

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.

Michel.LEGRAND@lgge.obs.ujf-grenoble.fr

Received and published: 3 July 2013

AU: First I would like to thank the author of the comments for showing his interest for our study and also to take time to write these detailed comments. In the following I (AU) will answer on all comments separately.

Comment: 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

C1358

organic material, recovering only up to a quarter of the insoluble matter.

AU: Yes it is right that the UV method is less efficient than the combustion method in oxidizing insoluble organic matter. However, as discussed in our paper, the efficiency of the UV method itself in oxidizing insoluble organic material is dependant on the amount of water insoluble material present in the samples, with higher efficiency for low content samples (Booth et al., 1998). In this way, it is possible that the UV method oxidizes most of insoluble material present at very low level in central Antarctic samples (containing typically less than 10 ppbC of WinOC) whereas we found that in summer Alpine snow containing more insoluble organic (typically 100 ppbC of WinOC) only a quarter of it was oxidized.

Comment: 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).

AU: It is correct that insoluble organic is always present in aerosol together with soluble organic but in general in lower proportion than soluble organic as referenced in our paper (typically one third instead of two thirds, Pio et al., 2007). Two other factors have to be considered to evaluate the respective amount of water soluble versus water insoluble amount of organic in precipitation. First, for insoluble organic fraction (WinOC), a less efficient scavenging by precipitation is expected compared to WSOC. Investigations made in air and precipitation at the mountain site of Sonnblick suggested that WinOC is 2 times less efficiently removed from the atmosphere by snow than sulfate (Cerqueira et al., 2010). Finally, water-soluble atmospheric gases also significantly contribute to the amount of water-soluble carbon present in snow and ice increasing the dominance of water-soluble fractions on water insoluble ones. From that a larger

C1359

dominance of water-soluble on water insoluble matter is expected in precipitation compared to aerosol.

Cerqueira M., Pio, C., Legrand, M., Puxbaum, H., Kasper-Giebl, A., Afonso, J., Preunkert, S., Gelencsér, A., and Fialho, P.: Particulate carbon in precipitation at European background sites, *J. of Aerosol Science*, 41, 51-61, doi:10.1016/j.jaerosci.2009.08.002, 2010.

Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochao, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., Schock, M.: Climatology of aerosol composition (organic versus inorganic) at non-urban sites on a west-east transect across Europe, *J. Geophys. Res.*, 112, D23S02, doi:10.1029/2006JD008038, 2007.

Comment: 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.

AU: We feel that your argument that organic matter dominates primary marine emissions of aerosol is an overstatement. First, it has to be clear that the number of 77% reported by Facchini et al., 2008 only concerns particles with size range close to 0.1 μm . In fact, Facchini et al. 2008 showed that the WIOM/SS (water insoluble organic matter to sea salt) ratio rapidly decreases with the size of aerosol: from 73% between 0.125 and 0.25 μm to 58% between 0.25 and 0.5 μm , 17% between 0.5 and 1 μm . Thus, even in remote region like central Antarctica where the mass size distribution of sea-salt particles peaks around 1 μm (Jourdain et al., 2008 or Udisti et al. 2012), the organic material related to sea salt would not be so dominant. To date, using the typ-

C1360

ical size distribution of sodium particle observed at central Antarctica and the ratio of WIOM to SS proposed by Facchini et al. (2008), we calculate a sea-salt concentration of 138 ng m⁻³ (sodium of 43 ng m⁻³) against 62 ng m⁻³ of OM (essentially WIOM). The corresponding WIOM/SS is of 45%. In addition to carbon, organic aerosol contains in variable amounts hetero-atoms (H, O, N, etc.). To account for these atoms, a conversion factor has to be applied. The mass conversion factor for WinOC would be close to 1.4 (Kiss et al., 2002). Using this value, we calculate OC (WinOC) of 44 ngC m⁻³, i.e. similar to the sodium concentration. Considering typical sodium concentrations of 20 ppb in central Antarctic snow we may expect less than 20 ppbC of WinOC there. The preceding calculation I report for central Antarctica is very likely overestimated since it has to be emphasized that the values of the WIOM/SS ratio from Facchini we used in our calculation correspond to sea spray aerosol produced during a phytoplankton bloom in the North Atlantic ocean and that in their review Gantt and Meskhidze (acpd, 12, 21779-21813, 2012) clearly stated that the relative abundance of organic matter in primary marine aerosol exhibits very high spatiotemporal variability driven by ocean biological productivity. As an example in summer at the Azores island, Pio et al 2007 found in PM_{2.5} aerosol 1160 ng m⁻³ of sodium (3710 ng m⁻³ of SS) against 170 ng m⁻³ of WIOM leading to a WIOM/SS ratio of only 6.5%.

In their recent study of submicron marine aerosol at Bird Island (54°S) in the South Atlantic Ocean, Schmale et al. (acpd, 13,8261-8332, 2013) reported that organic matter accounts for 22% (21% for non sea-salt sulphate, 7% ammonium, and 47% of sea salt). Of these 22% a quarter is made of MSA. Finally, Zorn et al. (acp, 8, 4711-4728, 2008) reported very low organics in submicron aerosol sampled in coastal Antarctic air masses (20 ng m⁻³ of organic matter compared to 310 ng m⁻³ of sulphate and 40 ng m⁻³ of MSA) in summer at 60°S. Note that such a dominant presence of sulphur with respect to organic in submicron aerosol at marine Antarctic region is rather consistent with what we reported for the atmosphere at Concordia (Figure 4 of our study). In the revised version we will mention the paper from Zorn et al. (2008).

C1361

Kiss, G., Varga, B., Galambos, I., and Ganszky, I.: Characterization of water-soluble organic matter isolated from atmospheric fine aerosol, *J. Geophys. Res.*, 107, 10.1029/2001JD000603, 2002.

Pio, C. A., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanchez-Ochao, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., Schock, M.: Climatology of aerosol composition (organic versus inorganic) at non-urban sites on a west-east transect across Europe, *J. Geophys. Res.*, 112, D23S02, doi:10.1029/2006JD008038, 2007.

Jourdain B., S. Preunkert, O. Cerri, H. Castebrunet, R. Udisti, and M. Legrand, Year round record of size-segregated aerosol composition in central Antarctica (Concordia station): Implications for the degree of fractionation of sea-salt particles, *J. Geophys. Res.*, 113, D14308, doi:10.1029/2007JD009584, 2008.

Udisti, R., U. Dayan, S. Becagli, M. Busetto, D., Frosini, M. Legrand, F. Lucarelli, S. Preunkert, M. Severi, R. Traversi, and V. Vitale, Sea spray aerosol in central Antarctica. Present atmospheric behaviour and implications for paleoclimatic reconstructions, *Atmos. Environ.*, 52, 109-120, doi: 10.1016/j.atmosenv.2011.10.018, 2012.

Comment: 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 microorganisms, ex-polymer 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.

C1362

AU: The samples collected by Antony et al. (2011) at around 250-300 km from the coast along the DML transect (close to around 3000 m elevation) have still larger WIOM with respect to SS (WIOC of 150 ppbC and less than 25 ppb of sodium) even the sea salt content in snow deposited in this region start to be typical of central Antarctica (less than 25 ppb of sodium). As calculated above, even using the high numbers from Facchini, we may expect less than 25 ppbC of WIOC there.

Comment: 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.

AU: I guess that these values of fulvic acid are from Calace et al. (2005). In fact Calace found more dissolved than particulate fulvic. For instance when reporting, as you mention above, 7 to 83 ppb at the sites far from the coast they report in the same samples 50-115 ppb of dissolved fulvic. More important in our paper we state: "Such a rather low abundance of organic carbon in Antarctica apparently conflicts with data reported by Calace et al. (2005) who reported from 52 to 92 ppb of dissolved fulvic acid in snow pit samples collected at Concordia. Indeed, if correct, such an abundance of the fulvic acid would imply the presence of at least 26-46 ppbC of DOC in Concordia snow. As shown in Table 3, our HULIS measurements made in several snow samples collected at Concordia indicate however far lower concentrations (from 1 to 3 ppbC)."

Comment: 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

C1363

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) 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.

AU: We basically disagree with your comment on the data from Grannas et al. (JGR, 2004) to explain discrepancies in the organic content of surface snow both at the South Pole and at Summit. First, Grannas et al. have calibrated their TOC Shimadzu measurements by using hydrogen phthalate (for organic carbon) and carbon-
C1364

ate/bicarbonate (for inorganic carbon). Second, the argument that you present based on the study of Findlay et al. is an overstatement. Indeed, while it is correct that the presence of very large dissolved inorganic carbon (DIC) may lead to overestimate of TOC, there is no way to explain the high TOC values reported by Grannas. Indeed, Findlay reported an overestimate by 20% when measuring a sample containing 5 mg L⁻¹ of OC and 45 mg L⁻¹ of dissolved inorganic carbon. Thus, to explain an overestimate by 400 ppbC of TOC due to the presence of DIC you need some 4000 ppbC of IC. That corresponds to 330 μ Eq L⁻¹ of HCO₃⁻ leading to pH close to 8. The typical pH of melted Antarctic snow is 5 (see Legrand, 1987, Legrand and Mayewski, 1997).

Legrand M., Chemistry of Antarctic snow and ice, J. de Phys., 48, 77-86, 1987.

Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, Reviews of Geophysics, 35, 219-243, 1997.

Comment: 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 around 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 occurring 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).

AU: You may be right in the case of DML samples, though I am not sure that such mountain rocks are an efficient source of dust (that is very different for soils of the dry valleys for instance). Anyway, the argument of a local source cannot stand for PEL samples and here again the dust concentrations reported by Antony et al. (2011) are still as high as 250 ppb at 100-200 km from the coast. Thus, we will change the wording in the revised manuscript (mentioning the high dust content in PEL samples only).

Comment: 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.

AU: Did the number of 22 ppb for MSA you mention is in ppbC as the unit we used for 1.3 ppb is ppbC in Table 3? If so, that means a mean PEL sample concentration of MSA of 175 ppb (22 ppbC). This value is very high compared to concentrations reported in previous studies carried out at coastal Antarctica (see a summary in Minikin et al., 1998 and references from Mulvaney and Wolff, 1994; Minikin et al. 1994 with values close to 15-30 ppb).

A. Minikin, M. Legrand, J. Hall, D. Wagenbach, C. Kleefeld, E. Wolff, E.C. Pasteur, and

C1366

F. Ducroz, Sulfur-containing species (sulfate and methanesulfonate) in coastal Antarctic aerosol and precipitation, *J. Geophys. Res.*, 103, 10,975-10,990, 1998.

Comment: 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; Haggler et al., 2007; Schneidemesser 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 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.

AU: Post depositional effects are expected to be stronger on organic gases initially trapped in snow than on organic aerosol phase. That is confirmed by the study from Anderson et al. (2008) showing that at Summit most of post depositional OC effects are due to fast formic and acetic acid (these two species being mainly present in the atmosphere as gases) re-emission from the snowpack. It is very likely that for OC values reported by previous studies in surface snow samples, samples have already experienced post-depositional loss. For instance, the surface snow sampling from Grannas (10 cm) at the South Pole would correspond to a snow deposited over the few months prior the sampling. Even sampling the upper 1-3 cm each day at Summit (some of

C1367

the samples might correspond to a fresh summer snow event at that site where snow events are more frequent), Hagler et al. only found a factor of two higher OC level with respect to older summer snow layers likely because most of post-depositional effects have already enough time to act. Note also that our comparison of snow and air at Concordia reveals a strong depletion of formic acid in snow with respect to the air compared to the situation of an organic aerosol (far less volatile) like MSA or HULIS or WSOC (see Table 3). Therefore it is likely that post deposition acts quickly and that we can still compare surface snow (or snow pit samples) aged of a few weeks or months with ice. However in the revised version we will address a bit more the above discussion.

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

C1368