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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

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Abstract

While it is now recognized that organic matter dominates the present-day atmospheric aerosol load over continents, its sources remain poorly known. The studies of organic species or organic fractions trapped in ice cores may help to overcome this lack of knowledge. Available data on the dissolved (or total) organic carbon (DOC or TOC) content of snow and ice often appear largely inconsistent and until now no critical review was conducted to understand the causes of these inconsistencies. To draw a more consistent picture of the organic carbon amount present in solid precipitation that accumulates on cold glaciers, we here review available data and, when needed, complete the data set with analyses of selected samples. The different data sets are then discussed by considering the age (modern versus pre-industrial, Holocene versus last glacial maximum) and type (surface snow, firn, or ice) of investigated samples, the deployed method (DOC, TOC) and the applied contamination control. Finally, the OC levels of Antarctic, Greenland and Alpine ice cores are compared and discussed with respect to natural (biomass burning, vegetation emissions) and anthropogenic source (fossil fuel combustion) contributions to atmospheric OC aerosol.

1 Introduction

Although the carbonaceous matter that includes elemental carbon (EC) and organic carbon (OC) is recognized as a major constituent of present-day atmospheric aerosol over continents (Putaud et al., 2004; Legrand and Puxbaum, 2007; Jimenez et al., 2009), there are still major gaps with respect to its sources. In the present-day continental atmosphere, on a mass carbon basis, the elemental carbon (or black carbon, BC) fraction accounts only for 15% of carbonaceous aerosol (see Pio et al., 2007 for Europe), while the dominant fraction consists of organic carbon (OC). Whereas it is rather well established that secondary productions dominate primary emissions of organic carbon (OC) aerosol, the chemical nature of gaseous precursors

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also documented organic aerosols like C2–C5 dicarboxylates (Legrand et al., 2007a), long chain (C14–C22) carboxylates (Kawamura et al., 1996) and humic like substances (HULIS) (Calace et al., 2005; Guilhermet et al., 2013). Finally, though being present at levels more than 2 orders of magnitude lower than those of others organic species, polycyclic aromatic hydrocarbons (PAHs) were also investigated in an Alpine ice core (Gabrielli et al., 2010).

In addition to these investigations of individual organic species, several studies were dedicated to evaluate the total amount of OC present in snow and ice from Greenland, Antarctica, and the Alps. To date the results reveal however several large inconsistencies. For instance, whereas biogenic organic species able to produce organic aerosol within the atmosphere are mainly emitted by vegetation present on continents, some OC concentrations reported for pre-industrial ice extracted at Antarctic sites are unexpectedly higher (80–360 ppbC, Federer et al., 2008) than those reported for Greenland (10–40 ppbC, Preunkert et al., 2011) and Alpine (45–98 ppbC, Preunkert et al., 2011) pre-industrial ice. Furthermore, available data on the OC amount present in the pre-industrial Antarctic ice range from less than 10 ppbC (Preunkert et al., 2011) to 80–360 ppbC (Federer et al., 2008).

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. The new data include OC measurements of surface snow and snow pit samples collected under stringent conditions in Antarctica and in the Alps. In addition, organic carbon investigations were also carried out on selected sections of pre-industrial Greenland ice extracted at the sites of Summit and NEEM (including ice layers with boreal forest fire inputs), and in Antarctic ice core sections covering the last great climate change (from the last glacial maximum to the Holocene). Finally, several organic carbon fractions including WSOC and HULIS were investigated in the 2011 yr-round atmospheric aerosol sampling carried out at Concordia station (Antarctica). These unique WSOC aerosol data from the lower atmosphere of the East

containing more than 50 ppbC. Due to the blank variability the uncertainty reaches 35 % at the 5 ppbC level.

Under working conditions applied in this study, the efficiency of the oxidation relative to the potassium hydrogen phthalate was found to range from 85 to 125 % for different water-soluble organic molecule standards (see details in Preunkert et al., 2011). That is true for organic species present at significant levels in natural ice such as short chain mono- and dicarboxylic acids and formaldehyde, as well as for a few other compounds whose presence in ice is expected but not yet quantified (i.e., methanol, and C2–C3 aldehydes as glyoxal, methyl glyoxal and glycolaldehyde). For long chain polyacids that are also present in snow such as HULIS, the efficiency of the oxidation was found to be slightly lower, i.e. 80 ± 2 %. The extent to which this method oxidizes the water insoluble organic material that may be present in snow and ice will be discussed in Sect. 3.2.1.

2.2 Ancillary chemical analysis

Most snow and ice samples in which the organic carbon content was measured in this study were also investigated for ions. For cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and NH_4^+), a Dionex ICS-1000 chromatograph equipped with CG12 and CS12 separator columns was used. For anions, a Dionex DX-600 equipped with AG11 and AS11 separator columns was run with a quaternary gradient of eluents (H_2O , NaOH at 2.5 and 100 mM, and CH_3OH). A gradient pump system allows the determination of inorganic species (F^- , Cl^- , NO_3^- , and SO_4^{2-}) as well as short-chain carboxylates. Investigated carboxylates including formate (HCO_2^-), lactate ($\text{CH}_3\text{CHOHCO}_2^-$), acetate (CH_3CO_2^-), glycolate ($\text{CH}_2\text{OHCO}_2^-$), and glyoxylate (CHOCO_2^-), oxalate ($\text{C}_2\text{O}_4^{2-}$), malate ($\text{CO}_2\text{CH}_2\text{CHOHCO}_2^{2-}$), malonate ($\text{CO}_2\text{CH}_2\text{CO}_2^{2-}$), succinate ($\text{CO}_2(\text{CH}_2)_2\text{CO}_2^{2-}$), and glutarate ($\text{CO}_2(\text{CH}_2)_3\text{CO}_2^{2-}$). The detection limits for major ions like ammonium, nitrate, and sulfate are close to 1 ppb, those for most carboxylates close to 0.1 ppb.

In addition to short chain carboxylates, other potential contributors to the OC content of solid precipitation like short chain aldehydes were investigated in some samples.

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First, HCHO was measured in a few snow pit samples collected at Concordia and in the Alps as well as in a few ice core sections from the Greenland NEEM site. Measurements were done with a fluorimetric method that is based on the liquid phase reaction of formaldehyde with acetyl acetone and a $\text{CH}_3\text{COONH}_4\text{-CH}_3\text{COOH}$ mixture (Hantzsch reagent). The deployed analyzer (Aerolaser AL4021) has a detection limit of 0.1 ppb (Legrand et al., 2007a). A few measurements of some other carbonyl compounds including acetaldehyde, propionaldehyde and acetone were achieved in Alpine surface snow as well as in Alpine ice covering the 1940s (Houdier et al., 2000). Hereby, only acetaldehyde was detected at a significant level (~ 4 ppb, i.e. 2 ppbC).

Water-soluble HULIS were investigated in several snow pit samples collected at Concordia and in the Alps. HULIS were extracted with a DEAE (diethylaminoethyl) resin and the quantification of their organic carbon content was made with a Shimadzu TOC analyzer (Guilhermet et al., 2013).

2.3 Sampling and sub-sampling of snow and ice

The OC content was investigated in various snow and ice samples collected on polar ice sheets (Antarctica and Greenland) as well as at the high-elevated Alpine site of the Col du Dôme (4250 m a.s.l., Mont Blanc Massif, French Alps). It has to be emphasized that, the measurement of OC, which is present at trace levels in precipitation of remote regions, is very sensitive to contamination from numerous organic gases present in the ambient air of laboratories. Thus the DOC (or TOC) content of snow deposits is documented until now only in snow samples collected under stringent conditions nearby the surface or in snow pits but not in firn cores. Note that this contamination problem does not hamper measurements of the water insoluble part of OC (WinOC) retained on quartz filters by filtering melted snow and ice samples (Legrand et al., 2007a).

2.3.1 Surface snow and snow pits

With only two studies conducted in Antarctica (at the South Pole and coastal areas, Table 1) and two studies performed at Summit in central Greenland (Table 2) the OC content of the surface snow pack remains poorly documented (see Sect. 3). With levels reaching several hundreds of ppbC, the Antarctic snow (both coastal and inland) appears unexpectedly rich in OC with respect to the one of central Greenland. Furthermore, the two central Greenland studies show differences by a factor of 4 in the OC abundance of surface snow (Table 2).

With the aim to enlarge this rather inconsistent data set, surface snow and snow pit samples were collected at Concordia located on the high East Antarctic plateau and at the Col du Dôme in the Mt Blanc massif. At Concordia, surface snow (0–5 and 5–10 cm depth) was collected in January 2010. Furthermore, twenty-four snow samples were collected in a 1 m deep snow pit dug in January 2012 at Concordia (Table 1).

At the Col du Dôme, the surface snow layer corresponding to a 3 day old snow precipitation event (having occurred 14 September 2012) was sampled (4 samples between 0 and 20 cm depth), together with the upper most 1.5 m of the snowpack permitting to document snow deposited during the entire summer 2012 as well as the winter 2011/2012 (18 samples). Finally, 4 surface summer snow samples were collected in June 2011 (Table 2).

All samples were collected in airtight glass bottles (Schott, Mainz, Germany) of different sizes (from 100 mL to 5 L). Indeed, whereas 100 mL bottles are adequate for OC sampling even for samples containing less than 5 ppbC of OC, a volume of 500 mL of melted snow is needed to reach a HULIS detection limit of 1 ppbC as required for Antarctic snow and for Alpine winter snow layers. Glass bottles were cleaned by rinsing them several times with ultrapure water (Purelab Ultra MK2 analytic system commercialized by ELGA LabWater/VWS (UK) Ltd, organic content of less than 2 ppbC) a few hours to days before sampling, and then tightly closed until sampling. At Concordia, snow samplings were conducted in the clean air sector located at a few hundred

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meters upwind from the main station. When needed, the snow sampling was done with a glass scraper that was previously washed with ultrapure ELGA water.

Blank measurements of the glass bottle cleaning and storage procedure were made by analysing the OC content of an ultrapure water volume of about 20 % the volume of bottle (i.e. similar to the minimum sample liquid volume collected by filling completely bottle with snow) poured in the respective bottles. The blank value was found to be close to the detection limit of 3–5 ppbC when blank measurements were performed no later than a few hours after the cleaning. Tests made on blank bottles which were put in sealed plastic bags together with those used to collect snow, revealed however that during the storage time between cleaning, sampling and analysis, contamination took place. A typical bottle blank value of 30–50 ppbC was observed when glass bottles were stored for two days in the lab after cleaning. Such a contamination over time of airtight glass bottles is consistent with observations from Preunkert et al. (2011) who reported a mean contamination of 0.13 and 25 ppbC h⁻¹ in a 4 mL volume of ultrapure water put in a 100 mL airtight glass bottle stored in the clean room and in a “general purpose” room of the lab, respectively. Note that when glass bottles were cleaned well before their use to sample snow, larger blank values were observed. For instance, the glass bottle blank of the flasks designed to sample a snowpit at Vostok (not shown) revealed a value close to 160 ppbC, likely due to the storage over several months under various atmospheres before and after the snow sampling. Therefore, the bottle cleaning of snow samples collected within this study (see Tables 1 and 2) was done only a few hours up to 3 days before sampling and a storage bottle blank was systematically analysed. With these precautions bottle blank values generally remained below 25 ppbC. Since these values are significant with respect to measured snow concentrations, they were subtracted from snow concentrations.

Another problem related to the use of Schott glass bottles to sample snow appears at the very low temperatures encountered in Antarctica (–30 °C). At these temperatures, snow grains that stick on the glass thread do not melt even when compressed in the thread plug of the glass bottle during closure of bottle. Thus the bottle cap does not

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close properly and significant contamination takes place during melting of sample at ambient lab temperature. For instance, on a total of 24 bottles used to collect snow pit samples at Concordia in 2012, nine bottles were found to remain well closed during the melting step, whereas fifteen bottles were not closed tightly showing higher DOC content (82 ± 24 ppbC instead of 30 ± 20 ppbC).

2.3.2 Ice core subsampling

OC investigations were conducted in ice cores extracted at various locations in Antarctica and Greenland, as well as at the Col du Dôme Alpine site. With the aim to investigate change of the OC level with respect to the proximity of the ocean in Antarctica, investigations were made on ice cores extracted at the high plateau (Vostok and Dome C) as well as at sites located closer to the coast (i.e. in the D47 core and at the top of the Caroline ice core drilled at the coast) (Table 1). The ages of the ice samples from the Antarctic ice cores were estimated by Parennin et al. (2004) for Vostok, by Jouzel et al. (1989) for Dome C, and by Ciais et al. (1994) for D47. In the case of the Caroline ice core drilled in the margin area of East Antarctica (Yao et al., 1990), the ice from increasing core depth originates from increasing distance from the coast. In Table 1, based on the study from Lorius and Merlivat (1997), we report therefore an estimate of the altitude origin of the investigated ice core sections corresponding to the Holocene. The Dome C and Caroline OC investigations include, for the first time Antarctic ice samples which correspond to the last glacial maximum (LGM).

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 Greenland ice and to examine the impact 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), on the OC levels. The age of ice from the Summit and NEEM sites were estimated by Clausen et al. (1997) and Rasmussen et al. (2013), respectively.

sample concentrations. HULIS were measured on 5 selected winter and summer filters using a filter surface of 36 cm² for each sample.

3 Results and discussions

3.1 Presentation of data obtained in this study

OC data of snow and ice samples obtained in this work are summarized in Table 1 for Antarctica and in Table 2 for Greenland and the Alps. Antarctic ice samples were not seasonally resolved, and values reported in Table 1 correspond to annual means. In contrast, all OC values reported for Greenland snow and ice layers from Summit and NEEM are seasonally resolved. As previously discussed in numerous publications (see Legrand and Mayewski (1997) and references therein), the seasonality of major ions in Greenland ice exhibits a sodium maximum during the winter season, a calcium peak in spring, and a maximum of ammonium and nitrate in summer (see the examples reported in Figs. 1 and 2). As seen in Fig. 1, the ice layer located at the top of the Summit ice core section exhibits a large increase of the ammonium level. As for the first time discussed by Legrand et al. (1992) such ammonium events that are accompanied by a large formate increase are related to plumes of boreal forest fires that can reach the Greenland ice cap in summer. Similarly, another forest fire event was detected in a NEEM ice core layer located at 140.15 m depth (see Fig. 2 and discussions in Sect. 6.2).

3.2 A critical discussion on data inconsistencies

As seen in Table 1, OC concentrations widely fluctuate from site to site and from very recent snow to old ice, the range being particular large for Antarctic samples (from less than 5 ppbC up to 900 ppbC, Table 1). Prior our shallow snow study conducted at Concordia, data tended to suggest that OC is more abundant in the recent snow layers than in ice. Since this tendency is even more pronounced in Antarctica than in

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to OC measurements. Whereas this procedure was applied by Hagler et al. (2007a), all the other studies using UV methods (Federer et al., 2008; Twickler et al., 1986; Preunkert et al., 2011; Legrand et al., 2007a, 2013) do not remove insoluble particles prior OC analysis.

If the water insoluble organic fraction (WinOC) of sample is large with respect to the one of water-soluble organic species, the direct use of an UV method without sample filtering would partly account for the above-discussed discrepancies. However, at the very remote places that we discuss here, insoluble organic carbon is not expected to dominate the organic carbon budget. As an example, the contribution of WinOC retained by filtering the samples through quartz filters has been documented for summer snow samples at Summit (Hagler et al., 2007a), showing on average a WinOC/DOC ratio close to 10% at that site. Given this low WinOC contribution, it is even possible that UV methods applied without sample filtering are able to partly (or totally) oxidize the particulate matter present in this kind of samples.

Federer et al. (2008) compared their UV method with a Sievers 900 TOC analyser and report a mean value of 145 ppbC measured with their UV system compared to 155 ppbC with the Sievers in a melted ice sample from Dye-3 (South Greenland). Given the certified blank for the Sievers vial (10 ppbC) the authors concluded that the difference between the two results is not significant. Using a hydrophilic PTFE filter (0.45 μm , Millex-LCR from Millipore) to remove particulate organic matter from samples, the authors filtered another melted ice sample from Dye-3. This time the unfiltered sample revealed an OC content of 204 ppbC against 190 ppbC measured in the filtered sample, that lead the authors to suggest that their UV method measures rather TOC than DOC in samples containing a small amount of insoluble organic matter. In addition, their results suggest that particulate organic content of precipitation at remote sites such as Greenland contributes for a minor fraction to the total organic content. Attempts made by Preunkert et al. (2011) to quantify the recovery of their method for particulate carbon of melted ice samples were unsuccessful due to contamination occurring during sample filtering. Preunkert et al. (2011) therefore reported their data as dissolved

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that the corresponding ice was extracted by using a drill fluid whereas other data were obtained from ice cores extracted by dry drilling. In addition, OC sampling of the Talos Dome ice was done continuously by applying a melting head on the ice (Federer et al., 2008). From our experience, OC measurements are very sensitive to the presence of cracks in the ice, especially when a fluid was used for the drilling. For instance, one of the three NEEM ice sections (186.6 m depth, Table 2) was damaged with a visible inner crack. Although having cleaned it with the same procedure than the other NEEM ice sections, the 3 pieces of ice from this section clearly indicated a remaining huge contamination (mean value of 570 ± 50 ppbC) and required a subsequent intensive rinsing of the melting glass device over several days to recover typical blank levels. From that it can be concluded that the melting head used for the ice decontamination had either crossed existing micro-cracks or induced the formation of new ones, which allowed penetration of drilling liquid inside the Talos Dome OC samples. It is also interesting to examine OC measurements made on ice from the 905 m long Dome C ice core that contains cracks but was extracted in 1978 using a thermal drill but without fluid. As seen in Table 1, in spite of the presence of cracks, OC values observed in this kind of ice remain fairly close to 10 ppbC suggesting that cracks efficiently re-close rapidly after the core extraction limited any subsequent contamination during storage of ice cores.

4 Towards a more comprehensive picture of the OC content of snow and ice

Several points emerge from the above discussions on existing inconsistencies in the OC literature data. It has to be noted that, the differences related to the insoluble OC recoveries of the deployed (UV versus combustion) methods cannot account for observed large inconsistencies. Instead, the inconsistencies highlighted in Tables 1 and 2 seem to be often related to contamination problems during sampling and storage of snow, as well as to the ice quality and/or its degradation (i.e. formation of cracks) during the subsampling.

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Discarding values obtained in snow sampled into plastic bags or stored into not properly closed glass bottles, an OC concentration of around 10–15 ppbC seems to be a typical value for Antarctic surface snow (Table 1). With the single exception of Talos Dome, most of OC concentrations observed in good quality Holocene ice range between 5 and 10 ppbC. 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 snowpit 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). Note also that OC values observed in the Holocene ice indicate values close to 5 ppbC at Vostok and slightly higher ones in Caroline ice (~ 10 ppbC) corresponding to precipitation deposited initially between 1320–1550 m elevation. More data are however needed to increase the significance of such a difference and to discuss a possible contribution of the Antarctic ocean to the budget of organics in Antarctic snow.

As done for Antarctica, the consistency of the various OC data gained in Greenland is examined after having excluded the ones obtained from snow sampled into plastic bags (Table 2). Annual mean values observed within this study in 60 pre-industrial Summit ice samples that were not influenced by biomass burning inputs (see Sect. 3.1) are close to 12 ± 7 ppbC. These values are consistent with the more limited Summit data set (10 samples) reported by Preunkert et al. (2011) (23 ± 11 ppbC). A similar range is observed in the NEEM pre-industrial ice (19 ± 7 ppbC, Table 2). Over the more recent years (2002–2005) at Summit, Hagler et al. (2007a) reported a mean annual DOC value of 40 ppbC (i.e., at least twice higher than the pre-industrial level). As further discussed in Sect. 6.2, this difference may be attributed to man made activities. In addition, the latter study reported also a mean DOC value close to 110 ppbC for the 2006 surface summer snow at Summit (Table 2). As discussed by Anderson et al., (2008), it seems that most of post depositional OC effects at that site are due to formic

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to the presence of methanesulfonate in Greenland. Finally, Fig. 3 reports for the first time the OC speciation of Antarctic snow. Compared to the other sites, C1–C3 mono-carboxylic acids and HCHO represent a weaker contribution (11 % of OC). In addition, not only MSA but also HULIS represents a significant fraction of WSOC at that very remote site. The conclusion drawn for the case of the Alps that C1–C3 mono-carboxylic acids and HCHO represent the most important water-soluble organic gases contributing to the OC content of ice and that consequently the OC* quantity corresponds to OC aerosol, remains likely also true for Greenland and Antarctica except if oceans surrounding the Greenland and Antarctic ice caps emit other water-soluble organic gases than monocarboxylic acids and/or formaldehyde. One possible candidate is dimethylsulfoxide (DMSO), a water-soluble gas produced by the DMS/OH oxidation via the addition channel that is particularly efficient at low temperatures. Typical concentrations of 3 ng C m⁻³ STP of DMSO, which sporadically reach 20 ng C m⁻³ STP, were observed in summer at coastal Antarctica by Jourdain and Legrand (2001). However, as discussed by Legrand et al. (2001), once trapped in the liquid phase (cloud or hydrated aerosol), DMSO is quickly oxidized into MSA. Therefore the contribution of oxidation by-products from DMS emitted by the ocean at high latitudes, contribute rather to the OC* aerosol fraction (via MSA) than to the fraction related to water-soluble organic gases. In the following we assume therefore that the OC* quantity calculated as [OC]–[Monoacid-C]–[HCHO-C] would correspond to OC aerosol fraction in Greenland and Antarctica snow and ice.

6 Atmospheric implications

In this section we will discuss to what extent the observed spatial variations of the OC ice contents are consistent with our present knowledge of organics in the atmosphere. After that, we will initiate a discussion on the origins and potential atmospheric implications of some observed temporal changes detected in Antarctica, Greenland and

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layers often develop. Second, atmospheric gases like HCOOH and CH₃COOH are weak acids, for which incorporation in precipitation strongly depends on cloud pH and cloud water liquid content. Third, at least in Greenland, snow emissions are suspected to strongly control atmospheric concentrations observed in the very stable lowermost atmosphere lying over this ice cap (Dibb and Arsenault, 2002). One consideration that will be relevant in further discussions of these species is the fact that in the present-day atmosphere they are mainly secondary produced from biogenic precursors mainly emitted by the continental biosphere (Paulot et al., 2011). The weak contribution of anthropogenic sources to the budget of monocarboxylic acids was also supported by the examination of their long-term ice core trends in Greenland (Legrand and De Angelis, 1996) and in the Alps (Legrand et al., 2003).

The main cause leading to the observed increase of the OC content from Antarctic to Greenland and from Greenland to the Alpine pre-industrial ice is related to an increase of the OC* fraction. Using concentrations of monocarboxylic acids and HCHO reported in Table 3, we calculate that in surface snow OC* increases from ~ 13 ppbC (annual mean) in Antarctica, to 44 ppbC (summer) in Greenland, and ~ 210 ppbC (summer) in the Alps. To relate these snow values with atmospheric observations we also compare snow and air concentrations of sulfate and ammonium at the three sites. At Concordia, sulfate and ammonium data suggest that 1 gram of snow roughly contains the amount of aerosol present in 1 m³ STP of air. The 13 ppbC of OC* found in Concordia surface snow are consistent with the WSOC level observed in the atmosphere (annual mean of 13 ngC m⁻³ STP). At Summit, sulfate and ammonium data suggest that in summer 1 gram of snow roughly contains the amount of aerosol present in 0.5 ± 0.2 m³ STP of air. In this way, the 44 ppbC of OC* found in Greenland summer snow are consistent with the WSOC level observed in the atmosphere (summer mean of 77 ngC m⁻³ STP). In contrast to the case of Antarctica and Greenland for which surface snow and atmospheric measurements cover roughly the same time periods, for the Alps values reported for atmospheric aerosols were obtained in summer 2004 by Legrand et al. (2007b) and Preunkert et al. (2007) whereas summer snow concentrations cover

of the chemically unidentified fraction of DOC, it is difficult at this stage to discuss further the causes of these changes.

Our Greenland study documents for the first time the DOC content together with its speciation along forest fire events (Figs. 1 and 2). The pioneer study from Legrand et al. (1992) already revealed an input of formate in such events. Here, we can extend the examination of the organic composition of such perturbation. As seen in Fig. 2, it appears that the main contributors to the increase of DOC along such event are monocarboxylates (77%) mainly as formate, chemically unidentified species (20%), and to a lesser extent dicarboxylates (2%) mainly as oxalate, and HCHO (1%). We have to point out here that in contrast to background formate levels that are likely present in the form of formic acid, the formate observed along with forest fire events is present in the form of ammonium formate aerosol. As discussed in Sect. 5, the HULIS level is not yet documented in Greenland snow and ice. These species may account for the unknown contribution in forest fire events since they are known to be formed during incomplete breakdown of polymeric plant matter (Mayol-Bracero et al., 2002).

Finally, as seen in Table 1, though being still limited to a few samples, the Antarctic data gained on the Caroline ice core suggest a significant decreasing level of OC during the ice age compared to the Holocene. Note that, even probably slightly contaminated due the presence of cracks (see Sect. 3.2.2), the Dome C data also tend to suggest lower levels during ice age than during the Holocene. One possible cause for this decrease during ice age would be the lowering of continental biogenic emission (vegetation) following colder and drier conditions.

7 Conclusions and prospective

Available data on the dissolved (or total) organic carbon content of snow and ice from Antarctic, Greenland and Alpine ice cores were critically reviewed to understand the causes of existing inconsistencies. Most of large inconsistencies were found to be related to contamination problems during sampling and storage of snow, as well as

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degradation of the ice quality (presence of cracks) rather than to the different recovery of deployed (UV versus combustion) methods in oxidizing insoluble OC material present in samples. Discarding outliers from data, a more consistent picture with respect to our knowledge of OC sources, that are predominantly present over continents, emerges. For instance, the typical annual pre-industrial ice content is close to $\sim 5\text{--}10$ ppbC in Antarctica, 20 ppbC in Greenland and 70 ppbC in the Alps. The investigation of chemical organic species present in snow and ice showed that, whatever the site (Antarctica, Greenland, or Alps), the C1–C3 monocarboxylic acids and HCHO represent the most important water-soluble atmospheric organic gases contributing to the OC content of ice and that the remaining amount of OC denoted OC* ($[\text{OC}^*] = [\text{OC}] - [\text{Monoacid-C}] - [\text{HCHO-C}]$) would correspond to atmospheric OC aerosol. C2–C5 dicarboxylic acids, HULIS, and sometimes methanesulfonate were found to contribute to the OC* quantity but a large fraction remained chemically unidentified.

A preliminary discussion was done on the change from pre-industrial to present-day atmosphere that was detected in the Alps and Greenland. In a recent study, the case of the alpine OC trend in summer ice was recently documented by DO^{14}C measurements suggesting that in spite of three times higher levels in the 70s and 80s compared to prior World War II, a major fraction of OC is biogenic in origin. Many environmental parameters may have caused strengthened biogenic emissions of atmospheric WSOC including warmer temperatures, higher atmospheric CO_2 , enhanced oxidative capacity of the atmosphere. For Greenland, it has to be emphasized that the OC increasing trend since pre-industrial era is documented only by the level in pre-industrial ice level and in snow collected over the very recent years in snow-pits. A complete study of the change between the pre-industrial times and the present-day is limited by the fact that the cleaning of the firn material in view of OC measurement remains a difficult work. Finally, this paper reports for the first time a few data on the natural variability of the OC content of ice in relation with sporadic arrival of forest fire plumes over Greenland or response to the last glacial/interglacial transition in Antarctica.

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Table 1. Organic carbon content measured in snow and ice from various Antarctic sites. TOC refers to total organic carbon concentrations obtained with a catalytic combustion (CC) method. All other values that were obtained with a UV oxidation method without filtration of samples would correspond to dissolved organic carbon (DOC) but also to a large part of the particulate organic fraction present at levels of a few ppbC (less than 10% of DOC, see discussion in Sect. 3.2.1). For the methods: NDIR CO₂ refers to a non-dispersive infrared CO₂ detector, Conduc. to a CO₂ electrolytic conductivity detector. PE denotes the use of polyethylene vials. S refers to summer season. N are the numbers of analysed samples.

Sites, Elevation (m a.s.l.)	Material, Age	OC in ppbC (N)	Method	Vials	References
South Pole (2850)	Surface snow, S 2001 AD	TOC = 400 ± 130 (11)	CC/NDIR CO ₂	PE	Grannas et al. (2004)
Concordia (3250)	Surface snow, S 2010 AD	14–27 (2)	UV/NDIR CO ₂	Glass	This work
Concordia (3250)	Snow pit, 2002–2012 AD	10–150** (24)	UV/NDIR CO ₂	Glass	This work
Princess Elizabeth Land (0–2210)	Surface snow*	88 < TOC < 928 (38)	CC/NDIR CO ₂	PE	Antony et al. (2011)
Dronning Maud Land (610–3015)	Surface snow*	13 < TOC < 345 (20)	CC/NDIR CO ₂	PE	Antony et al. (2011)
Victoria Land, Antarctic coast	Snow pit, 1989–2000 AD	TOC < 96 (36)	CC/NDIR CO ₂	PE	Lyons et al. (2007)
Vostok (488)	Ice, 9970 BP	5.2 ± 1.7 (7)	UV/NDIR CO ₂	Glass	Preunkert et al. (2011)
Vostok (488)	Ice, 8300 BP	5.8 ± 1.4 (3)	UV/NDIR CO ₂	Glass	This work
D47 (1500)	Ice, 1280 AD	1.7 ± 1.7 (2)	UV/NDIR CO ₂	Glass	Preunkert et al. (2011)
D47 (1500)	Ice, 1660 AD	6.2 ± 5.8 (7)	UV/NDIR CO ₂	Glass	This work
South Pole (2850)	Ice, 1010 BP	7.4 (1)	UV/NDIR CO ₂	Glass	Preunkert et al. (2011)
Dome C (3240)	Ice, 10 300 BP	21.1 ± 4.5 (4)	UV/NDIR CO ₂	Glass	This work
Dome C (3240)	Ice, 19 600 BP	14.5 ± 5.4 (7)	UV/NDIR CO ₂	Glass	This work
Caroline (~ 1320)	Ice, Holocene	10.9 ± 3.7 (9)	UV/NDIR CO ₂	Glass	This work
Caroline (~ 1550)	Ice, Holocene	9.0 ± 4.5 (8)	UV/NDIR CO ₂	Glass	This work
Caroline (~ 3000)	Ice, LGM	5.0 ± 3.8 (7)	UV/NDIR CO ₂	Glass	This work
Caroline (~ 3000)	Ice, LGM	5.3 ± 3.7 (16)	UV/NDIR CO ₂	Glass	This work
Talos Dome (2300)	Ice, 4350–4650 BP	80–360 (continuous)	UV/Conduc.	–	Federer et al. (2008)

* Sampling year not specified.

** Numerous samples were contaminated following difficulties to properly close the cap of glass bottle at cold temperatures (see details in Sect. 2.3.1).

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Table 2. Same as Table 1 for OC content of snow and ice from various Greenland sites and the Alps. Values are reported as DOC when samples that were measured with a UV oxidation method were previously filtered to remove particulate organic material (see Sect. 3.2.1). All other values that were obtained with a UV oxidation method without filtration of samples would correspond to TOC and DOC in the case of snow and ice from Greenland and the Alps, respectively (see Sect. 3.2.1).

Sites, Location, Elevation (m a.s.l.)	Material, Age (AD)	OC in ppb C (N)	Method	Vials	References
Summit, central Greenland (3240)	Surface snow, S 2006	DOC = 111 ± 45 (S) (219)	UV/Conduc.	Glass	Hagler et al. (2007a)
Summit, central Greenland (3240)	Snow pit, 2001–2002	400 (W) < TOC < 580 (S) (4)	CC/NDIR CO ₂	PE	Grannas et al. (2004)
Summit, central Greenland (3240)	Snow pit, 2002–2006	20 (W) < DOC < 55 (S) (29)	UV/Conduc.	Glass	Hagler et al. (2007a)
Summit, central Greenland (3240)	Ice, 1020	10 (W)–40 (S) (10)	UV/NDIR CO ₂	Glass	Preunkert et al. (2011)
Summit, central Greenland (3240)	Ice, 1557–1559	8 (W)–35 (S) (22)	UV/NDIR CO ₂	Glass	This work
Summit, central Greenland (3240)	Ice, 1400–1402	6 (W)–20 (S) (20)	UV/NDIR CO ₂	Glass	This work
Summit, central Greenland (3240)	Ice, 1298–1300	6 (W)–80** (S) (21)	UV/NDIR CO ₂	Glass	This work
NEEM site, Greenland (2450)	Ice, 684–686	10 (W)–33 (S) (6)	UV/NDIR CO ₂	Glass	This work
NEEM site, Greenland (2450)	Ice, 1465–1466	17–116** (8)	UV/NDIR CO ₂	Glass	This work
Dye 3, Greenland (2486)	Snow pit, 1982–1984	30 (W)–320 (S) (19)	UV/NDIR CO ₂	Glass	Twickler et al. (1986)
Mt Blanc, French Alps (4250)	Surface snow, Sep. 2012	107 ± 12 (4)	UV/NDIR CO ₂	Glass	This work
Mt Blanc, French Alps (4250)	Snow pit, 2011	304 (S) (4)	UV/NDIR CO ₂	Glass	This work
Mt Blanc, French Alps (4250)	Snow pit, 2012	70 (W)–210 (S) (18)	UV/NDIR CO ₂	Glass	This work
Mt Blanc, French Alps (4250)	Ice, 1952–1976	270* (S) (26)	UV/NDIR CO ₂	Glass	Legrand et al. (2007a)
Mt Blanc, French Alps (4250)	Ice, 1971–1988	86 (W)–201 (S) (137)	UV/NDIR CO ₂	Glass	Legrand et al. (2013)
Mt Blanc, French Alps (4250)	Ice, 1925–1936	45 (W)–98 (S) (105)	UV/NDIR CO ₂	Glass	Preunkert et al. (2011)
Mt Blanc, French Alps (4250)	Ice, 1925–1936	128* (S) (4)	UV/NDIR CO ₂	Glass	Legrand et al. (2007a)
Mt Blanc, French Alps (4250)	Ice, 1921–1951	44 (W)–91 (S) (335)	UV/NDIR CO ₂	Glass	Legrand et al. (2013)

* Values obtained without subtracting the blank of the ice decontamination procedure (~30 ppb C, Legrand et al., 2007a). When seasonally resolved, data are reported for summer (S) and winter (W). ** refer to values observed in layers from Summit and NEEM containing input from biomass burning events (see Figs. 1 and 2).

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Table 3. Air and snow concentrations of various species observed at Concordia, Summit, and Mt Blanc. Species include atmospheric gases (HCOOH, CH₃COOH, and HCHO) and aerosol such as water-soluble organic carbon (WSOC), Humic like substances (HULIS), methanesulfonate (CH₃SO₃⁻), dicarboxylates, sulfate, ammonium, and sodium. For OC concentrations of snow, we also report (values under parenthesis) the calculated OC* fraction (see Sect. 5).

	Concordia (central Antarctica)		Summit (central Greenland)		Mt Blanc (French Alps)	
	Air (annual)	Snow (annual)	Air (summer)	Snow (summer)	Air (summer)	Snow (summer)
HCOOH	43 pptv (23 ng C m ⁻³ STP) ^b	0.3 ppb C ^a	500 pptv (268 ng C m ⁻³ STP) ^{d–e}	2.4 ppb C ^k	300 pptv (160 ng C m ⁻³ STP) ^o	49 ppb C ^a
CH ₃ COOH	27 pptv (30 ng C m ⁻³ STP) ^b	0.9 ppb C ^a	400 pptv (430 ng C m ⁻³ STP) ^{d–e}	7.2 ppb C ^k	278 pptv (300 ng C m ⁻³ STP) ^o	8 ppb C ^a
HCHO	50 pptv (27 ng C m ⁻³ STP) ^c	0.4 ppb C ^a	150 pptv (80 ng C m ⁻³ STP) ^f	1.6 ppb C ^l	400 pptv (215 ng C STP) ^{p–q}	3.6 ppb C ^a
WSOC/OC	13 ng C m ⁻³ STP ^a	~ 15 ppb C ^a (13 ppb C)	77 ng C m ⁻³ STP ^g	55 ppb C ^m (44 ppb C)	150 ng C m ⁻³ STP ^r	270 ppb C ^a (209 ppb C)
HULIS	1.6 ng C m ⁻³ STP ^a	2 ppb C ^a	ND	ND	ND	30 ppb C ^a
CH ₃ SO ₃ ⁻	8.5 ng (1.1 ng C) m ⁻³ STP ^a	1.3 ppb C ^a	5 ng (0.6 ng C) m ⁻³ STP ^h	0.3 ppb C ^k	0	0
Diacids	0.3 ng (0.08 ng C) m ⁻³ STP ^a	0.05 ppb C ^a	< 5 (1.4 ng C) m ⁻³ STP ^j	< 0.8 ppb C ⁿ	20 ng C m ⁻³ STP ^r	16 ppb C ^a
SO ₄ ²⁻	55 ng m ⁻³ STP ^a	53 ppb ^a	200 ng m ⁻³ STP ^h	100–200 ppb ^{k–m}	400 ng m ⁻³ STP ^o	255 ppb ^a
NH ₄ ⁺	3.2 ng m ⁻³ STP ^a	2.6 ppb ^a	30 ng m ⁻³ STP ^l	10 ppb ^t	110 ng m ⁻³ STP ^o	190 ppb ^a

^a This work, ^b Legrand et al. (2012), ^c Hutterli et al. (2004) (see also comments in Sect. 4.2), ^d Dibb and Arsenault (2002), ^e De Angelis et al. (2012), ^f Jacobi et al. (2002), ^g Hagler et al. (2007b), ^h Jaffrezo et al. (1994), ⁱ Jaffrezo et al. (1998), ^j Silvente and Legrand (1993), ^k Legrand and Mayewski (1997), ^l Hutterli et al. (1999), ^m Hagler et al. (2007a), ⁿ Legrand and De Angelis (1996), ^o Preunkert et al. (2007), ^p Fried et al. (2008), ^q Kormann et al. (2003), and ^r Legrand et al. (2007b).

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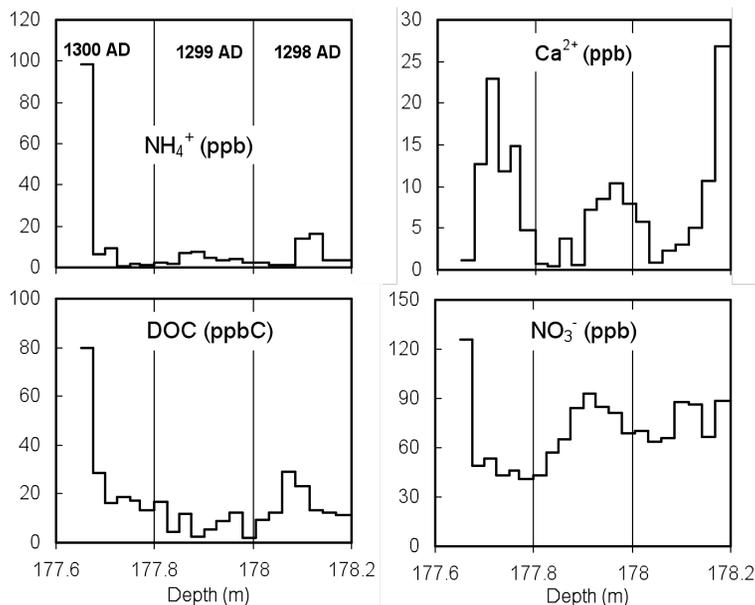


Fig. 1. Concentrations of ammonium, calcium, nitrate, and organic carbon along a 55 cm long ice core section extracted at Summit (central Greenland). Vertical lines refer to winter characterized by nitrate and ammonium minima, and sodium maximum (not shown). The calcium maximum is in spring. Note that the OC concentrations are higher in summer than in winter. As discussed in Sect. 3.1, the presence of a high level of OC in summer 1300 AD corresponds to a forest fire event as indicated by the large amount of ammonium and formate present in this layer (see also Fig. 2).

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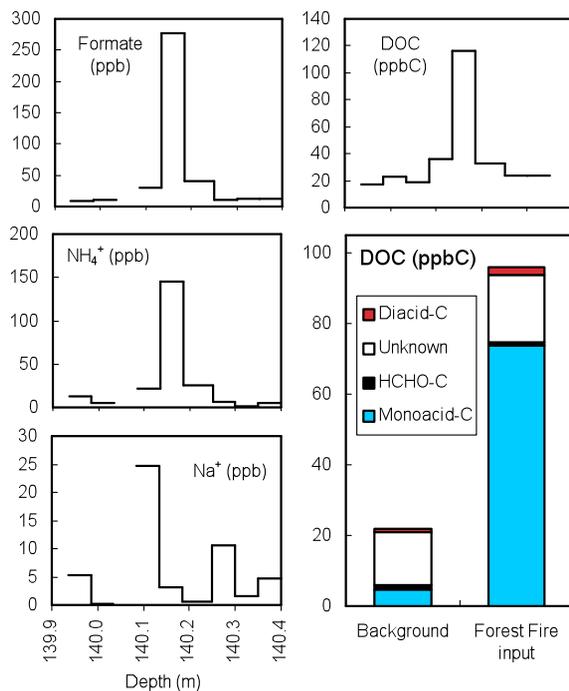


Fig. 2. Chemical signature of a forest fire event recorded in the NEEM ice site (dated to 1465 AD, see Sect. 2.3.2). Characterized by a large amount of ammonium and formate, the event took place in summer as suggested by the sodium minimum of this layer. Comparison of the organic carbon speciation along and outside the event (bottom right) indicates an input of OC mainly in the form of formate, to a lesser extent of dicarboxylates and other unidentified organic species (see Sect. 6.2).

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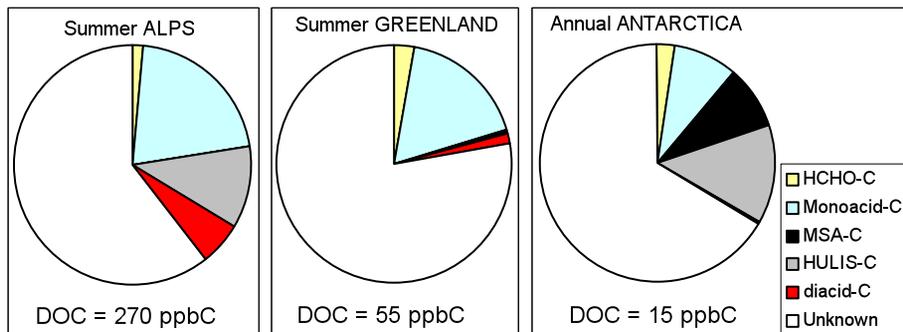


Fig. 3. From left to right: Chemical composition of DOC present in recent summer snow layers at the Col du Dôme and Summit sites, in recent annual snow layers at Concordia (see Sect. 4). The identified organic species include formaldehyde, C1–C3 monocarboxylic (formic, lactic, acetic, glycolic, and glyoxylic) acids, CH_3SO_3^- , C2–C5 dicarboxylic (oxalic, malic, malonic, succinic, and glutaric) acids, HULIS, and the remaining unidentified fraction of OC (see Sect. 4).

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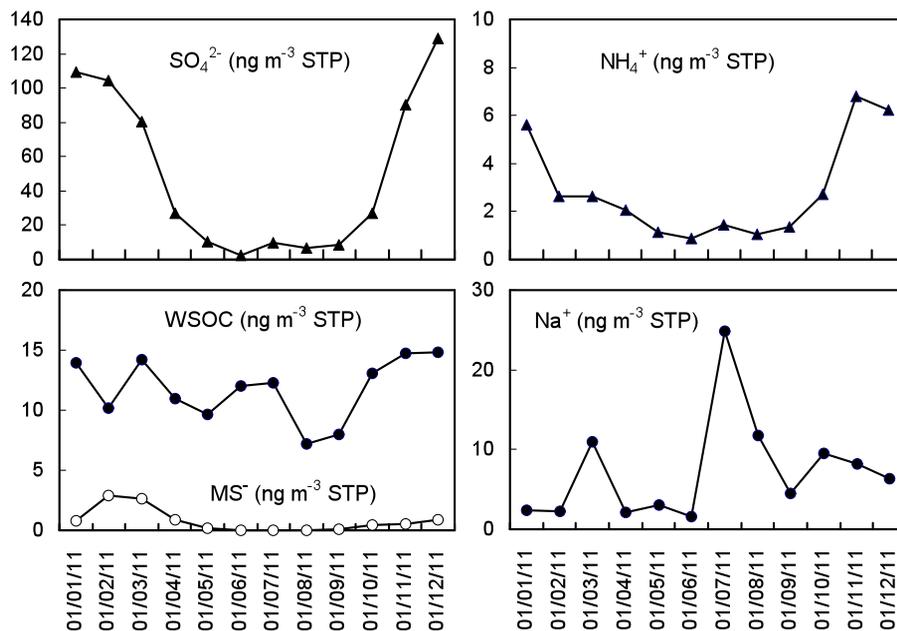


Fig. 4. Year-round bulk aerosol composition observed at Concordia in 2011. Note the higher sodium values in winter than in summer and the well-marked maximum of sulfate and methanesulfonate (CH_3SO_3^-) in summer (see discussions in Sect. 6.2).

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