

Towards a quasi-complete reconstruction of past atmospheric aerosol load and composition (organic and inorganic) over Europe since 1920 inferred from Alpine ice cores

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Abstract

Seasonally resolved chemical ice core records available from the Col du Dôme glacier (4250 m elevation, French Alps) are here revisited in view to reconstruct past aerosol load of the free European troposphere from prior World War II to present. The extended array of inorganic (Na^+ , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-}) and organic (carboxylates, HCHO, HUmic LIke Substances, dissolved organic carbon, water insoluble organic carbon, and black carbon) compounds and fractions already investigated permit to examine the overall aerosol composition and its change over the past. It is shown that the atmospheric load of submicron aerosol has been increased by a factor of 3 from the 1921–1951 to 1971–1988 years, mainly as a result of a large increase of sulfate (a factor of 5), ammonium and water-soluble organic aerosol (a factor of 3). It is shown that not only growing anthropogenic emissions of sulfur dioxide and ammonia have caused the enhancement of the atmospheric aerosol load but also biogenic emissions producing water soluble organic aerosol. This unexpected change of biospheric source of organic aerosol after 1950 needs to be considered and further investigated in scenarios dealing with climate forcing by atmospheric aerosol.

1 Introduction

The reconstruction of our changing atmosphere from the present-day polluted atmosphere back to preindustrial times, and the evaluation of the subsequent radiative impact are strongly needed to improve our understanding of present and future climate. From this point of view, the knowledge of past atmospheric changes in aerosol load and composition are required to predict future climate, particularly at regional scales.

The decrease of SO_2 emissions resulting from an improvement in the quality of fuel and emission abatements over the three last decades has led to a decrease of sulfate levels in the atmosphere over large industrialized regions, including Europe (Mylona, 1996). In the present-day European atmosphere, organic matter is recognized to be

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a major constituent of aerosol (Putaud et al., 2004; Pio et al., 2007). There are however still major deficits in knowledge with respect to its sources. For instance, the relative contribution of natural and anthropogenic sources to the present-day organic carbon (OC) aerosol as well as the variability of natural sources over the past is not well known. That contrasts with inorganic aerosol like sulfate for which source apportionment (natural versus anthropogenic) has been established and past anthropogenic emission inventories exist (see Mylona, 1996, for Europe). The study of chemical impurities trapped in solid precipitation accumulated over the past on cold glaciers, represents a unique and powerful way to reconstruct our changing atmosphere from the pre-industrial era to present-day (see Legrand and Mayewski, 1997, for a review).

To our knowledge, the most extended array of chemical species investigated in ice deposited since the beginning of the 20th century was obtained in ice cores extracted at the Col du Dôme (CDD, 4250 m.a.s.l.) glacier site located in the Mount Blanc massif (French Alps). Investigations included inorganic ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) and short chain (C_1 – C_5) mono- and dicarboxylates. The organic fraction was also documented along these ice cores for its dissolved organic (DOC) fraction, formaldehyde (HCHO), and Humic Like Substances (HULIS) (see Legrand et al. (2013) and references therein) which were investigated for the first time in ice. The CDD ice cores were shown to record quite well the seasonal cycle of chemical species in contrast to those extracted at other Alpine sites like Colle Gnifetti (4450 m.a.s.l., Swiss Alps) where, to the benefit of an extended archived time period, the preservation of winter layers is often incomplete even nearby the surface (Preunkert et al., 2000; Wagenbach et al., 2012). Although a rapid annual ice layer thinning appears with depth in the CDD ice cores, they own a good preservation of seasonal variations back to 1925 in relation with a high snow accumulation at the surface (3 m water equivalent). This large snow accumulation also minimized diffusional and depositional perturbations of the record of gases like nitric acid (Preunkert et al., 2003) or formic and acetic acids (Legrand et al., 2003). Finally, it is important to emphasize that nearby the CDD drill site stands the Vallot observatory (4360 m.a.s.l., 400 m southeast of the Col du Dôme

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drill site) where several atmospheric sampling campaigns were conducted (Preunkert et al., 2002, 2007; Legrand et al., 2005). Atmospheric information available here are very useful in view to invert chemical ice core records in terms of past atmospheric concentrations of water soluble gases and aerosols.

In this paper we review all chemical (organic and inorganic) records available in ice cores extracted from the high-elevated CDD Alpine site in view to extract comprehensive information on the past change of aerosol load and composition over Europe from 1920 to the recent decades.

2 Ice core dating, sampling and analyses

2.1 Dating

Since 1994, three ice cores were drilled close to bedrock at virtually the same place at the Col du Dôme glacier site (4250 m a.s.l.), located nearby the Mont Blanc summit. Whereas the C10 ice core (126 m long) and its twin (C11, 140 m long drilled less than 50 m away from the C10) were extracted in 1994, the CDK ice core (124 m long) was drilled in 2004.

The overall glacio-chemical setting of the CDD site and the accurate dating of its snow and ice layers are described in Preunkert et al. (2000). In brief, the dating was first established by counting annual layers along the ammonium C10 profile and the identification of the 1963 tritium or ^{137}Cs bomb peak. The dating of C10 was estimated to be better than ± 2 yr after 1954, ± 4 yr in the 1940's, and ± 5 yr around 1920. Based on examination of the ammonium profile, each annual layer was divided into two parts corresponding to winter and summer snow deposition following the procedure detailed in Preunkert et al. (2000). From that, the individual means of summer and winter half years were calculated for all chemical species.

Pieces of ice from the C11 core were used for some discontinuous chemical investigations. Its dating was established by scaling down the dating established on the C10

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core by checking the time horizons of 1954 and 1963 in the two ice cores (Legrand et al., 2007a). As seen in Fig. 1, the C11 ice core summer half year means of sulfate and nitrate are in very good agreement with the C10 ones over the 1925–1994 period.

5 The dating of the more recently drilled CDK ice core was more complicate to establish as detailed in Legrand et al. (2013). The dating was attempted by counting annual layers along the ammonium profile as done for C10. However, between 65.5 and 67.5 m water equivalent (mwe) the ammonium seasonal cycle vanishes and sulfate and nitrate exhibit unexpected low values. Below 67.5 mwe the ammonium seasonal signature recovers and remains easily detectable down to 91.5 mwe. Tritium measurements revealed that ice layers corresponding to the main bomb peak were definitely
10 missing in this core. It was concluded that a crevasse might have developed upstream of the borehole, having caused a hiatus in the CDK ice core stratigraphy. As suggested by tritium values, the CDK ice located below 67.5 mwe was deposited prior to 1954. The dating for the 67.5–91.5 mwe part of the CDK core was established by comparing
15 the stratigraphies of various species (ammonium, nitrate, sulfate, calcium, and others) with those of the C10 core. From that, Legrand et al. (2013) concluded that the CDK layers deposited between 86.0 and 67.5 mwe cover the 1925–1954 time period with an uncertainty of ± 4 yr. As seen in Fig. 1, the derived CDK ice core summer half year means of sulfate and nitrate appear again in very good agreement with the C10 ones
20 over the 1925–1994 period.

2.2 Sampling and analysis

For each species of concern, details on sampling and working conditions applied for analysis can be found in the references reported in Table 1. Depending on measurements, ice samples were cleaned mechanically in a cold room or by washing them
25 in ultrapure water. For determination of ions and HCHO, pieces of ice were cleaned under a clean air bench located in a cold room (-15°C) using an electric plane device. For HULIS measurements, ice was decontaminated in a clean room by washing it in three successive baths of ultrapure water produced by a Maxima HPLC system

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(Elga). Among all measurements, the one of DOC was found to be the most sensitive to contamination. To remove the contaminated outer part of ice pieces prior to DOC analysis, a special glass device was designed in which pieces of ice are cleaned with ultrapure water (Elga) and kept melting (Preunkert et al., 2011). During the ice melting, an inert gas atmosphere is maintained inside the glass receptacle to prevent contact of sample with ambient air of the lab. Note that until now cleaning of samples for DOC determinations can only be applied to ice material but not to porous firn. Only ions were determined along the firn part of the cores. These samples were cleaned similarly to the ice samples with a plane. For most species, blanks of the ice decontamination procedure were found to be insignificant with respect to respective levels found in the ice cores.

For cations (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and NH_4^+), a Dionex 500 chromatograph equipped with a CS12 separator column was used. For anions, a Dionex 600 equipped with an AS11 separator column 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 ($\text{CO}_2\text{CH}_2\text{CHOHCO}_2^-$), malonate ($\text{CO}_2\text{CH}_2\text{CO}_2^-$), succinate ($\text{CO}_2(\text{CH}_2)_2\text{CO}_2^-$), and glutarate ($\text{CO}_2(\text{CH}_2)_3\text{CO}_2^-$).

HCHO was measured by a fluorimetric method based on the liquid phase reaction of formaldehyde with acetyl acetone and a $\text{CH}_3\text{COONH}_4$ – CH_3COOH mixture (Hantzsch reagent). Water-soluble HULIS were extracted by using a DEAE (Diethylaminoethyl) resin and the quantification of the organic carbon content of the HULIS fraction was made with a Shimadzu TOC analyzer (Guilhermet et al., 2013). The dissolved organic content (DOC) of ice samples was determined by using a commercial Phoenix 8000 device (Teledyne Tekmar company), which was modified to allow DOC determinations at the level of a few ppbC (Preunkert et al., 2011). In brief, the liquid sample is first mixed with phosphoric acid and sparged to drive off inorganic carbon. Next, the sample

is transferred to a reactor where an UV lamp together with the use of synthetic air as a carrier gas oxidizes organic carbon into CO₂ hereafter quantified in a Non-Dispersive Infrared (NDIR) detector.

3 Presentation of available data

3.1 Saharan dust events

Saharan dust plumes that sometimes reach Western Europe also affect the Alps and disturb the chemistry of snow deposits. Following Wagenbach et al. (1996) these events can be identified as calcium rich alkaline snow layers. The acidity (or alkalinity) of samples can be evaluated by checking the ionic balance between anions and cations with concentrations expressed in micro-equivalents per liter (μEq L⁻¹):

$$[H^+] = ([F^-] + [Cl^-] + [NO_3^-] + [SO_4^{2-}] + [MonoAc^-] + [DiAc^{2-}]) - ([Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] + [NH_4^+]) \quad (1)$$

$$\text{with } [MonoAc^-] = [HCO_2^-] + [CH_3CHOHCO_2^-] + [CH_3CO_2^-] + [CH_2OHCO_2^-] + [CHOCO_2^-] \quad (2)$$

$$\text{and } [DiAc^{2-}] = [C_2O_4^{2-}] + [CO_2CH_2CHOHCO_2^{2-}] + [CO_2CH_2CO_2^{2-}] + [CO_2(CH_2)_2CO_2^{2-}] + [CO_2(CH_2)_3CO_2^{2-}] \quad (3)$$

To date, along the C10 ice core, Preunkert et al. (2001a) identified 98 summer (on a total of 762 samples) and 4 winter (on a total of 337 samples) samples as suspected to be contaminated by Saharan dust. The ionic budget of a CDK snow layer containing Saharan dust is reported in Fig. 2 along with the one of its averaged adjacent summer layers. It can be seen that, in addition to the large enhancement of the alkalinity

3.2 Seasonality of the snow and ice CDD chemical records

Numerous atmospheric studies carried out at elevated sites in Europe have revealed a well-marked summer maximum of various chemical species in relation to a more efficient upward advection of air masses from the boundary layer in summer than in winter (Baltensperger et al., 1997; Kasper and Puxbaum, 1998; Pio et al., 2007; Hammer et al., 2007). This was also seen at the very high-elevated site of the Vallot observatory located nearby the CDD drill site (Preunkert et al., 2002; Legrand et al., 2005). Thus, the interpretation of long-term chemical records extracted from small-scale Alpine glacier in terms of past atmospheric chemistry has to carefully consider possible changes in the surface topography and snow deposition characteristics upstream to the drill site. As shown by Preunkert et al. (2000) along the C10 core for instance, the ratio of winter to summer net snow accumulation is decreasing from 1 near the surface to 0.5 at 74 mwe. Therefore a direct examination of averaged ice concentrations without any seasonal dissection would induce a non-atmospheric effect in ice core records there. Therefore, and taking advantage of a good preservation of the seasonal signal down the length of the CDD ice cores (see Sect. 2.1), winter and summer long term trends were examined separately in all previous CDD ice core studies.

The above-mentioned seasonal change of the air mass upward transport is associated with a geographical change of source regions impacting high-elevated Alpine sites. The sources of atmospheric aerosol that are trapped in the CDD snow layers were investigated by performing source-receptor calculations using the regional EMEP chemical transport model. For sulfate and ammonium, Fagerli et al. (2007) showed that Spain, Italy, France and Germany are the main contributors at the CDD site in summer, whereas in winter more European wide and trans-Atlantic contributions were found. Note that this conclusion is an additional argument for a separated examination of summer and winter trends extracted from the CDD ice records.

Table 1 summarizes the available various seasonally resolved records covering changes from prior World War II to the recent decades. Investigated chemical species

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are present in the atmosphere either as aerosol, or gases, or both. In the following we critically review all investigated species in view to select those contributing to the atmospheric aerosol load.

4 Snow and ice content versus atmospheric aerosol

4.1 Inorganics

In the following we examine which inorganic species trapped in ice provide relevant information on past atmospheric aerosol. Sulfate and all cations are atmospheric aerosol components. Other inorganic anions are present in the atmosphere in the gas (their acidic form) and aerosol phase (Table 1).

For nitrate, the most abundant inorganic anion present in CDD ice after sulfate (see Fig. 4), the atmospheric gas-aerosol partitioning is highly variable, generally in favor of aerosol (up to 50 % of total nitrate) in the boundary layer compared to the free troposphere (Dibb et al., 2003). Kasper and Puxbaum (1998) reported similar amount of nitrate in gas and aerosol phase at Sonnblick (3106 m a.s.l.) in summer, but four times less aerosol than nitric acid in winter. Except in the presence of Saharan dust particles (alkaline material) that sporadically affect Alpine sites (see Sect. 3.1), we can assume that at the remote CDD site, when present, particulate nitrate is mainly in the form of ammonium nitrate (NH_4NO_3). This aerosol is formed when ammonia is present in excess with respect to a full neutralization of sulfuric acid aerosol. On an equivalent basis (i.e. in $\mu\text{Eq m}^{-3}$), the mean composition of atmospheric aerosol collected on quartz filters at Vallot in summer since 1999 (detailed working conditions are reported in Preunkert et al., 2002) indicates similar mean concentrations of ammonium and sulfate ($[\text{NH}_4^+] = 10.8 \mu\text{Eq m}^{-3}$ and $[\text{SO}_4^{2-}] = 10.3 \mu\text{Eq m}^{-3}$). Though samplings on quartz filters are well known to lead to variable losses of NH_4NO_3 at temperatures higher than 10°C (Hering and Cass, 1999), the temperature of sampling filters at the Vallot observatory that remains close to zero even in summer may have minimized this negative artifact.

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The slope of the linear relationship between ammonium and sulfate concentrations close to 1.1 (Fig. 5) suggests that, in addition to $(\text{NH}_4)_2\text{SO}_4$, around 10 % of ammonium are present as another chemical form (i.e. likely NH_4NO_3). Total nitrate collected by using both quartz and nylon filters (Preunkert et al., 2002) in summer at Vallot indicates a mean concentration of $4.5 \mu\text{Eq m}^{-3}$. The observed mean excess of ammonium with respect to $(\text{NH}_4)_2\text{SO}_4$ would correspond around $1 \mu\text{Eq m}^{-3}$ of nitrate in the form of NH_4NO_3 , the remaining part of nitrate ($3.5 \mu\text{Eq m}^{-3}$) being present as gaseous nitric acid. That leads to a gas aerosol partitioning of nitrate favoring nitric acid (80 % HNO_3 against 20 % NH_4NO_3 aerosol). During a short summer campaign conducted at Vallot in 2004 under typical summer conditions, Preunkert et al. (2007) investigated the nitrate partitioning by sampling HNO_3 on coated denuder tubes and particulate nitrate on a quartz filter mounted behind the tubes. They also found that on average around 20 % of total nitrate was present in the aerosol phase.

The similar abundance of ammonium and sulfate seen in summer aerosol at Vallot since 1999 is consistently with the composition of snow deposited between 1995 and 2004 ($[\text{NH}_4^+] = 8.5 \mu\text{Eq L}^{-1}$ and $[\text{SO}_4^{2-}] = 8.0 \mu\text{Eq L}^{-1}$, Fig. 4). When SO_2 emissions in Western Europe reached their maximum in the 70's (see Sect. 5), sulfate CDD snow concentrations largely exceeded ammonium ones ($13.2 \mu\text{Eq L}^{-1}$ against $7.8 \mu\text{Eq L}^{-1}$, Fig. 4). Under these conditions sulfate would be mainly present as ammonium bisulfate whereas ammonium nitrate would have been not produced. Note that given the relative abundance of ammonium with respect to sulfate in summer snow deposited between 1922 and 1942 ($[\text{NH}_4^+] = 3.4 \mu\text{Eq L}^{-1}$ and $[\text{SO}_4^{2-}] = 2.6 \mu\text{Eq L}^{-1}$, Fig. 4), on a total of $1.6 \mu\text{Eq L}^{-1}$ of nitrate, at least $0.8 \mu\text{Eq L}^{-1}$ of nitrate would correspond to ammonium nitrate. In conclusion, at present (after 1999) the nitrate only contributes to the CDD aerosol load at a level of around $1 \mu\text{Eq m}^{-3}$ (i.e. 60 ng m^{-3}). This contribution would rather similar between 1920 and 1940 but lower in the 70's characterized by a more acidic atmosphere related to larger SO_2 emissions. In winter, whatever the time period, sulfate is always in excess with respect to $(\text{NH}_4)_2\text{SO}_4$ and a significant contribution of NH_4NO_3 to the atmospheric aerosol load at CDD is unlikely.

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The most abundant halogen in CDD ice is chloride. Its budget has been discussed by Legrand et al. (2002), showing that in addition to soil and halide aerosols, chloride also originates from HCl emitted by biomass burning, coal combustions and waste incineration. The presence of HCl in the summer atmosphere at CDD was confirmed by atmospheric measurements made with denuder tubes in 2004 by Preunkert et al. (2007) at Vallot. Legrand et al. (2002) estimated a mean halide Cl contribution of 7 ppb (on a total chloride of 10 ppb) and 10 ppb (on a total chloride of 30 ppb) in winter and summer CDD snow and ice layers, respectively. The authors calculated a mean level of Na^+ (corrected from its leachable fraction from mineral dust) of 7 ppb in summer and 4 ppb in winter CDD snow and ice layers. These levels of sodium and chloride (corrected from the mineral dust contribution) suggest that sea-salt aerosol would, at the best, contribute for ~ 20 ppb in CDD snow and ice layers. The chloride contribution from soils is considered in the following paragraph.

Given the low contribution of sea-salt aerosol in the CDD snow deposits, it can be assumed that calcium is mainly related to mineral dust aerosol. The CDD calcium levels (after correction from Saharan dust, see Sect. 3.1) range from 40 to 80 ppb in summer (Fig. 3) and from 5 to 15 ppb in winter. A crude estimate of the total mass atmospheric concentration of mineral dust aerosol (including its chloride contribution) in Europe can be obtained by multiplying the calcium concentration by a factor of 4.5 (Putaud et al., 2004)

As discussed by Preunkert et al. (2001a), the fluoride content in CCD ice originates in soil dust aerosols and HF emitted from coal burning and release from aluminum smelters. In contrast to chloride the gas-aerosol partitioning of fluoride has not been documented in the atmosphere at the CDD site. However, given the low level of total fluoride observed in the ice (up to 3 ppb on average in summer in the 70's), we neglected this species in the following calculations of the aerosol mass.

The respective contribution of the different types of inorganic aerosol (sea-salt, mineral dust, and S and N derived aerosol) to the total aerosol load and their change from 1921–1951 and 1971–1988 are summarized in Table 2.

4.2 Organics

Until very recently, information on the load and composition of carbonaceous aerosol archived in ice remained very limited. Several studies have already investigated the long-term trend of elemental carbon (EC) or black carbon (BC) fraction in ice from various Alpine glaciers, such as the Mt Rosa (Lavanchy et al., 1999) and Fiescherhorn glacier (Jenk et al., 2006) in Switzerland, but also in the C11 core of CDD (Legrand et al., 2007a). In the present-day European atmosphere, on a mass carbon basis, this fraction only accounts for 15 % of carbonaceous aerosol (Pio et al., 2007). The reconstruction of past changes of the remaining part of carbonaceous aerosol (organic carbon, denoted OC) preserved in ice is a challenge since only the water insoluble organic carbon (WinOC) fraction can be measured directly in ice, while the dissolved organic carbon (DOC) content measured in ice represents both the water-soluble organic carbon (WSOC) aerosol and water-soluble organic gases (Fig. 7). Similarly, the measurement of total organic carbon (TOC) content of ice also accounts for the presence of organic gases.

An extended array of organic species including DOC, C₁–C₃ monocarboxylates, C₂–C₅ dicarboxylates, formaldehyde, and for the first time HULIS, were recently investigated in the CDK ice cores (Legrand et al., 2013). The chemical speciation of the DOC content in CDK ice reported in Fig. 8 represents the unique case for which more than 50 % of the DOC content in a hydrometeor is chemically identified. This percentage becomes even higher (67 to 73 %) in ice corresponding to the first part of the 20th century (1921–1951). The extended knowledge of the chemical speciation of DOC was successfully explored to estimate the fraction that can be attributed to atmospheric WSOC aerosol. Among identified species that contribute to the DOC ice content (Fig. 8), formaldehyde and C₁–C₃ mono-carboxylic acids are organic gases that have been solubilised in precipitation, whereas C₂–C₅ dicarboxylic acids and HULIS represent a part of WSOC aerosol. From the examination of the atmospheric abundance and water solubility of other short-chain organic gases having a polar character,

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Legrand et al. (2013) concluded that the determination of light monocarboxylic acids together with that of HCHO in ice have likely permitted to quantify most water soluble organic gases contributing to the DOC content of ice. The unknown fraction of the DOC should therefore be mainly related to atmospheric WSOC aerosol, and the quantity denoted WSOC* calculated as the sum of HULIS, diacids and unknown in ice would correspond to WSOC atmospheric aerosol. It has to be emphasized that in the European atmosphere WSOC aerosol generally dominates WinOC aerosol (Pio et al., 2007). In addition to carbon, organic aerosol contains in variable amounts heteroatoms (H, O, N, etc.). To account for these atoms, a conversion factor has to be applied. The conversion factor is only known for chemically identified species. For instance, the mass conversion factor ranges from 3.7 for the C2 diacid (oxalic acid) to 2.2 for the C5 diacid (glutaric acid). Though HULIS are a class of compounds (not a single species), a conversion factor close to 2.0 can be assumed. However, as seen in Fig. 8, most of the WSOC* carbon mass remains chemically unidentified, the unknown fraction accounting for 60 and 75 % in ice deposited over the 1921–1951 and 1971–1988 years, respectively. Therefore we have calculated the mass corresponding to WSOC* by using the mean mass conversion factor (2.1) estimated by Kiss et al. (2002) for the whole atmospheric WSOC aerosol.

Until now, the levels of BC and WinOC in CDD ice were only documented on discontinuous samples, 49 discontinuous summer ice samples and 5 winter samples selected along the C11 ice core (Legrand et al., 2007a). In summer, BC and WinOC levels slightly increase from 1921–1951 to 1971–1988 (from 5 to 13 ppbC and 25 to 50 ppbC, respectively). In winter, BC and WinOC levels remained close to 5 and 20 ppbC, respectively. Though further works are here clearly needed to document more continuously summer and winter layers, we made an attempt in Table 2 to calculate an order of magnitude of the contribution of these two carbonaceous components to the total aerosol mass. The mass conversion factor for BC would be close to 1.1 for this highly condensed aromatic structure (Kiss et al., 2002). For WinOC, we have assumed an intermediate conversion factor (1.4) lying between the BC and WSOC ones.

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The respective contribution of the different types of carbonaceous aerosol (WSOC, WinOC, and EC) to the total aerosol load and their change from 1921–1951 and 1971–1988 are summarized in Table 2.

5 The changing aerosol load and composition over Europe from 1920 to 1990

5 Figs. 1 and 6 show the key periods of the history of the nitrogen and sulfur pollution over Europe. As already discussed by Preunkert et al. (2001b) on the basis of the C10 core, the regular increase of both summer and winter sulfate levels from 1925 to 1980 followed by a decrease resulting from improvements in the quality of fuel and emission abatements (Mylona, 1996), can be recognized in the CDD ice archives. Conversely,
10 as discussed by Preunkert et al. (2003), the nitrate levels show a persistent increase until 1994.

Interestingly, the CDK ice core data reported in Fig. 6, which enlarge the covered time period with respect to the C10 core studies over more recent years, indicate that sulfate continues to decrease from 1994 to 2004 in agreement with a lasting reduction of SO₂ emissions in Western Europe until the beginning of the 21st century. In agreement with
15 SO₂ emissions from Western Europe reported in Fig. 9, the recovered sulfate level in summer 2004 is close to the one observed in the early 50's. Instead, nitrate ended to increase only after 1995 (Fig. 6), consistently with the start of a slight decrease of NO emissions (Fig. 9). As shown in Fig. 6, the CDK ice record shows an increase by
20 a factor of 3 of ammonium concentrations between 1940 and 1995. This record, which contrasts with the sulfate trend, is qualitatively in agreement with the historical NH₃ emission trend (Fig. 9), but emissions increased only by a factor of two. As discussed by Fagerli et al. (2007), since the production of ammonium aerosol is limited by the availability of sulfuric and nitric acids, for which concentrations have increased more
25 than the ammonia emissions up to 1980, a larger proportion of NH₃ is converted to ammonium aerosols in 1980 than in 1925. Finally, while NH₃ emissions inventories do not yet report any decrease, the ammonium CDK record suggests a weak decrease

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after 2000. This may be related to a strong enough reduction of sulfuric acid leading a decreasing production of ammonium aerosol.

The cause of the increase by a factor of 2 of calcium after 1950 (Fig. 6) may have several causes since as pointed out by Putaud et al. (2004), this aerosol fraction includes all water insoluble and non-carbonaceous components (e.g. soil dust, road dust, and fly ash). Man made activities (road dust or agricultural activities for instance) or drier meteorological conditions may have contributed to this change of the background mineral dust atmospheric load in Europe. Further work is here clearly needed to better understand the causes of the observed calcium changes. For instance, studies using trace elements and isotopes (Sr and Nd for instance) would help to better decipher Saharan dust and background soil dust, road dust from natural soil weathering, etc.

The WSOC* fraction increased by a factor of 3 and 2 from 1920 to 1990 in summer and winter, respectively (Fig. 6). The summer WSOC* change was highlighted by the ^{14}C signature of the DOC content of ice found by May et al. (2013). Examining the time lag of the DO^{14}C in ice with the $^{14}\text{CO}_2$ around the bomb peak of 1965, the authors clearly concluded that the main biogenic source contributing to the DOC in ice in summer is the living biosphere, while biomass burning represents a very weak source. One of the major consequences of this result is that only $\sim 15\%$ of the WSOC* increase is related to enhanced fossil fuel emissions whereas $\sim 85\%$ of the increase relate to the living biosphere (Legrand et al., 2013). There are many possible causes that may have strengthened either biogenic precursors of atmospheric WSOC (e.g. the temperature) or the gas-particle conversion rate (e.g. ozone concentrations). However, since a large part of the increase of WSOC* in summer appears to be related to the chemically unidentified fraction (see Fig. 6), it remains difficult to discuss this summer trend in terms of possible involved gaseous precursors (isoprene, monoterpenes) emitted by vegetation.

Based on discussions in Sect. 4, Table 2 summarizes the estimated mass concentrations of the different aerosols present in winter and summer CDD ice layers corresponding to the years 1921–1951 and 1971–1988. In view to get an idea of the

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past change of aerosol load and composition we tentatively inverted these ice core concentrations to corresponding ambient air concentrations and compared them with atmospheric data gained in summer 2004 at the Vallot site.

Preunkert et al. (2002) found that atmospheric sulfate levels of 800 ng m^{-3} STP in summer at the CDD site correspond to 650 ppb in corresponding snow layers. These values were used to invert sulfate ice concentrations into atmospheric concentrations. A similar firn-air relationship was also used for other water-soluble submicron aerosols like ammonium aerosols, and WSOC. For insoluble fractions like WinOC and BC, a less efficient scavenging by precipitation is expected. Investigations made in air and precipitation at Sonnblick suggested that WinOC and BC are 2 and 5 times less efficiently removed from the atmosphere by snow than sulfate (Cerqueira et al., 2010). On this basis, we have multiplied the ice levels of WinOC by a factor of 2 and those of BC by a factor of 5 to account for these less efficient incorporation in precipitation prior applying the preceding firn air relationship.

Though not yet documented, the size of sea-salt aerosol at the top of the Alps would be larger than the preceding submicron aerosols. For this aerosol component, we still have applied the same firn-air relationship to invert ice core sea-salt content. Note that, even uncertain, given the low abundance of this aerosol fraction, the results will not modify the overall obtained composition of aerosol. Concerning calcium, it would lead to erroneous calculations to invert dust ice concentrations with a similar firn-air relationship than the one used for preceding species. Indeed, Puxbaum and Tschernwenka (1998) showed that the ratio of calcium present in snow and rime at Sonnblick is far higher than for sulfate (0.5 instead of 0.2). This calcium enrichment in the ice phase suggests that in contrast to sulfate, mainly present in rime, dust aerosol can be scavenged by ice crystals (the mineral aerosol might act as ice condensation nuclei). Preunkert and Wagenbach (1998) reported a firn air relationship some 6 times higher for calcium than for sulfate at Colle Gnifetti. With a mean calcium level of 35 ng m^{-3} STP in aerosol collected at Vallot in summer since 1999 (see Sect. 4.1), the mean calcium concentration in summer snow of around 75 ppb (Fig. 3) indicates

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also a better scavenging of calcium with respect to sulfate by a factor of 3. The dust contribution was calculated by assuming that this aerosol is three times more efficiency scavenged by snow than sulfate and WSOC.

The inverted summer ice concentrations corresponding to the years 1921–1951 and 1971–1988 are compared in Fig. 10 with atmospheric observations made in summer 2004 at the Vallot observatory. As already mentioned in Sect. 4.1, during this campaign, sulfate, ammonium, and particulate nitrate were documented (Preunkert et al., 2007). A mean calcium level of 36 ng m^{-3} STP was observed (unpublished data). The different carbonaceous aerosol fractions were also measured showing concentrations of 50, 100, and 150 ng C m^{-3} STP for BC, WinOC, and WSOC, respectively (Legrand et al., 2007b). In Fig. 10, the dust fraction is considered separately from the other inorganic fraction since this aerosol fraction would stay in the coarse size range. Indeed, it was shown that background crustal aerosol at Colle Gnifetti exhibits a diameter close to 2.5 microns (Wagenbach and Geis, 1989).

Figure 10 shows that, in addition to an increase by a factor of 2 of the coarse dust aerosol from 1920 to present-day, load and composition of submicron aerosols in summer have changed over time. From 1921–1951 to 1971–1988, the atmospheric load of submicron aerosol has been enhanced by a factor of 3 mainly due to the large change of N and S derived aerosols and watersoluble organic matter (WSOM). Compared to the situation encountered over the 1971–1988 years, the submicron aerosol load has re-decreased in 2004 mainly in relation to the strong decrease of sulfate (a factor of 2) whereas N derived aerosol and WSOM remained quasi unchanged. Whereas the observed long-term trend of ammonium, nitrate, and sulfate are in very good agreement with our knowledge of growing emissions of NH_3 , NO_x , and SO_2 , the change of WSOM needs further investigations. Indeed, though clearly attributed to the biosphere by DO^{14}C measurements, its chemical speciation is still too poorly documented to identify the precursors (isoprene, monoterpenes) and thus the causes of the increase.

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Seasonally resolved chemical ice core records extracted from the high-elevated Alpine site of the Col du Dôme glacier were revisited to reconstruct past change of atmospheric aerosol load and composition over Europe from 1920 to present. The extended array of investigated inorganic (Na^+ , Ca^{2+} , NH_4^+ , Cl^- , NO_3^- , and SO_4^{2-}) and organic (carboxylates, HCHO, HUmic Like Substances, dissolved organic carbon, water insoluble organic carbon, and black carbon) compounds and fractions permit to examine the key aerosol components (sea salt, mineral dust, nitrogen and sulfur related aerosol, and carbonaceous aerosol). It is shown that coarse aerosol related to background mineral dust and possibly also of Saharan dust events have increased by a factor of around two. The total load of submicron aerosol has increased by a factor of 3 from the 1921–1951 to 1971–1988 years, mainly as a result of a large increase of sulfate (a factor of 5), ammonium and water-soluble organic matter (a factor of 3). Whereas a strong reduction of sulfate had occurred after the 80's, the level of nitrogen derived aerosol and water-soluble organic matter remains in the present-day atmosphere almost as high as in the 80's. Therefore, not only inorganic pollution by NH_3 , SO_2 , and NO_x have led to enhanced atmospheric aerosol load over Europe but also biogenic emissions of precursors of water soluble organic matter that have increased by after 1950. This rather unexpected change of biospheric emissions would motivate further atmospheric and ice core studies to highlight possible causes of these change of natural emissions.

Acknowledgements. Funding was provided by the European Community via contract ENV4-CT97 (ALPCLIM), ENV4-CT96–5051 (Environment and Climate Research Training), and the Ministry for Science and Research of Baden-Württemberg within the collaboration program between Region Rhône-Alpes and Baden-Württemberg. The drilling operation to extract the CDK ice core at Col du Dôme was supported by the EU CARBOSOL project (contract EVK2 CT2001-00113). Finally the study of organics in the CDK ice cores was funded by the CNRS-DFG bilateral project entitled “Secondary organic aerosol production in the lower free troposphere over western Europe”. We would like to thank Dietmar Wagenbach from IUP Heidelberg for

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Table 1. Summary of chemical species (or fractions) that were investigated on a continuous (or quasi-continuous) and seasonally resolved basis along CDD ice cores, its physical state in the atmosphere, and references of the respective original studies. For a species X , the α value corresponds to the estimated X to calcium mass ratio in Saharan dust (Preunkert, 2001). They were used to correct concentrations from Saharan dust inputs by using calcium ($[X]_{\text{corrected}} = [X] - \alpha[\text{Ca}^{2+}]$).

Species in ice	Atmospheric phases	α	References
F^-	Gas (HF)/aerosol	2×10^{-3}	Preunkert et al. (2001a)
Cl^-	Aerosol/gas (HCl)	0.06	Legrand et al. (2002)
NO_3^-	Gas (HNO_3)/aerosol	0.01	Preunkert et al. (2003)
SO_4^{2-}	Aerosol	0.59	Preunkert et al. (2001b)
NH_4^+	Aerosol	0.03	Fagerli et al. (2007)
$\text{Na}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$	Aerosol	0.03–0.07	Legrand et al. (2002)
Monocarboxylates ($\text{HCO}_2^-, \text{CH}_3\text{CO}_2^-$)	Gas (HCOOH , CH_3COOH)/aerosol	0.01–0.02	Legrand et al. (2003)
Dicarboxylates (C2–C5)	Aerosol	0.01	Legrand et al. (2013)
HULIS	Aerosol	0	Guilhermet et al. (2013)
HCHO	Gas	0	Legrand et al. (2013)
DOC	Gas/aerosol	0	Legrand et al. (2013)
EC/WinOC*	Aerosol	0	Legrand et al. (2007a)

* Only discontinuous sampling (see Sect. 4.2).

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Table 2. Mass concentrations in Summer (S) and winter (W) CDK ice of various types of aerosol. The ways to calculate the mass of sea-salt (from Na^+ and Cl^-), dust (from Ca^{2+}), and organic matter (OM) (from WSOC* and WinOC) are detailed in Sect. 4.

Species (in ppb)	1921–1951	1971–1988	Enhancement factor
Sea salt S	20	20	1
Sea salt W	13	13	1
Dust S	195	380	2
Dust W	30	30	1
$(\text{NH}_4^+ \text{ and } \text{SO}_4^{2-})$ S	204 (254*)	830	4.1 (3.3)
$(\text{NH}_4^+ \text{ and } \text{SO}_4^{2-})$ W	45	136	3
OM (WSOC*) S	110	308	2.8
OM (WSOC*) W	54	113	2.1
OM (WinOC) S	35	70	2
OM (WinOC) W	35	35	1
BC S	6	14	2.3
BC W	6	6	1

* denotes value accounting for the presence of particulate nitrate (see Sect. 4.1).

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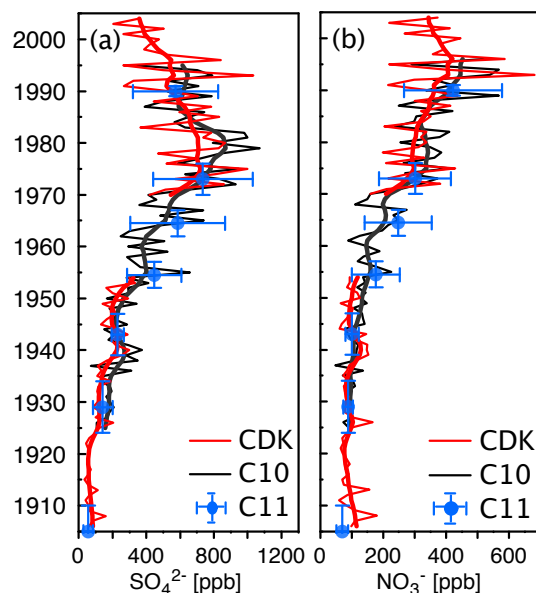


Fig. 1. Comparison of summer half-year means of sulfate and nitrate along the C10, C11, and CDK ice cores. For C10 and CDK, the thin solid lines refer to individual summer means and the thick solid lines to the smoothed profiles (singular spectrum analyses, time window of 5 yr). For C11, the discontinuous sampling (blue dots) is reported with vertical bars referring to the standard deviations related to sample content variability and horizontal bars to the covered time periods. C10 data are from Preunkert et al. (2001b, 2003), C11 data from Legrand et al. (2007a), and CDK data from Legrand et al. (2013). All data were corrected from the Saharan dust contribution (see Sect. 3.1). Adapted from Legrand et al. (2013).

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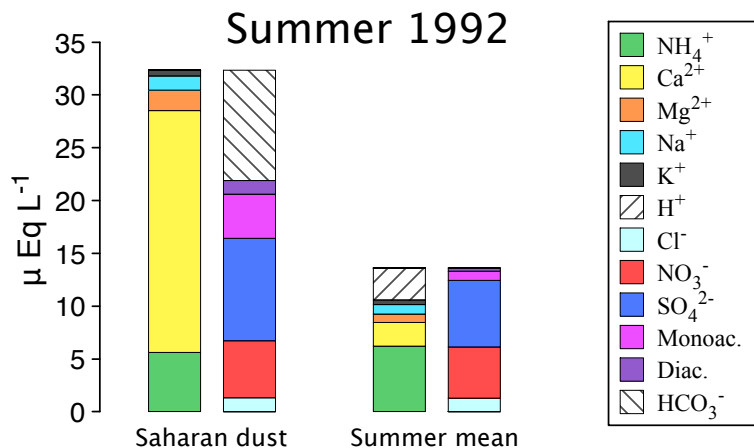


Fig. 2. Ionic content of CDK snow layers deposited during summer 1992. Left: a snow layer containing Saharan dust. Right: average over 1992 summer layers adjacent to the dust layer. Abbreviations Monoac. and Diac. stand for C1–C3 monocarboxylates and C2–C5 dicarboxylates, respectively (see Eqs. 2 and 3 in Sect. 3.1).

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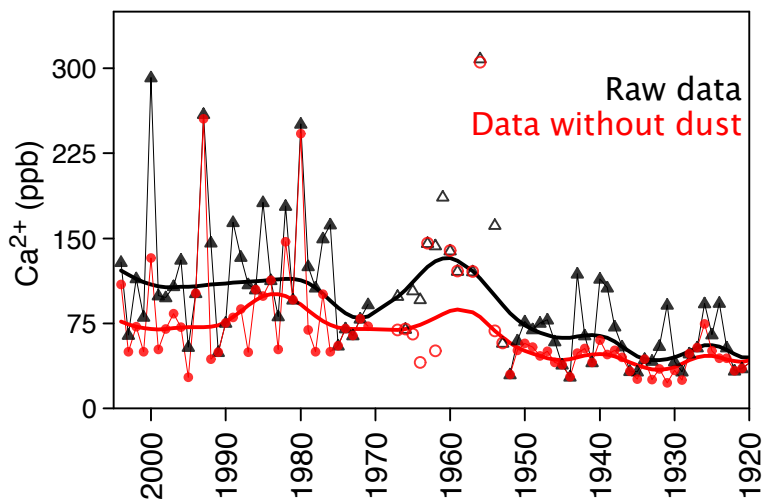


Fig. 3. Summer half year means of calcium along the well-dated part of the CDK ice core (solid dots). The open points correspond to samples from the C11 ice core (see Sect. 2.1). The thick solid lines are robust spline smoothing (Bloomfield and Steiger, 1983). Black dots and lines refer to raw data, red ones to data after having discarded Saharan dust events (see Sect. 3.1).

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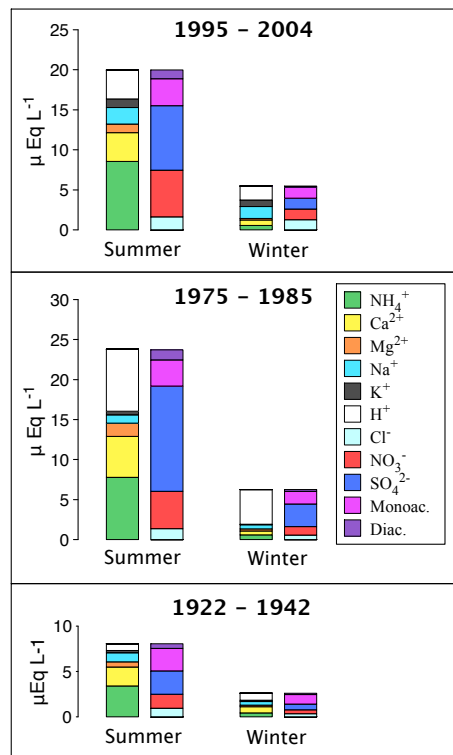


Fig. 4. Overall mean ionic composition of snow and ice layers deposited in summer (left panels) and winter (right panels) over three different time periods in the CDK core. Abbreviations Monoac. and Diac. stand for C1–C3 monocarboxylates and C2–C5 dicarboxylates, respectively (see Eqs. 2 and 3 in Sect. 3.1). Individual summer and winter half year means were calculated after having corrected data from the contribution of Saharan dust (see details in Sect. 3.1).

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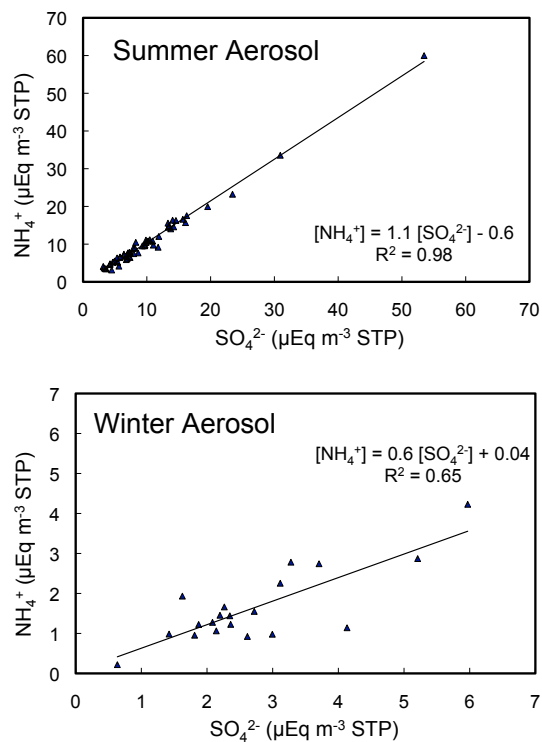


Fig. 5. Ammonium as a function of sulfate in atmospheric aerosol sampled at the Vallot observatory in summer (top panel) and winter (bottom panel) between 1999 and 2010. Concentrations are given in $\mu\text{Eq m}^{-3} \text{STP}$.

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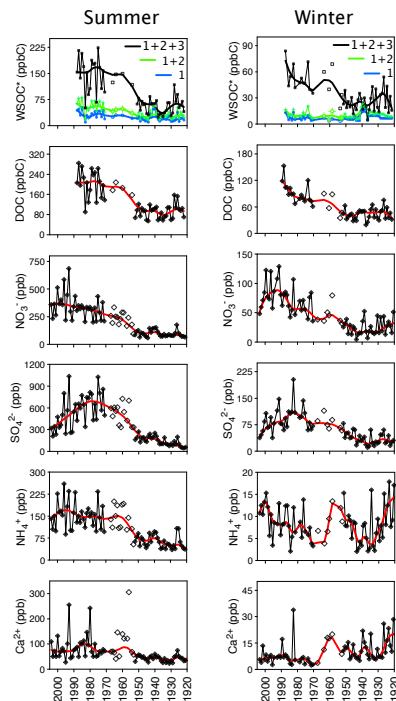


Fig. 6. Long-term trends extracted from summer (left panel) and winter (right panels) CDK snow and ice layers. From top to bottom: proxy of water-soluble organic carbon (WSOC*, see Sect. 4.2), dissolved organic carbon (DOC), nitrate, sulfate, ammonium, and calcium. On the WSOC* panel, the numbers 1, 2, and 3 refer to HULIS (blue line), the sum of HULIS and dicarboxylates (green line), and the sum of HULIS, dicarboxylates and Unknown fraction (black line) (see Sect. 4.2). For calcium, the Saharan dust events have been removed from the data. The solid symbols correspond to the well-dated part of the CDK ice core, the open symbols to samples from the C11 ice core (see Sect. 2.1). The thick solid lines are robust spline smoothings. Except for NH_4^+ and Ca^{2+} , the panels are adapted from Legrand et al. (2013).

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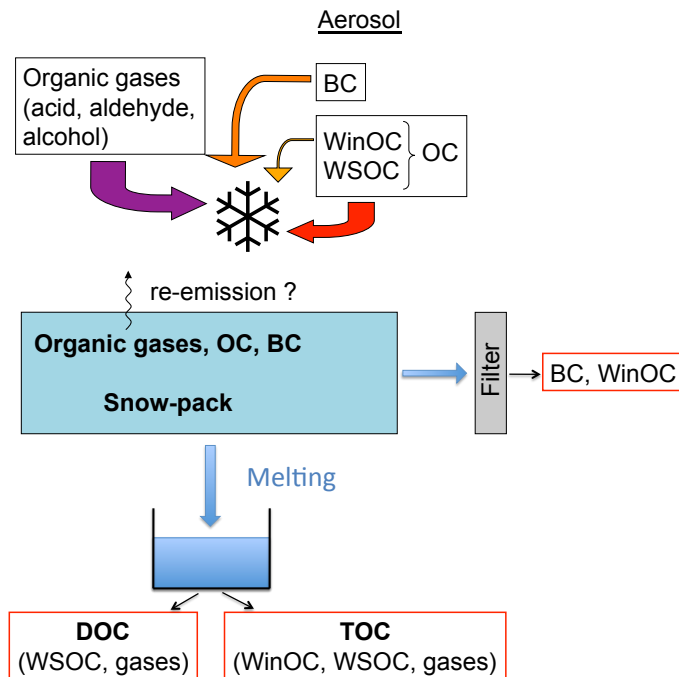


Fig. 7. The different atmospheric organic fractions trapped in ice. They include black carbon (BC), organic carbon (OC) and its two sub-fractions (water soluble and water insoluble organic carbon denoted WSOC and WinOC, respectively). DOC and TOC refer to dissolved and total organic carbon, respectively. Adapted from Legrand et al. (2013).

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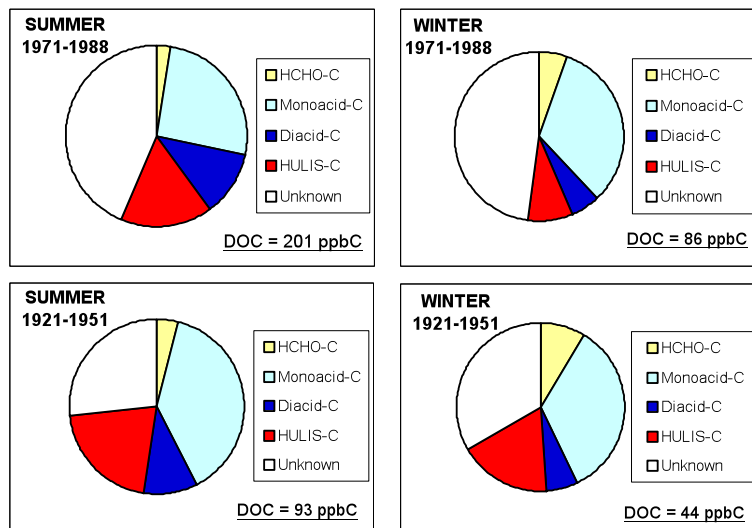


Fig. 8. Chemical composition of DOC present in winter and summer CDK ice layers corresponding to the first (1921–1951) and second (1971–1988) half of the 20th century. The identified organic species include formaldehyde, C1–C3 monocarboxylic (formic, lactic, acetic, glycolic, and glyoxylic) acids, C2–C5 dicarboxylic (oxalic, malic, malonic, succinic, and glutaric) acids, HULIS, and the unidentified fraction of DOC (see Sect. 4.2). Adapted from Legrand et al. (2013).

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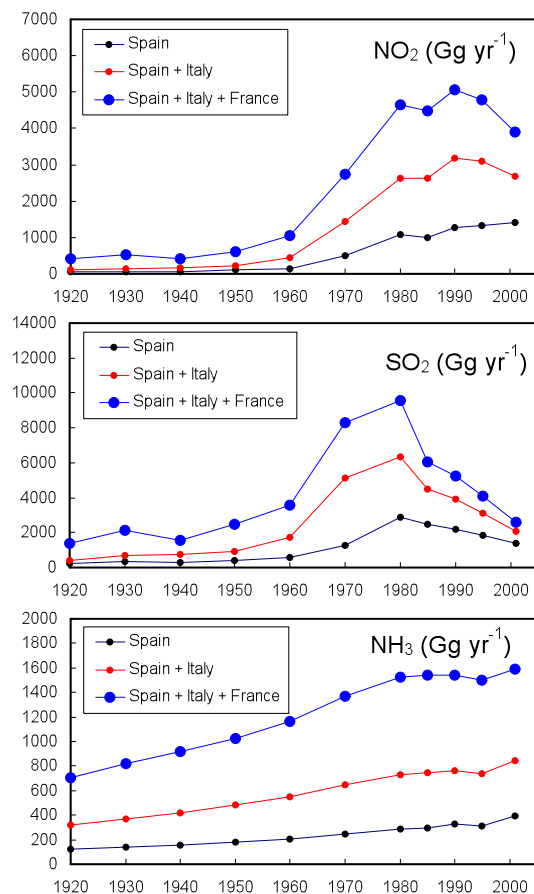


Fig. 9. Emissions of NO₂, SO₂, and NH₃ from Spain, Italy, and France from 1920 to 2001. Adapted from Fagerli et al. (2007).

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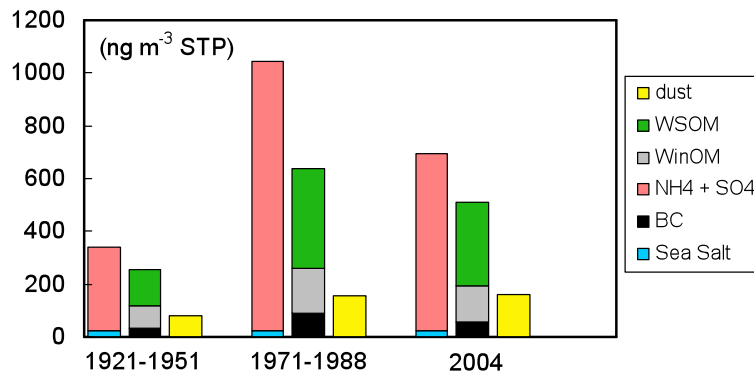


Fig. 10. Temporal changes of summer mass concentrations of different aerosols at the CDD site. For the 1921–1951 and 1971–1988 years, atmospheric concentrations were estimated by inverting ice concentrations (see Sect. 5) whereas the 2004 concentrations are data gained during a field atmospheric campaign conducted in summer 2004 (Legrand et al., 2007b; Preunkert et al., 2007).

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