

First of all, we would like to thank the reviewers for their helpful and constructive comments. These were used to clarify some aspects of the paper and in particular to facilitate its reading by colleagues who are not familiar with snow studies. Other changes were made, as detailed below, where we report our reaction to each one of the reviewers comments and suggestions, and the relevant changes in the revised version.

### **Referee 1**

The general comment does not call for any particular response.

#### **Specific comment 1: clarity.**

- The referee states that he/she is not a snow expert (as is a large fraction of ACP readers). We therefore took the requests for clarification very seriously. The very first sentence of the revised version (lines 35–39) explains the different phases presents in the snow and defines the term “snowpack”. Subsequently, we avoid the ambiguous term “ice lattice” and instead use “ice crystalline lattice” to avoid misunderstandings (e.g. line 61).
- We clarify the difference in the conclusions reached by Houdier et al. (2002) and by Couch et al. (2000). The former were not able to reach a clear-cut conclusion as to the location of acetaldehyde in snow, while the latter concluded that acetaldehyde was adsorbed onto snow crystal surfaces (lines 90 and 93).
- The objectives and interests of this new study have been stated more clearly and in a more detailed manner at the end of the introduction. Briefly, different thermodynamic and kinetic conditions such as those prevailing near Fairbanks are likely to reveal different aspects of the acetaldehyde-snow interactions (lines 98-101 and 112-120).
- We clarify the last sentence of the introduction regarding the measurement of acetaldehyde mixing ratios in the air. The problem is not sensitivity, but the fact that snowpack air is inevitably diluted with atmospheric air with current sampling techniques. This effect is especially strong in shallow seasonal snowpacks, as we encountered (lines 126-129).
- In the ordinates of Figures 1 and 2, we replaced “Height” with “Height above ground” to avoid misunderstandings.

#### **Specific comment 2: Interpretation of the results.**

- We agree with the referee that  $P_{\text{CH}_3\text{CHO}}$  is certainly not constant, and that assuming that it is constant, as we do, results in errors. However, we argue that  $P_{\text{CH}_3\text{CHO}}$  is probably not the most important cause of variation of the snow concentration in  $\text{CH}_3\text{CHO}$ ,  $X_{\text{CH}_3\text{CHO}}$ . For example, Guimbaud et al. (2002) observed that  $P_{\text{CH}_3\text{CHO}}$  above the snowpack varied by less than a factor of 3 over the season at Alert, Canadian Arctic. Of course, variations of  $P_{\text{CH}_3\text{CHO}}$  in snowpack interstitial air were certainly somewhat larger, but other variables probably affected  $P_{\text{CH}_3\text{CHO}}$  in a more important manner. These include snow specific surface area (SSA) which varied between 71 and 577  $\text{cm}^2/\text{g}$  (factor of 8) and temperature, which varied between  $-37$  and  $0^\circ\text{C}$ . For a temperature-dependant process with an activation energy of 40  $\text{kJ/mol}$ , such a temperature change will produce variations of a factor of 22. Assuming  $P_{\text{CH}_3\text{CHO}}$  constant therefore neglects the smallest cause of variation and focusses on the most important aspects. Furthermore, the referee is not correct in assuming that variations of  $P_{\text{CH}_3\text{CHO}}$  of a factor of 2 will result in similar variations in  $X_{\text{CH}_3\text{CHO}}$ . Equations (1) and (2) show that this depends on the value of the factor “n” which is unknown for acetaldehyde. For HCl,  $n=2.73$  so that a variation of  $P_{\text{HCl}}$  by a factor of 3 will result in a variation of  $X_{\text{HCl}}$  by a factor of only 1.4. Moreover, if  $\text{CH}_3\text{CHO}$  is present in organic particles and not in the snow crystals,

such thermodynamic considerations will not apply. Lastly, the diffusion coefficient suggested by the referee probably does not apply to acetaldehyde, whose diffusion coefficient in ice has never been measured. Given the size of the molecule, it appears highly uncertain that it could diffuse that fast in ice. For example, the small chloride ion diffuses much slower than that (Thibert and Domine, 1997). In any case, to test the potential effect of changes in  $P_{\text{CH}_3\text{CHO}}$ , we have redone calculations supposing that  $P_{\text{CH}_3\text{CHO}}$  increases linearly by a factor of 3 between 1 December and 1 April, and found that it did not affect our conclusion, as now detailed in the text. For the adsorption hypothesis (Fig. 3),  $R^2$  changes from 0.0759 to 0.0135 and for the dissolution hypothesis (Figure 4)  $R^2$  changes from 0.2589 to 0.2766. Even a variation of  $P_{\text{CH}_3\text{CHO}}$  by a factor of 10 over the season has little effect on  $R^2$  values (0.0041 for adsorption and 0.1483 for dissolution). This therefore confirms that  $P_{\text{CH}_3\text{CHO}}$  is not an important variable to understand the location of acetaldehyde in snow. Extensive changes in the text have been done lines 271 to 289 to explain these aspects on the adsorption hypothesis. The effects of variations in  $P_{\text{CH}_3\text{CHO}}$  on the dissolution hypothesis are discussed lines 332-334.

- A plot of  $X_{\text{CH}_3\text{CHO}}$  vs. SSA is suggested by the reviewer to test the adsorption hypothesis. Adsorption is highly temperature-dependent, so that data would have to be regrouped within narrow temperature ranges for this plot to be meaningful. We estimate that 8 ranges would be required, and the number of points within each range would not be sufficient. In any case, Figure 3 is not complicated, it is just the representation of the usual adsorption equation.

- The reviewer also suggests to correlate  $X_{\text{CH}_3\text{CHO}}$  with density to test the dissolution hypothesis. But  $X_{\text{CH}_3\text{CHO}}$  is an intensive variable that is not related to density by any physical or chemical relationship we know of, so we do not understand what information could be obtained here. Since density is not, to our current understanding, a crucial variable, we only give a brief description of the density profiles lines 209-220, and refer the reader to the detailed work of Taillandier et al. (2006) for details.

#### Specific comment 3: Other possible approaches.

- The reviewer misunderstands our approach and conclusion on possible precursors of acetaldehyde in snow. On the contrary, the mechanism involved in the generation of acetaldehyde from precursors is relevant, as it is the addition of the derivatizing agent (DNSAOA) that pulls reaction 1 to the right and therefore produces acetaldehyde in solution. In any case, further work beyond the scope of this paper is required for a complete understanding of these interferences. Perhaps our analytical method can provide information on the structure of organic macromolecules present in snow, but this is speculation we do not wish to start developing here.

- Indeed, measuring compounds other than acetaldehyde cannot hurt. We also measured formaldehyde, which is subjected to totally different processes, as will be detailed in a subsequent publication. However, understanding the behavior of formaldehyde did not help us with acetaldehyde.

- Yes, measuring  $P_{\text{CH}_3\text{CHO}}$  above the snow may have been a useful substitute for measurements within the snow. However, Guimbaud et al. (2002) showed that the snow-atmosphere gradient in  $P_{\text{CH}_3\text{CHO}}$  reversed sign over the season, so that using atmospheric  $P_{\text{CH}_3\text{CHO}}$  values may also have been misleading.

- Indeed, measuring acetaldehyde in filtered and unfiltered samples may be interesting. However, reactions generating acetaldehyde from precursors may take place as soon as the snow is melted so the interpretation of the results may be ambiguous. We will nevertheless attempt to do that as soon as the opportunity shows up.

## Referee 2

The general comments request changes on several aspects: glycolysis and biological activity, and chemical reactivity of HULIS.

The reviewer rightly mentions that glycolysis is an anaerobic process, and also suggests that we try to quantify the possible productivity of microorganisms in the snow we studied. The reviewer appears to be well familiar with biological processes and strongly stresses the relevant aspects in his/her review. However, we mentioned the biological aspect only for the sake of completeness, after all other possibilities had been explored, and we never suggested that we thought it was the most important process. While the reviewer is correct, we feel there is no need to develop an aspect that remains a speculation in the discussion and which is probably minor. Nevertheless, we agree that some points deserve clarification. We now stress that glycolysis is an anaerobic process, but mention, with the support of references, that anoxic environments do exist in soils and snow, very next to oxic environments. We clearly state that the possible implication of glycolysis is speculation at this point, and we present this as no more than an idea in the final part of the discussion section (lines 410-413). Regarding the suggestion to make a quantitative evaluation of the possible productivity of bacteria, we feel this is not warranted here. Indeed, since we do not know the amount and strains of bacteria, any estimate would have such a huge error bar that we do not see how it would improve the discussion, especially given that this point is again, not presented as crucial.

The fact that HULIS photochemistry may produce acetaldehyde is an interesting point, which was already alluded to in our discussion. We have however made that more explicit, mentioning the term HULIS and citing Guzman, as recommended by the reviewer. (lines 392-403).

### Specific questions

Points 1 and 2. Exactly. The purpose of spraying water onto the sheet was to test for contamination. We have changed the wording (lines 134-136) to remove any ambiguity.

Point 3. A seasonal cycle indeed is possible, even likely. We have now discussed that lines 284 to 289 and 332-334, as already detailed in the response to reviewer 1.

Point 4. Unfortunately, there are very few studies on the thermodynamics of solid solutions in ice. The only sufficiently detailed studies we are aware of are those of Thibert and Domine (1997 and 1998), dealing with the HCl-ice and HNO<sub>3</sub>-ice systems. There is no study of the solubility in ice of a non-dissociating acid and there is very little understanding of what determines the value of  $n$ . For lack of a better or more plausible alternative, we suggest here that  $n=1$ , but have added a few lines to indicate that  $n$  may also be equal to 2 (lines 358-361) if the incorporation of acetaldehyde in ice generates a defect. We are sorry, but currently we believe that nothing more can be said on  $n$ .

Point 5. We now use "snowpack" throughout.

Points 6 to 9. The reviewer suggests to regroup the discussion of snowpacks to a supplementary information section. We do not agree to that. The reviewer does not appear to be interested in snow details, but we on the contrary think that those aspects are important and should be placed where they are: in the main body of text. Numbering the snowpack types as 1, 2 and 3, does not seem a good idea, as these number do not convey any intuitive

information, contrary to the names “ground”, “plastic” and “table”. We believe that readers interested in snow details will much prefer our presentation.

Point 10. The water did not freeze in the vials because they were kept in a cooler. This was clearly indicated line 172.

Point 11-15 and 18-22. We considered these minor points, all dealing with style, with interest and followed some of them. Others were not followed, however, because they were mostly a matter of personal style, and such points are typically within the freedom and preference of writing of the authors.

Point 16. The sampling frequency was exactly as stated. It appears that the reviewers would like us to say that sampling was regular but that was not the case. The only extra explanation we could give would be to detail which snowpack was sampled at what date, but that is probably of no interest to any reader. Frankly, we believe that the brief description of the sampling frequency that we give is perfectly fine.

Point 17. Again, it appears that the reviewer has little interest in snowpack details. We strongly disagree with this suggestion. These snowpack details will be important to many readers and are best left here. Again, we think that regrouping data that we feel are crucial in a SI section is not a good idea at all.

Point 23. The size of the symbols in Figures 1, 2 and 5 was increased.