

# ***Interactive comment on “Water-soluble organic carbon in snow and ice deposited at Alpine, Greenland, and Antarctic sites: a critical review of available data and their atmospheric relevance” by M. Legrand et al.***

**M. Legrand et al.**

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Reply to reviewer C. Halsall (Referee No 1). In the following we (AU) will reply to all comments separately.

Comment: Points of note: The authors are to be congratulated for picking apart differences in analytical techniques and for utilising the operationally-defined fractions of OC (e.g. WSOC, HULIS etc) with regards to interpreting OC data.

What is interesting (but also troubling) is that sealed collecting vessels generally show

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higher blank OC levels the longer they are left prior to analysis. This is especially important with regards to Antarctic samples, when sample vessels may be in storage for much long periods compared to samples collected elsewhere.

AU: The cause of such an increase of the blank in airtight glass bottles is because the bottles are rinsed but not dried and therefore a skin of water remains in the bottle during storage. In this way, the small but continuous exchange between the outside air and the inside of the bottle permits dissolution of organic gases in the left water.

Comment: On page 9 the authors expand on this issue and state that for their sampling work in Antarctica and the Alps, the blanks generally remained below 25 ppb C, yet for vessels (containing purewater) analysed only a few hours after cleaning, blanks were close to detection limits of 3- 5 ppb C. Given the importance of blank artefacts and the low levels of OC reported in Antarctica (re: Table 1), it would be useful if the authors could report method detection limits (i.e.  $MDL = \text{mean blank} + 3 \times \text{Std Dev}$ ), rather than the arbitrary ‘twice the variability’ reported on page 5 (this is not used in analytical chemistry). If blank subtraction has been undertaken, then the  $MDL = 3 \times \text{Std Dev}$ . The authors could also expand on why they felt that blank subtraction was necessary for some samples (i.e. Antarctic snow) and yet not for others (e.g Alps). Surely blank subtraction will have a pronounced impact on the ensuing dataset and make comparisons difficult with data where this procedure had not been conducted.

AU: Thanks for your comment on the blanks. Following your comment we clarified the text. First, the blank value reported in page 5 (23) is related to the analytical device and not to the sampling procedure, storage or decontamination. We took as detection limit twice the standard deviation (as generally done by geochemists). We here correct the wording “twice variability” by “twice the standard deviation” in the revised. We also recognize that chemists more commonly use 3 times the standard deviation rather than twice but we feel both are OK as far as it is clearly specified.

Concerning the blank of the glass bottle cleaning and storage procedure used to sam-

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ple snow (discussed in page 9), we make clearer that “With these precautions bottle blank values generally remained below 25 ppbC. Since these values are significant with respect to measured snow concentrations, the corresponding glass bottle blank of the sampling series was subtracted from snow concentrations.” In fact you may have been confused by the remark we put at the bottom of Table 2 for some alpine ice “Values obtained without subtracting the blank of the ice decontamination procedure ( $\sim 30$  ppbC, Legrand et al., 2007a).” In fact the decontamination procedure used for ice sections in this previous study gave higher blanks than the one described in section 2.3.2 (see below). Therefore to avoid confusion, in the revised version we report this value as “blank corrected value from Legrand et al. (2007a)”. We also specify at the end of section 2.3.2 that concerning the sampling of ice core sections that don’t use any storage in glass bottles, the blank of the decontamination procedure was found to be below the detection limit.

Comment: Given the water-soluble nature of various OC fractions it is surprising that the authors fail to mention the possibility of OC migration within the snow following seasonal warming of the perennial snowpack, particularly in Alpine or Greenland snow. Migration of OC with meltwater may blur temporal trends and affect winter and summer accumulation patterns. Could the authors comment on this ?

AU: Yes you are right that the ice records of any water soluble chemical species would be altered if the temperatures at sites are warm enough to permit significant melting of snow. In the case of the Col du Dôme glacier in the Alps presented in our study, with a firn temperature of  $-12^{\circ}\text{C}$  the site is typical of the recrystallization-infiltration zone of the glacier (i.e. when melt water percolation exists but is refreezing immediately at the surface without percolation within lower layers). In our case at the Col du Dôme, melt layers never exceeded a few cm, that remains small compared to the annual layer thickness (Preunkert et al., Tellus, 2000). Such a good preservation of the seasonal cycle is confirmed by the observed strong summer to winter ratio for concentrations of a typical water-soluble species like ammonium.

Comment: Minor errata Page 2, line 25: . . .secondary production dominates. . . AU:  
Done

Page 4, line 4: others AU: Done

Page 22, line 13: permits Au: Done

Page 26, line 26: Most of the large.. AU: Done

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Interactive comment on Clim. Past Discuss., 9, 2357, 2013.

**CPD**

9, C1417–C1420, 2013

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