

Interactive comment on “n-Aldehydes (C₆–C₁₀) in snow samples collected at the high alpine research station Jungfraujoch during CLACE 5” by K. Sieg et al.

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Reply to Referee 2

The authors appreciate the Reviewer's thoughtful comments, which helped to improve the paper. The suggestions for improvement of manuscript have been considered as far as possible during preparation of revised version of this manuscript. The responses to the comments accompanied by the original comments are given below.

Referee:

This paper reports concentrations of higher aldehydes in fresh snow sampled at

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Jungfraujoch and attempts to interpret them. The measurements are interesting, appear to be conducted well, and add to the small body of data available on higher aldehydes in snow. The discussion can be divided in 2 parts: first the physical mechanism of incorporation of these aldehydes in snow, then their possible chemical mechanism of formation in the atmosphere. While the data are interesting, I was disappointed by the interpretation and the discussion. The authors are studying a complex reactive multiphase system consisting of 3 or 4 phases: air, aerosols, snow and most likely super cooled water droplets. They perform just one measurement of melted snow and analyze one family of chemical species. In my opinion, it is close to impossible to interpret the data under those conditions. As a result, their conclusion that higher aldehydes are in aerosols scavenged by snow, although reasonable, cannot be substantiated by the data and are only speculative. Likewise, their proposed formation mechanisms of aldehydes, in the absence of data on co-products or on the postulated initial reactants, although again plausible, are only speculative. In an attempt to make constructive comments, I very strongly recommend that their data be analyzed in the light of the aerosol measurements that were also performed within CLACE 5. There appears to be some data sharing issues in the consortium, but these need to be resolved in the interest of science. Furthermore, I am surprised to see that the physical state of the snow was not observed. In particular, what was the degree of riming? How can chemical data of soluble compounds be interpreted if the fraction of rimed ice onto snow crystals is not estimated? The authors themselves seem to be aware of this, as they cite Kalina and Puxbaum (1994) and Poulida et al. (1998) and it is therefore extremely surprising that the adequate observations were not made. They can also read Mitchell and Lamb (1989), JGR 94, 14831. In summary on my general impression, I suggest that future campaigns be organized in such a way that more phases and chemical species are analyzed simultaneously, and that an adequate data sharing protocol be agreed upon, to make the best possible use of the data. Unfortunately, at present, given that too many variables are left unconstrained, I do not see how the quality of this paper can be improved to meet my idea of ACP standards.

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Response:

Concentrations of C6-C10 n-aldehydes were analyzed in the present study for the first time in fresh fallen snow at the high alpine research station Jungfraujoch. The dominating aspect of the study was the source identification of n-aldehydes. The obtained data set provides evidence that the atmospheric n-aldehydes are preferentially of direct and indirect biogenic origin. Evidence for a contribution of direct biogenic emission to the atmospheric n-aldehyde concentrations is provided by the detection of the same set of n-aldehydes in direct emissions from vegetation in previous studies (cited in the manuscript) and in snow samples from Jungfraujoch in the present study. An exception was visible with respect to n-hexanal, being present in high abundance preferentially in the snow samples. Additionally, indirect biogenic emissions can contribute to the atmospheric concentrations of n-aldehydes, through oxidation of precursor compounds (fatty acids and alkenes) of biogenic origin. Moise and Rudich (2002) and Thornberry and Abbatt (2004) proposed the formation of n-nonanal and n-hexanal in the atmosphere through cleavage of double bonds in unsaturated fatty acids (namely oleic acid and linoleic acids) by ozonolysis. The predominance of n-hexanal and n-nonanal within the C6-C10 n-aldehyde pattern in the snow samples collected at Jungfraujoch during CLACE 5 is therefore a strong argument for a preferential origin of the aldehydes from oxidation of biogenic unsaturated fatty acids and alkenes in the atmosphere. Particularly, the high concentrations of n-hexanal in the snow samples from Jungfraujoch argue for a major contribution of indirect biogenic emissions to the total content of n-aldehydes. However, the proportion of the origin of the n-aldehydes from both sources cannot be determined in detail so far.

Apart from the source appointment of the n-aldehydes also the uptake mechanisms of the compounds into the snow is an important scientific aspect. We are aware that our data from the analysis of snow can only provide hints with respect to the relevance of the different possible uptake mechanisms. We fully agree with the referee that our suggestion of incorporation of the n-aldehydes into the snow preferentially through par-

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ticle scavenging has to be supported by further evidence. This requires the analysis of n-aldehydes simultaneously in different phases (gas phase, aerosol particles, snow, supercooled droplets) found at Jungfraujoch. Therefore, we appreciate the referee's suggestion that future campaigns should be organized in such a way that more phases and chemical species are analyzed simultaneously. However, from the analytical point of view, it will be difficult to distinguish between the proportion of n-aldehydes present in the gas phase and the proportion sorbed to particles. In order to obtain sufficient particles for the analysis of the sorbed n-aldehydes, long collection times will be required to obtain sufficient analyte amounts required for GC/MS analysis. Long collection times can alter significantly the amount of VOCs and SVOCs adsorbed on the particles during sampling either by volatilization or chemical reaction. An improvement of the analytical procedures to enable the analysis of C6-C10 n- aldehydes in all phases (particles, gas phase and snow) is desired but requires ambitious and time-consuming experiments before application in new sampling campaigns will be successful. The chapter discussion of the revised manuscript and especially the subsection "uptake mechanism of n-aldehydes into snow" has been rewritten to consider the suggestions of the referee as far as possible.

Minor comments include:

1- Adsorption is ruled out as an incorporation mechanism (p. 8080, l. 17). However, testing this requires strict sampling and analysis procedures, given the reversibility of the process, as stressed by the authors. Species can desorb, but can also adsorb from ambient air. Not enough experimental details are given to tell whether adsorption can indeed be tested.

Response: We agree that adsorption of organic compounds on ice surfaces is a reversible process and that it is difficult if not impossible to quantify the extent to which adsorption of the n-aldehydes from the gas phase to the ice phase is relevant as an uptake mechanism and responsible for the measured concentration of n-aldehydes in snow. Therefore, it is not possible to rule out adsorption of the analytes from the gas

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phase to the ice surface as an additional uptake process. This aspect has been considered in the new version of the manuscript.

2- P. 8081, l. 5. A variable degree of riming could also explain the large variations in the concentrations of aldehydes in snow. Riming acts on gases solubility and also on aerosol scavenging. In one precipitation event, riming can vary on the timescale of minutes, so that it is essential to observe the degree of riming of the sample taken.

Response: We agree with the referee. Future field campaigns which focus on uptake mechanism of organic compounds into snow and ice should establish an experimental procedure which allows the determination of the degree of riming.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 8071, 2009.

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