

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.

R. Antony

runa@ncaor.gov.in

Received and published: 26 June 2013

This paper provides an overview of available data on organic carbon in snow and ice cores from polar as well as non-polar sites and provides new data on water-soluble organic carbon measurements in surface snow and snow-pit samples in both Antarctica and the Alps. The authors also discuss data discrepancies arising from the use of different measurement techniques and conclude that most of the large inconsistencies were related to sample contamination as well as degradation of the ice quality. While the paper is of interest as available TOC data are very sparse for polar regions,

C1259

especially Antarctica, there are some critical issues that need to be addressed and re-evaluated by the authors. Below, I list some issues that should be considered when revising the manuscript.

Comment 1

The authors used the UV oxidation method for analysis of OC in snow and ice cores. As is well known, and as the authors themselves demonstrate, the UV oxidation method is far less efficient than combustion method in oxidizing insoluble organic material, recovering only up to a quarter of the insoluble matter. While using this method, for measuring OC in Antarctic snow, the authors assume that insoluble organic carbon is not a significant fraction of the organic carbon budget in the Antarctic. It is however, well established that insoluble components are always present together with soluble ones in both coarse and fine fraction of marine aerosol (Calace et al, 2001; Bigg et al, 2004; Leck & Bigg, 2005; Facchini et al, 2008) and that they make up a non-negligible part of the insoluble material in Antarctic snow especially the coastal sites (Calace et al, 2001). Concurrent laboratory and field measurements have shown that up to 77% of the primary marine aerosols is constituted of water insoluble organic carbon and composed mainly of phytoplankton exudates occurring as fine particulates or large colloids (Facchini et al 2008). Also, as organic carbon in marine aerosols is mainly concentrated in the sub-micrometer size fraction and have higher mobility and life span (Saltzman et al 1986; Calace et al 2005; Fattori et al 2005) it is possible that it may be transported to longer distances from the coast.

As TOC includes both soluble as well as particulate organic matter, it is therefore obvious, that the TOC data reported for Antarctic snow especially the coastal samples using UV oxidation method will be low compared to measurements carried out using the combustion method (which efficiently oxidizes water-soluble as well as insoluble organic particles). Previous studies in the Princess Elizabeth Land (PEL) and Dronning Maud Land (DML) region have shown significant influence of sea-spray associated organic matter and insoluble material such as bacteria and other micro-organisms, ex-

C1260

opolymer secretions of microalgae and bacteria in the snow samples (Antony et al 2011). It is not surprising therefore that reported TOC values for coastal snow in this study using the UV oxidation method are lower than that reported for coastal DML and PEL using the combustion method. Study of fulvic acids in fresh snow collected in coastal (up to 10 km) and in inland sites such as those in this study (Dome C and Talos Dome), showed that while dissolved fulvic acid concentrations were not significantly different, particulate fulvic acid concentrations in coastal samples are significantly higher (19 to 440 ppb) than those found in the sites far from the coast (7 to 83 ppb). Thus, given the high concentrations of particulate organic matter in Antarctic snow, it is most likely that the authors missed out on a significant fraction of the organic matter using the UV method, especially in the coastal snow samples and their method measures DOC rather than TOC. Thus, caution has to be exercised while comparing the 'DOC' measurements obtained in this study with TOC data reported by others.

Similarly, in section 3.2.2, lines 7-15, the authors argue that the higher OC values reported for summit snow by Grannas et al. (2004) (400–580 ppbC) compared to those reported by Hagler et al. (2007) (111 ± 45 ppbC) is most likely as a result of contamination due to the sampling material used. I would like to highlight two points here: 1) the authors carried out tests and report no significant contamination of sample from the HDPE carboys that were used for the collection of snow samples. 2) Grannas et al. (2004) estimate TOC by the difference between total carbon (TC) and inorganic carbon (IC) i.e., $TOC = TC - IC$. It is known that analytical methods that are configured to measure TOC as the difference between TC and IC, leads to overestimation of TOC and the magnitude of the overestimation varies with the amount of dissolved inorganic carbon (DIC), wherein samples that have a greater proportion of inorganic carbon will result in a greater overestimation (Findlay et al 2010). On the other hand, the analysis of TOC/DOC as non-purgeable organic carbon (NPOC) - wherein, the sample is acidified and sparged before analysis to drive off inorganic carbon and the remaining carbon then oxidized to measure OC- is completely unaffected by variation in DIC. The measurement efficiencies also affect the magnitude of this DIC effect. TOC (TC-IC)

C1261

analysis tends to have greater variation in measured values than the NPOC analysis because IC often accounts for a significant portion of the TC, and the errors in the two values are additive, which significantly affects TOC values. Also, for samples having very low OC, the CO₂ in the air dissolves in the sample and is measured as IC, causing the concentrations to vary. Thus, differences between a TOC value from TC-IC method and TOC value from NPOC method can be quite significant and can affect results and alter conclusions drawn from comparing data sets obtained using these 2 methods. Therefore, the analytical approach used by Grannas et al ($TOC = TC - IC$) is most likely responsible for the high OC values reported compared to that of Hagler et al. (acidify and sparge). The same would be true for South Pole snow since samples were analyzed by the TC-IC method.

Thus, some level of uncertainty across methods is expected in terms of absolute concentration of OC and variability in samples. The analytical approach used should therefore be taken into account to ensure that appropriate comparisons are being made across different samples and systems and caution exercised while drawing direct comparisons between samples analyzed using different methods.

Comment 2

The authors argue that the surface snow samples collected in the margin areas of DML and PEL have high TOC as they were collected in low density polyethylene bags. It may be noted that issues related to contamination from the sample bag material was addressed by Antony et al (2011), and a detailed account was provided by them on precautions taken during sub-sampling in order to avoid contamination from the sampling bag material. The author's assumption of contamination based on the 'high' dust concentrations in these samples is also not legitimate. The DML surface snow samples were collected from ~110 km from the coast to about 300 km inland traversing the Wohlthat Mountains - an imposing mountain chain in the DML that represent an extensive exposed rock area in this sector of East Antarctica. In Antarctica, an additional input of dust particles to the ice sheet can derive from ice-free terrains frequently occur-

C1262

ring in mountain ranges and such exports can be quite relevant. Even small amounts of dust have the potential to influence the overall budget in low deposition environments such as the East Antarctic ice Sheet (Delmonte et al 2013). Thus, in addition to other possible sources, dust in the DML snow samples has a significant input from the exposed mountain ranges, resulting in slightly higher values in these samples. The values are comparable to dust concentration of 16 to 1892 ppb (annual avg. 62 to 346 ppb) in a series of snow cores collected in the DML, including sites in close proximity to the Wohlthat mountain range (Mahalinganathan et al, unpublished data).

Comment 3

The authors suggest that MSA and HULIS represents a significant fraction of the water soluble OC in Antarctic snow. Using the OC value of 14-27 ppb (Table 1) and an average MSA value of 1.3 ppb (Table 3) reported for Concordia snow, MSA constitutes up to 10% of the water soluble organic carbon fraction. Rough calculations based on mean MSA (22 ppb; Antony et al 2010 and unpublished data) available for the surface snow samples from the PEL region show that the MSA values detected in snow would imply the presence of at least 220 ppb OC in the PEL snow samples. As shown by Antony et al (2011), the mean TOC value of 259 ppb recorded for the PEL snow samples is well within the expected range, providing further evidence that the reported TOC values are reliable.

Comment 4

There have been several reports demonstrating that organic compounds are subject to post-depositional processing resulting in significant depletion of organic carbon within the polar snowpack (Jaffrezo et al. 1994; Dibb and Jaffrezo, 1997; Hagler et al., 2007; Schneidmesser et al 2012). The author's assumption that there is no significant loss of volatile organic carbon after snow deposition (Section 3.2) is based on just 2 measurements of surface snow samples from Concordia (which has low OC concentrations, likely due to its location in the interior East Antarctic plateau and high elevation

C1263

of ~3250 m.a.s.l). Conclusions on post-depositional changes in OC cannot be made by comparing surface snow samples at Concordia with that of ice cores at other sites, as OC concentrations are subject to variations depending on sampling location as well as age/depth of the ice core. It would have been more apt if comparisons were made between OC concentrations at different depths using the snow core collected at Concordia, but unfortunately many of the core samples were contaminated, not allowing for such a comparison. The increasing evidence for post-depositional chemical alterations of organic compounds in accumulated ice and snow suggests that more systematic investigations over longer time periods are needed in order to yield better insights on post-depositional chemical changes in ice.

While, the author's attempt to provide a critical review of available data on OC in both temperate and polar snow samples is very useful, it is crucial that a common set of samples be compared across different analytical methods. Unlike concluded by the authors, it seems that the existing inconsistencies in the OC datasets, especially for surface snow, is in fact most likely due to the differences in the methods employed for OC estimation. As the authors use the limited OC data sets for drawing comparisons and for interpretation of OC trends, they should take into consideration the analytical approach used to ensure that robust comparisons have been-and can be-made. Only then, can appropriate conclusions be drawn from comparing data of different types (surface snow, firn or ice), age (modern, pre-industrial, Holocene, last-glacial maximum), spatial sites (elevation and distance from the coast) and location (Greenland, Antarctica, non-polar regions).

Additional References

Galace, N., B. M. Petronio, R. Cini, A. M. Stortini, B. Pampaloni, and R. Udisti (2001), Humic marine matter and insoluble materials in Antarctic snow, *Int. J. Environ. Anal. Chem.*, 79, 331–348.

E. K Bigg, C. Leck, L. Tranvik (2004) Particulates of the surface microlayer of open

C1264

water in the central Arctic Ocean in summer, *Marine Chemistry*, 91, 131– 141.

Leck, C.; Bigg, E. K. Biogenic particles in the surface microlayer and overlaying atmosphere in the central Arctic Ocean during summer. *Tellus B* 2005, 57, 305–16.

Facchini, M. C.; Rinaldi, M.; Decesari, S.; Carbone, C.; Finessi, E.; Mircea, M.; Fuzzi, S.; Ceburnis, D.; Flanagan, R.; Nilsson, E. D.; de Leeuw, G.; Martino, M.; Woeltjen, J.; O'Dowd, C. D. Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates. *Geophys. Res. Lett.* 2008, 35, L17814.

Saltzman, E. S.; Savoie, D. L.; Prospero, J. M.; Zika, R. G.; Mosher, B. Elevated atmospheric sulfur levels off the Peruvian coast. *J. Geophys. Res.* 1986, 91 (D7), 7913–7918.

Calace, N.; Cantafora, E.; Mirante, S.; Petronio, B. M.; Pietroletti, M. Transport and modification of humic substances present in Antarctic snow and ancient ice. *J. Environ. Monit.* 2005, 7, 1320–1325.

Fattori, I.; Becagli, S.; Bellandi, S.; Castellano, E.; Innocenti, M.; Mannini, A.; Severi, M.; Vitale, V.; Udisti, R. Chemical composition and physical features of summer aerosol at Terra Nova Bay and Dome C, Antarctica. *J. Environ. Monit.* 2005, 7, 1265–1274

Findlay, SEG, McDowell, WH, Fischer, DT, Pace, ML, Caraco, NF, Kaushal, SS, Weathers, KC (2010) Total carbon analysis may overestimate organic carbon content of fresh waters in the presence of high dissolved inorganic carbon *Limnol. Oceanogr. Methods* 8, 196-201.

B. Delmonte, C. Baroni , P.S. Andersson, B. Narcisi , M.C. Salvatore , J.R. Petit, C. Scarchilli, M. Frezzotti , S. Albani , V. Maggi (2013) Modern and Holocene aeolian dust variability from Talos Dome (Northern Victoria Land) to the interior of the Antarctic ice sheet. *Quaternary Science Reviews*, 64, 76-89.

Jaffrezo J.L., Clain M.P. & Masclet P. (1994) Polycyclic aromatic hydrocarbons in the polar ice of Greenland - geochemical use of these atmospheric tracers. *Atmospheric C1265*

Environment 28,1139-1145.

Dibb, J.E. and J.L. Jaffrezo. (1997) Air-snow exchange investigations at Summit, Greenland: An overview. *Journal Of Geophysical Research-Oceans*, 102(C12), 26795–26807.

Hagler, G. S. W., M. H. Bergin, E. A. Smith, J. E. Dibb, C. Anderson, and E. J. Steig (2007), Particulate and water-soluble carbon measured in recent snow at Summit, Greenland, *Geophys. Res. Lett.*, 34, L16505

Erika von Schneidemesser, James J. Schauer, Martin M. Shafer & Michael H. Bergin (2012) Measurement of loss rates of organic compounds in snow using in situ experiments and isotopically labelled compounds. *Polar Research* 31, 11597

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