Clim. Past Discuss., 9, C1409–C1416, 2013
www.clim-past-discuss.net/9/C1409/2013/

Climate of the Past
Discussions
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# *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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Received and published: 10 July 2013

Responses to reviewer 2. In the following we (AU) will answer on all comments separately

Anonymous Referee #2

Comment: The manuscript is a mixture of a review with few new data.

AU: Yes but as argued in the introduction they were selected to highlight existing inconsistencies: "With the aim to improve our understanding of these discrepancies, this paper carefully reviews available data and, when needed, provides new ones on the OC content of selected snow and ice samples."

Comment: Some of the discussions/conclusions, for example the long-term trends from pre-industrial to recent years for Greenland and the Alps, are not well supported by the presented data, but are based on other publications. For the interpretation of temporal trends the data basis in this manuscript seems to be too small. Even at one single site I expect to see year-to-year fluctuations of the OC concentration due to variations in source strengths, transport, precipitation etc. With all the problems related to the different techniques applied, any statements on temporal trends are weakly supported by the data. Therefore, I suggest omitting this paragraph.

AU: we think your view on section 6.2 (temporal trend) is somewhat pessimistic. Firstly, in addition to present the first year-round atmospheric WSOC aerosol record obtained over the high Antarctic plateau, this section presents Greenland data documenting for the first time the DOC content together with its speciation along forest fire events (Fig. 1 and Fig. 2). Also concerning the new set of data presented in this study we specify in section 2.3.2: "Ice cores extracted from Summit (central Greenland) and NEEM (North Greenland) were investigated with the aim to extend the limited number of OC data available from pre-industrial Greenland ice (prior this study, only the year 1020 AD has been documented by Preunkert et al. (2011), Table 2). That also aimed to examine the impact on the OC levels of boreal forest fire plumes, that were shown to often occur in summer (Legrand et al., 1992; Legrand and De Angelis, 1996; Savarino and Legrand, 1998). In this way, 6 and 9 years covering pre-industrial time were investigated in the NEEM and Summit ice, respectively. Later on in section 6.2 we discuss these data as follows: "In Greenland, the 15 investigated pre-industrial years (Table 2) indicate winter levels generally staying below 10 ppbC and summer levels ranging between 20 and 40 ppbC. Compared to the 4 recent years investigated by Hagler et al. (2007a) at Summit (20 ppbC in winter and 55 ppbC in summer, Table 2), these pre-industrial Greenland values are slightly lower (20 ppbC in winter and 55 ppbC in summer, Table 2)."

Secondly, concerning the alpine samples, in section 2.3.1 we motivate a bit more the use pit samples collected at Col du Dôme: " These pit samples were collected to document present-day levels that cannot be examined within firn cores (see Sec. 2.3) limiting examination of temporal trend to the end of the 80's (i.e at the age of the firn/ice transition at the site)."

Later on in section 6.2, we discuss these data as follows: In the alpine ice, the OC levels increased by a factor of $\sim 2$ both in winter and summer between the 1921-1951 and the 1971-1988 years (Table 2). The summer and winter levels observed in pit samples covering the year 2012 remain similar to those observed over the years 1971-1988 (Table 2), which tend to suggest that no large further increase of levels had occurred between the 80's and present. Note that even limited to the year 2012, these data seem to be representative of the very recent time period. Indeed, the mean 2012 summer levels of sulfate (350 ppb), nitrate (380 ppb), and ammonium (144 ppb) are very similar to corresponding typical levels detected in the middle of the 00's (300 ppb of sulfate, 370 ppv of nitrate, and 145 ppb of ammonium, Preunkert and Legrand (this issue)). Finally at the end of the section 6.2 we report, based on very significant number of measurements (40), a significant decrease of OC during the ice age compared to the Holocene: as far as I know this finding is unique.

At the end, note that the first sentence of section 6.2 is rather safety "Preliminary discussions on the causes of some observed temporal changes including seasonal variations, the possible trend from the pre-industrial to the present-day atmosphere, and the response to natural events such as sporadic arrival of forest fire plumes or climatic variations (last glacial/interglacial transition) are here presented."

Comment: For a critical review of existing data there is not sufficient discussion of the methods used by other groups. Instead only the UV-oxidation method is presented in detail. TOC data obtained with catalytic combustion are generally higher which is here attributed to sample contamination due to the use of PE bags. This is contradicting the original work in which blanks are given and corrected for.

AU: It is very well known that sampling snow in PE bags is not adequate for several organic species including monocarboxylic acids (Legrand and Saigne, 1988), ot formaldehyde (Legrand et al., 2007). Here is also the fundamental reason we are unable to sample firn cores that were stored and retrograded from the fields in sealed PE bags. Finally, in the study from A. Grannas et al. (2004) reported blank values concern only blank of water used to generate standard but no blank of bags are reported.

Legrand M., and C. Saigne, Formate, acetate and methanesulfonate measurements in antarctic ice: Some geochemical implications, Atmos. Environ., 22, 1011 17, 1988.

Legrand, M., S. Preunkert, M. Schock, M. Cerqueira, A. Kasper-Giebl, J. Afonso, C. Pio, A. Gelencsér, and I. Dombrowski-Etchevers, Major 20th century changes of carbonaceous aerosol components (EC, WinOC, DOC, HULIS, carboxylic acids, and cellulose) derived from Alpine ice cores, J. Geophys. Res., 112, D23S11, doi:10.1029/2006JD008080, 2007.

Comment: wonder if part of the discrepancy is due to the different technique and the different component (DOC versus TOC). Is UV oxidation as efficient as catalytic combustion? It is discussed in detail that UV oxidation may lead to a 10% overestimation because of oxidation of particulate OC when not filtering. The efficiency was tested on phthalate, mono- and dicarboxylic acids, and other C2 and C3 species. However, more than 50% of the OC in the snow samples is not identified, probably including compounds (microorganisms?) which are more resistant to UV oxidation.

AU: This alternative possibility has been extensively discussed in section 3.2 entitled TOC or DOC ? The efficiency of the UV method was also tested for bigger organic molecules like humic acids. I here report for your information the details on that as written in the analytical paper from Prenkert et al. (EST, 2011): "In the pre-modified configuration, nitrogen was used as carrier gas and an oxidant (ammonium persulfate) solution was added in the UV reactor in order to reach the complete oxidation even for some complex organic molecules like humic acids. As discussed below, to reach blank values as low as possible, we avoided the addition of oxidant solution in the UV reactor. Instead we used synthetic air as carrier gas (instead of nitrogen) from which oxygen increases the oxidation efficiency. Under these working conditions the efficiency of the oxidation relative to the potassium hydrogen phthalate was found to range from 85 to 125% for different organic molecules standards (Table S1, Supporting Information). That is true for organic species present at significant levels in natural ice such as monocarboxylic acids (lactic, acetic, glycolic, formic, glyoxylic), dicarboxylic acids (glutaric, malic, succinic, malonic, and oxalic), formaldehyde, as well as others not yet measured in ice but whose presence is expected including methanol, C2-C3 aldehydes (glyoxal, methyl glyoxal and glycolaldehyde). For long chain polyacids that are also expected to be trapped in snow (humic like substances, HULIS) the efficiency of the oxidation was found to be slightly low 80 ± 2 %."

Now concerning microorganisms, you are right that they may resist to UV oxidation. So the next important question is how much carbon is related to their presence in snow. To estimate the amount of carbon related to cells present in snow we can use data from Whitman et al. 1998 that report an organic carbon content in prokaryotic cell of 5-20 fg/cell for water prokaryotes, up to 65-86 fg/cell for soil bacteria. Using the maximum value of 86 fg/cell for organic carbon content per prokaryotic cell and the numbers of cells found by Chuvochina et al. 2011) in snow layers at the Col du Dome site (200 cell mL-1), we calculate a C mass of 17*10-12 gC g-1 (i.e. well below 1 ppbC).

Whitman, W.B., D.C. Coleman, and W.J. Wiebe, Prokaryotes : The unseen majority, Proc. Natl. Acad. Sci. USA, 95, 6578-6583, 1998.

M.S. Chuvochina, D. Marie, S. Chevaillier, J.-R. Petit, P. Normand, I.A. Alekhina, and S.A. Bulat, Community variability of bacteria in Alpine snow (Mont Blanc) containing saharan dust deposition and their snow colonisation potential, Microbes Environ. Vol. 26, No. 3, 237–247, 2011, doi:10.1264/jsme2.ME11116.

Comment: Part of the difference in Antarctica might also be explained by the distance to the ocean, which is a source of organic carbon. I therefore do not expect a typical OC concentration in Antarctica, as stated on page 2374, top.

AU: Thanks for this important and useful comment. Indeed this point was not enough discussed in the manuscript.

Firstly, in section 3.2.2 we now mention: "Other available Antarctic data reported in Table 1 concern ice. Hereby OC values are consistently in the range of 10 ppbC at all Antarctic sites except those from Talos Dome that indicate values from one to several hundreds ppbC. The proximity of the ocean to the site compared to sites located above 3000 m elevation is likely not the cause of these high levels. Indeed, as seen in Table 1, the ice section from the Caroline site originating from a 1300 m elevation area still indicates a mean OC value as low as 11 ppbC. Unexpectedly, the Talos Dome OC values exceed even those observed in pre-industrial ice from Greenland, a region located far closer to strong emissions of various organic compounds from the continental biosphere. The particularity of the Talos Dome ice samples lies in the fact that the corresponding ice was extracted by using a drill fluid whereas other data were obtained from ice cores extracted by dry drilling."

Later on, end of section 6.1 was reworded as: "Such spatial changes are consistent with present-day observations made over continents and oceans. For instance, a two-year-round climatology of organic aerosols was conducted in 6 sites located along a west-east transect extending from the Azores in the mid-Atlantic ocean to K-Puszta (Hungary) in central Europe by Pio e al. (2007). Hereby it was shown that OC is more than 10 times less abundant at the oceanic site of Azores (380 ngC m-3 STP) than over the European continent (4900 ngC m-3 STP at K-Puszta, 3400 ngC m-3 STP at Schauinsland in the Black Forest, Germany). Even being far weaker than continental sources, the marine source still may represent a source of OC aerosol for Antarctica as sometimes proposed (Calace et al., 2005; Antony et al., 2011). However, even in the marine boundary layer, the importance of emissions of organic aerosol is still the subject of debate (see the recent review from Gantt and Meskhidze (2012)). To date, with respect to a global sea-salt emission reaching 1000 Tg yr-1 (Eriksson, 1959), the averaged global emission of submicron marine OC aerosol averaged 10 Tg yr-1 with a range of one order of magnitude depending of studies, locations, and of the proximity of biologically productive waters. To date, the unique study from Zorn et al. (2008) carried out in summer marine Antarctic air masses reported only 20 ng m-3 of OC compared to 40 ng m-3 of MSA and 310 ng m-3 of sulfate in the submicron fraction of aerosol. Further works are here clearly needed to evaluate the role of marine emissions on the OC budget of Antarctic aerosol."

Gantt, B., and N. Meskhidze: The physical and chemical characteristics of marine primary organic aerosol: a review, Atmos. Chem. Phys., 13, 3979–3996, doi:10.5194/acp-13-3979-2013, 2013.

Zorn, S. R., Drewnick, F., Schott, M., Hoffmann, T., and Borrmann, S.: Characterization of the South Atlantic marine boundary layer aerosol using an aerodyne aerosol mass spectrometer, Atmos. Chem. Phys., 8, 4711–4728, doi:10.5194/acp-8-4711-2008, 2008.

Comment: It would be helpful to define at the beginning the various carbon fractions (DOC, TOC, particulate OC, WinOC, OC* etc.) and to use it strictly throughout the manuscript. For example the term "organic aerosol fraction" page 2376, last line, is not precise.

AU: Yes but most of these abbreviates are already defined at the beginning of the paper, DOC and TOC in the abstract, EC, OC, WinOC, and WSOC in the first paragraph of the introduction. It is difficult to define OC* at the beginning since its concentrations are calculated (see line 16, page 2376). In the text when concerning aerosol the wording OC is clearly defined. We agree that it is not so clear for the OC content in snow and ice (when needed we clarified the wording in the revised version).

Comment: It is not clear if the DOC values presented include HCHO-C and monoacid-C? Are these volatile compounds not lost during sparging of inorganic carbon?

AU: As stated above the method gives excellent recovery even for species as volatile as many carboxylic acids and formaldehyde and methanol. Further details can be found in the supporting information available in the paper from Preunkert et al. (2011).

Comment: The seasonality of DOC shown in Fig. 1 is not at all clear. There is a peak in 1300 AD (forest fire) and a small one in 1298 AD, but none in 1299 AD.

AU: Thanks for this comment: Indeed, it is a fact the 1299 summer is the single case (on 15 years) for which the summer maximum is not detectable. In the revised version we will change the wording accordingly.

Minor comments: Page 2360, line 6: Gabrieli et al. AU: Thanks, Done

2361, lines 13-14: Give more details: Power of UV lamp, external or internal irradiation, material of extraction set-up. AU: We think that these information are not absolutely needed in this paper since the method has been already published and calibrated (Preunkert et al., 2011). However for your information the power of the lamp is 13Watts, it is an internal irradiation within a glass reactor and a carrier gas is used to transfer the CO2 produced from the sample.

2369, lines 21-24: Give reference for this statement. AU: The reference is the same that for the next sentence (i.e. Booth et al., 1998)

2373, line 11, it can be supposed . . (not concluded) AU: Right, Done

Caption Fig. 1: sodium maximum, DOC (instead of OC) concentrations AU: Done

Caption Fig. 2: DOC (instead of OC) concentrations AU: Done

Caption Fig. 3 and 4: MSA instead of CH3SO3- (consistent with legend) AU: Done

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