases through porous snow. For this reason, a correlation between grain boundary content and diffusivity cannot be given and thus the grain boundary content of the snow-maker snow does not need to be known with highest precision. We believe that the comparison is thus valid.

Furthermore, we argue that the overall uncertainty in the grain boundary content of

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the snow-maker snow is small as the snow-maker snow formed by nucleation of water from the gas-phase making the formation of polycrystalline snowflakes very unlikely. This key-difference in preparation of the two snow samples makes them very different in their grain boundary content.

2) Can the authors provide a sentence or two to explain the purpose and why NO was used in their experiments?

The diffusivity of NO through porous snow is well established and the observed diffusion profiles were used to discard experiments where the structure of the snow sample was damaged during preparation, or where the sample holder was not gas-tight.

We give this information when we first mention the use of NO in the revised manuscript and also add the NO source in Figure 1.

3) In section 2.2, the authors mentioned that before entering the snow diffusion chamber, the gas flow was cooled by passing it over an ice surface. How sure are the authors that a portion of their acetone or methanol was not adsorbed on this ice surface prior to entering the snow diffusion chamber? And did the authors account for this loss?

We apologize for this misleading sentence. The carrier gas was humidified before the VOC were added. Otherwise, methanol and acetone would certainly have adsorbed to the ice in the humidifier.

We have changed the description of the experiment accordingly.

4) A number of groups using different experimental techniques have shown that liquid like layers can exist at temperatures as low as 243 K. At a temperature of 263K, a liquid layer has to be present why did the authors kept referring to their ice surface as dry ice? With this layer present, I would guess that the solubility of methanol and acetone will be different, why did the authors explain the fast recovery of methanol at 263 as an artifact by CIMS (p:6144) and not due

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to presence of the liquid layer (solubility, chemistry, etc).

7) In section 3.2 (P: 6145, lines 10-15), the authors stated that the dissolution of these volatile species in the disordered layer on the surface of ice is not an important factor; however, in section 5 (p:6150, lines 6-7) the author surface adsorption dominates as long as water layers are not present. I think the authors here are giving contradictory statements.

The diffusion of trace gases through the open pore space is always a combination of gas-phase diffusion through the open pore space and interaction with the ice surface. If interaction with the ice surface occurs, this can only slow down the diffusivity compared to the diffusivity of non-interacting gases, but it can't accelerate diffusion beyond the diffusivity in the gas phase alone. For this reason, we concluded that the surface disorder or qll couldn't explain the observation of faster recovery.

We further like to emphasise that qll does not mean that a true liquid covers the ice, i.e. it is not a 3 phase system, only solid ice and the gas-phase are present (dry snow). In field studies, partial melting of the snow often occurs (wet snow). Working with snow made from clean water, we can exclude the presence of melt water in our experiments. The results give no indication that the surface disorder leads to a significant change in the sorption behaviour of methanol or acetone to snow.

Being an interface phenomenon the total volume of the qll is rather small, and the properties of the qll are different from liquid water. (It might still be valid to parameterize the interaction of some trace gases with the qll using properties of liquid water, but our results clearly show that there is no need to do so for these VOC's.) Thus results from this study cannot be applied directly to wet snow, where the fraction of melt water is much higher than the volume of the qll.

We have emphasized the difference of wet and dry snow more clearly in the introduction and explained our conclusion about the artefact in more detail. We hope that this also resolves questions 4 and 7.

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5) Henry's coefficient can change with temperature; did the authors take this into account when doing their simulation –Langmuir vs. Henry?

Yes, this was taken into account.

We have added this information to the discussion.

8) Since ice phase diagrams for a number of volatile species do not exist, do the authors know if acetone and methanol are in ice regime at 223 K? HCHO for instance is not.

Indeed, this is critical. We have ensured that we are in the ice regime at higher temperatures (i.e. concentrations of VOC are too low to induce melting). Other studies have shown that adsorption of methanol and of acetone to ice can be well described by surface adsorption to ice in the temperature range of 195 to 230 K (for both species; Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J. and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V — heterogeneous reactions on solid substrates, *Atmos. Chem. Phys.*, 10(18), 9059–9223, doi:10.5194/acp-10-9059-2010, 2010.) This might indicate that we have been working within the ice stability regime. Direct experimental proof that we worked in the ice stability regime comes from our earlier spectroscopic investigations of the adsorption of acetone to ice at 218 K (Starr, D. E., Pan, D., Newberg, J. T., Ammann, M., Wang, E. G., Michaelides, A. and Bluhm, H.: Acetone adsorption on ice investigated by X-ray spectroscopy and density functional theory, *Phys. Chem. Chem. Phys.*, 13(44), 19988–19996, doi:10.1039/c1cp21493d, 2011.)

We have added this information to the manuscript.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 6131, 2013.

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