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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General Comments

The authors report field measurements of acetaldehyde concentration in the Alaskan subarctic snow pack and the specific surface area of snow layers. They intend to test two hypotheses, 1) that acetaldehyde is adsorbed onto the surface of snow crystals, and contrary 2) that acetaldehyde is dissolved in the ice lattice of the snow crystals. Based on their data, and after applying a treatment that assumes the partial pressure of acetaldehyde is constant, under the risk of providing misleading conclusions, they propose that the lack of any correlation in their measurements can not be explained through the previous hypotheses. Their reasoning directs the discussion into a third (experimentally unsupported) alternative. They suggest that acetaldehyde is either contained or dissolved within organic aerosol particles trapped in snow, or that acetaldehyde is produced during the hydrolysis of unknown precursors trapped in snow, during the analytical procedure involving melting the snow samples.

I would suggest a revision with corrections, clarifications, and addition of the references cited in this revision prior to acceptance of this manuscript however. The discussion is somewhat disappointing in its description of how high acetaldehyde concentrations are generated. The authors must be very careful using the term glycolysis on page 19698 (lines 1-7). The most general definition of glycolysis is the metabolic pathway that converts glucose into pyruvate (Nelson et al., 2000). For simple anaerobic fermentations a final product can be ethanol (lactate is another possibility). Acetaldehyde is only a catabolic intermediate towards the production of ethanol and seems unlikely to be isolated in the environment. More concerning is the presence of oxygen in the field environment. Their proposal suggests that fermentative microorganisms produce acetaldehyde in the presence of 21% O2 because snow constantly exchanges air with the atmosphere. The reader should be aware that at least conditions of hypoxia, meaning a concentration of less than 2 ppm O2, are required for fermentation, what makes that part of their proposal unsustainable. The authors should calculate the rate of production of acetaldehyde by microorganisms that are able to live in snow and for that calculation should extrapolate to the low temperature range of the investigation. The activation energy for the proposed pathway is strongly dependent on temperature as explained in the literature (Price and Sowers, 2004) and the thermal variations undergone by field samples over the campaign would affect the production rates considerably. Humic-like substances (HULIS) have been identified in both modern and ancient ice, despite the remote marine setting of the ice field (Grannas et al., 2006) and their presence proves that organic aerosol HULIS are scavenged by snow. In fact, the proposal that organic species trapped in snow or ice can produce degradation products of HULIS has been touched on by other authors, e.g., the photodecomposition of humic-like chromophores sporadically injected as contaminants into glacial ice is potentially able to simultaneously explain CO and CO2 anomalous spikes (Guzman et al., 2007), and a tie in to these concepts would be helpful.

Specific Questions

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Page 19688, Methods:

1) What do the authors mean by “We tested by analyzing water sprayed onto the sheet that it did not release aldehydes”? Should not be easier to explain that this was a control experiment? Please clarify and contrast to the last proposal of the paper that sustains that precursors in the aerosol and trapped in the snow pack can generate acetaldehyde.

2) Have the authors performed a blank or background test to ensure that no acetaldehyde is released from the polyethylene plastic?

3) How does the five months time scale affect the experimental results? Is there any possibility for a seasonal cycles that could affect the quantification of acetaldehyde?

Page 19693, 4.1 Adsorption and dissolution hypotheses:

4) What are the criteria for constraining the vales of n, the number of entities created by adsorption of CH3CHO on/in the ice surface/volume? Please provide a reference for a non-dissociating acid case with n = 1, of a molecule with similar properties of acetaldehyde? What is the base for considering the partial pressure of acetaldehyde Pacetaldehyde constant if there is a dynamic partitioning between the condensed and gas phases? Under the authors’ assumption, the concentration of acetaldehyde in the condensed phase also remains constant for the Henry’s law to be valid.

Other points, suggestions, and corrections

5) Title and Manuscript: Please, unify the terminology by using only snow pack or snowpack in the text, captions, and title.

Page 19688, Methods:

6) It seems convenient to add a supplementary information (S.I.) file to the manuscript. The S.I. file should provide a diagram of what the author describes for the different types of samples studied. This will allow the authors to concentrate the methods sec-

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tion by just mentioning the three types of samples and will leave the details for those really interested in the experimental/field setup to read the S.I. file.

7) It would be better to change the terminology. Classify the ground, plastic, and table snow pack in type 1, 2, and 3 in the diagram. Thereafter the terminology should be kept in the text.

8) Lines 21-22. Include the location of the thermsistors in the S.I. scheme Section 2.2 (Snow sampling):

9) Lines 10-14: Authors should leave the detailed description of the snow crystals shapes and layer for the S.I. file too.

10) Line 17: It seems surprising that water did not freeze in the vials. How do the authors discard there is no dilution error from any water remaining in the vials? For future work it could be convenient to purge the vials with an inert gas before leaving to the field.

Page 19690, 2.3 Analytical procedures:

11) Lines 7-8: Substitute: "It is noteworthy that ... ... campaign," for "The limit of detection was lowered to 0.05 ppbw"

12) Line 9: Delete "here"

13) Line 10: Substitute "samples" with "sample"

14) Lines 13-14: Delete "(" before Legagneuz and add it before "2002"

Page 19690, 3 Results:

15) Line 17: Delete "November and April" if it is already known from the experimental section that samples were taken between December and April. Clarify in the experimental section if samples of snow were taken starting in December or November.

16) Lines 17-20: Authors should try to explain in a simpler way these lines. For exam-

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ple: Field samples were collected every week (or with a weekly frequency).

Page 19690, 3.1 Vertical profiles of density and specific surface area:

17) It appears that the most important result to be mentioned here includes lines 9-13. The remaining part of this section should be shorter and details moved to the S.I. file. After the changes, the short paragraph remaining can be incorporated to another section.

Page 19693, 4.1 Adsorption and dissolution hypotheses:

18) Lines 17-18: Consider writing “taking advantage of the wide range of temperatures observed” instead of “we will take advantage of . . .” or change the current statement

Page 19694:

19) Lines 24-29: Condense text into a range of minimum (in the dark) and maximum (in the sunlight) values’ of acetaldehyde concentrations (e.g., range 10–100 pptv) and list all the references at the end of the sentence.

Page 19695:

20) Lines 3-9: Write in a completely different way this idea. The data reported by Petitjean et al., (2009) is reliable. It has been obtained under well controlled laboratory conditions.

Page 19696:

21) Lines 13-14: Substitute “is not expected to dissociate” with “can be considered an undissociated species” or “is an undissociated species”

Page 19697:

22) Line 5: delete “probably”

23) I would recommend increasing the size of the symbols in Figures 1-5.

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References

Grannas, A. M., Hockaday, W.C., Hatcher, P.G., Thompson, L.G., and Mosley-Thompson, E.: New revelations on the nature of organic matter in ice cores, J. Geophys. Res., 111, D04304, 2006.

Guzman, M. I., Hoffmann, M. R., and Colussi, A. J.: Photolysis of pyruvic acid in ice: Possible relevance to CO and CO2 ice core record anomalies, J. Geophys. Res., 112, D10123, 2007.

Nelson, D. L., Cox, M. and Lehninger, M.: Principles of Biochemistry, 3rd ed., 1200 pp., W. H. Freeman, New York, (2000).

Price, P. B., and Sowers, T.: Temperature dependence of metabolic rates for microbial growth, maintenance, and survival, Proceedings of the National Academy of Sciences of the United States of America, 101, 4631-4636, 2004.

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