Atmos. Chem. Phys. Discuss., 9, C6901–C6905, 2009
www.atmos-chem-phys-discuss.net/9/C6901/2009/
© Author(s) 2009. This work is distributed under
the Creative Commons Attribute 3.0 License.

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Acetaldehyde in the Alaskan subarctic snow pack" *by* F. Domine et al.

Anonymous Referee #1

Received and published: 9 November 2009

General comment

This article reports measurements of acetaldehyde in the Arctic snowpack near Fairbanks Alaska, from Dec. 2003 to April 2004. Based on the results, the location of this compound in the snowpack (adsorbed at surface of snow crystals or dissolved in bulk ice) and its possible origin (gas or atmospheric particles. . .) are discussed. This is a very interesting work and interesting results, which definitely deserve publication in this journal. A few points, however, could be improved, such as the clarity of the text. I am not convinced either that the observations presented here are sufficient to conclude on the origin and location of acetaldehyde in snow. Physical and chemical processes in snow seem numerous and complex and the acetaldehyde measurements could have benefited from measuring other species at the same locations, such as inert tracers, which could have helped to distinguish between chemical and physical processes. But the present results might already contain valuable information. Although I am not an

expert in this particular field, I am making a few suggestions that I hope to be helpful for this or future discussion(s). Overall, I recommend publication of this manuscript with minor corrections.

Specific comments

1. Clarity

As the possible processes involving acetaldehyde in snow are numerous and complex, it is important that the observations are presented as clearly as possible before to discuss possible mechanisms to explain them. The text could be improved on this point.

- In particular, the specific phase of the snow (interstitial gas, liquid film, or solid bulk. . .) referred to in each sentence has to very clear, especially in the introduction where all these phases are discussed successively. Thus, could the authors, please, explain once and for all the generic term "snow", and that it refers to melted samples, thus includes bulk ice, potential liquid water, and perhaps even interstitial air (although the latter should have a negligible contribution to the samples). Same thing for the term "snowpack". Also, while this might be a well-known definition to specialists, the term "ice lattice" is confusing because it seems to refer at the same time to ice (solid bulk) and to "lattice", suggesting interstitial air. Please, could the authors go through the text again (in particular the introduction) and make sure that the phase(s) discussed are clear.

- The summary of previous observations could be clearer, too. For instance, the summary of the results of Houdier et al., (2002), p. 19686, li. 20-26, suggests that the observations were too complex to conclude on the origin of acetaldehyde. Yet, on p 19687, li. 2/3 the authors emphasize on the clear difference between these results and those of Couch et al. (2000). Please, try to state all the conclusions can be drawn from these previous works as clearly as possible, as these studies are already complicated enough.

- the specific objectives of the present study could also be explained more clearly. These objectives seems to be contained in one single sentence p. 19687 li. 5-7 “we have therefore performed a season-long study. . .”. But this sentence does explain how this study is going to help answering the questions that could not be answered by previous studies. In fact, the paragraph in li. 8 -21 is not very reassuring on this point, because it is not clear how observing different processes at a different location is going to help explain previous observations. On the other hand, the sentence on P.19691 li. 26/27 would be good justification of the objectives of this study.

- The last sentence of the introduction, li. 27-29 concerning measurement of the partial pressure of acetaldehyde in the interstitial air is not well written. Could this sentence be simplified into a statement such as “current techniques available to measure PCH3CHO are not sensitive enough to bring useful information. . .” ?

- in Figures 1 and 2, it is not completely clear what “height” means, and if the air/snow limit (top of the snowpack) is at 50 cm or at 0 cm. I understood that it was rather the former, but it could be useful to state it clearly in the text.

2. Interpretation of the results

The observations presented in this paper are complex, and I am not convinced that they can lead to a clear conclusion on the origin and location of acetaldehyde in snow. The few suggestions below might, however, help in the interpretation of the results.

- Of all the assumptions that can be made, the only one that I would definitely exclude is that PCH3CHO is constant in the interstitial air. Regardless of the type of equilibrium involved (air/ice surface or air/bulk) if acetaldehyde concentration varies by a factor 2 in the snow over 3 months, as shown by Figure 2, then it also varies in the air and vice versa. In ice at -15°C, D = 8 x 10(-11) cm2 s-1 (Domine et al., 2003), thus within 2 weeks acetaldehyde molecules have time to diffuse over 100 microns, and the bulk composition of ice crystals to adapt to changes in PCH3CHO (and, obviously, PCH3CHO would adapt instantly to changes in the bulk). Perhaps PCH3CHO does

not vary within the same series of measurements, but I would not attempt to interpret all the data with a single value of PCH3CHO.

- Instead of the complicated plot of Fig. 3, did the authors try to correlate XCH3CHO with SSA directly to test for adsorption at the surface of ice crystals ? If PCH3CHO and T are constant within each series of measurements, the plot might show series of parallel curves.

- Similarly, did the authors try to correlate XCH3CHO with the snow density (not shown in the paper, by the way, which could have been useful) to test for a possible air/bulk ice partitioning instead of Fig. 4 ? Such an equilibrium would seem a likely hypothesis, and I do not quite agree with the discussion of the authors p. 19695/19696, where PCH3CHO is assumed to be constant. Moreover, this discussion (p. 19696, li. 3 – 10) takes into account the shape of the snow crystals, while only their volume matters for a dissolution equilibrium.

3. Other possible approaches

As I am not a specialist in this field, it feels a little presumptuous to make suggestions on the measurements that should be made, or how they should be made. However I hope that the following suggestions are useful, if not for the present discussion, for future studies.

- if I understand well, it is shown in the last part of the paper that a precursor for acetaldehyde, acetaldehyde-di-n-hexyl acetal, tested positive for acetaldehyde with the analysis reagent, DNSAOA. The mechanism involved in this interference is not really relevant, the main point is that this reagent is susceptible to react positive for acetaldehyde with other compounds than acetaldehyde. Thus, before to discuss the potential origin of this compound in snow, it is important to find out which other compounds would also test positive for acetaldehyde, or find another method or reagent which would be specific to acetaldehyde.

- Apparently, many physical and chemical processes happen in snow simultaneously (diffusion, reaction...). Therefore, measuring only a reactive compound such as acetaldehyde is difficult to interpret. In future studies, measuring several compounds in the same samples, in particular inert tracers (CH4, noble gases...), or even different organic compounds with different reactivities, could help to distinguish the effects of diffusion and of chemical reactivity on the concentration profiles.

- If measuring the gas-phase concentration of acetaldehyde in the interstitial air is difficult, measuring it above the snowpack would have been helpful, as it would have given an order of magnitude for the air/snow partitioning coefficient, and the timescale and magnitude of the variations of this gas-phase concentration.

- another approach that could be useful, in particular to test the hypothesis of the presence of acetaldehyde in particulate matter in the snow, would be to separate dissolved and particulate organic matter in the samples, for instance by using filters, before to perform the chemical analyses.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 19683, 2009.