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Major 20th century changes of the content and chemical speciation of organic carbon archived in Alpine ice cores: Implications for the long-term change of organic aerosol over Europe

M. Legrand,¹ S. Preunkert,¹ B. May,² J. Guilhaumet,¹ H. Hoffman,² and D. Wagenbach²

Dissolved organic carbon (DOC) and an extended array of organic compounds were investigated in an Alpine ice core covering the 1920–1988 time period. Based on this, a reconstruction was made of the long-term trends of water-soluble organic carbon (WSOC) aerosol in the European atmosphere. It is shown that light mono- and dicarboxylates, humic-like substances, and formaldehyde account together for more than half of the DOC content of ice. This extended chemical speciation of DOC is used to estimate the DOC fraction present in ice that is related to WSOC aerosol and its change over the past. It is suggested that after World War II, the WSOC levels have been enhanced by a factor of 2 and 3 in winter and summer, respectively. In summer, the fossil fuel contribution to the enhancement is estimated to be rather small, suggesting that it arises mainly from an increase in biogenic sources of WSOC.

1. Introduction

[2] The reconstruction of the changing atmospheric aerosol load and composition from the present polluted atmosphere back to preindustrial times, and the evaluation of the subsequent radiative impact are strongly needed to improve our understanding and to forecast future climate, particularly at regional scales. Although carbonaceous matter is recognized as a major constituent of present-day atmospheric aerosol over continents, nearby the surface as well as in the free troposphere [for Europe, see *Putaud et al.*, 2004, *Pio et al.*, 2007], there are 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].

[3] 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 preindustrial era to present day [for a review, see *Legrand and Mayewski*, 1997]. The potential of high-elevation glaciers present in the Alps in Europe above 4000 m elevation (Mount Rosa and Mount Blanc glaciers) to provide relevant aerosol records was previously evaluated [*Preunkert et al.*, 2000]. On the basis of sulfate, which shows a dramatic post-1950 increase at the scale of Western/Central Europe, the significance of these proxy atmospheric records was assessed [*Preunkert et al.*, 2001a] using ice cores extracted nearby the Mount Blanc summit. Furthermore, it was shown that a regional chemistry-transport model, using past emission inventories of SO₂ in Europe, reproduces fairly well the long-term trends of sulfate extracted from Alpine ice cores characterized by an increase between 1920 and 1950, and then a significant decrease over the last decades [*Fagerli et al.*, 2007], suggesting that these archives can indeed help to reduce uncertainties in past emission inventories.

[4] In contrast to inorganic aerosol, information on the load and composition of carbonaceous aerosol archived in ice is still very limited. Focusing on the Alps, several studies have already investigated the long-term trend of the elemental carbon or black carbon fraction in ice extracted at different glaciers from Switzerland (Mount Rosa glacier [*Lavanchy et al.*, 1999] and Fiescherhorn glacier [*Jenk et al.*, 2006]) and France (Mount Blanc [*Legrand et al.*, 2007a]). The reconstruction of past changes of OC preserved in ice is a challenge since only the water-insoluble organic

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¹UJF-Grenoble 1/CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) UMR 5183, Grenoble, France.

²Institut für Umweltphysik, University of Heidelberg, Heidelberg, Germany.

Corresponding author: M. Legrand, UJF-Grenoble 1/CNRS, Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) UMR 5183, Grenoble, France. (mimi@lgge.obs.ujf-grenoble.fr)

carbon (WinOC) fraction can be measured directly in ice, whereas the dissolved organic carbon (DOC) content measured in ice represents both the water-soluble organic carbon (WSOC) aerosol and water-soluble organic gases. It has to be emphasized that in the European atmosphere, WSOC aerosol generally dominates WinOC aerosol [Pio *et al.*, 2007]. In spite of these difficulties, the pioneer study from Legrand *et al.* [2007a] suggested that in the Alps, the DOC ice record together with the one of light carboxylates might allow reconstruction of past WSOC changes over Europe. Although preliminary, this first attempt achieved on a discontinuous selection of summer samples suggested that the levels of OC aerosol have been enhanced by a factor of 2 to 3 after 1950 [Legrand *et al.*, 2007a]. In this study, only a small fraction of organic carbon aerosol was identified, namely, C₂–C₅ dicarboxylic acids that represent less than 10% of the DOC content of ice. Humic-like substances (HULIS) were also measured in ice but with a method that does not allow an accurate evaluation of their contribution in terms of carbon mass.

[5] With the aim to reconstruct past changes of atmospheric WSOC aerosols over Europe, an extended array of organic species was investigated in ice cores drilled at the Mount Blanc site. This includes continuous records of DOC, C₁–C₃ monocarboxylates, C₂–C₅ dicarboxylates, formaldehyde, and for the first time HULIS, which were measured on a carbon mass basis. Furthermore, an innovative approach based on ¹⁴C measurements in DOC was deployed to investigate the cause of past DOC changes. Data are discussed in three companion papers of which this is one. The present paper reports on the chemical speciation of DOC present in ice. From that, the fraction of DOC present in ice that is related to WSOC aerosol is estimated and its change over the past is discussed. The

second paper discusses the ¹⁴C signature of the DOC present in ice deposited over the 1945–1990 time period to quantify fossil fuel versus biogenic fractions and also to distinguish between biomass burning and living biosphere emissions [May *et al.*, this issue]. The third paper examines changes of the most abundant chemically identified WSOC aerosol fraction contributing to the DOC ice content, namely, HULIS. Data are discussed in terms of atmospheric HULIS budget over Europe that remains still poorly understood [Guilhermet *et al.*, this issue].

2. Ice Core Dating

[6] A 124 m long ice core (hereafter denoted CDK) was drilled in 2004 at the Col du Dôme (4250 m asl), located nearby the Mont Blanc summit (French Alps). The CDK ice core was drilled at virtually the same place as the C10 ice core (126 m long) extracted in 1994. The overall glacio-chemical setting of the Col du Dôme site and the accurate dating of the C10 ice core are described in Preunkert *et al.* [2000]. The C10 ice core was already successfully used to investigate the long-term trends of various atmospheric species (e.g., see Preunkert *et al.* [2001a] for sulfate and Preunkert *et al.* [2003] for nitrate). In a first step, the dating of the CDK ice core was attempted by counting annual layers along the ammonium depth profile as done for the C10 ice core and by comparing the depth stratigraphies of major ions (e.g., sulfate and nitrate) with the ones of the well dated C10 ice core. Based on the 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

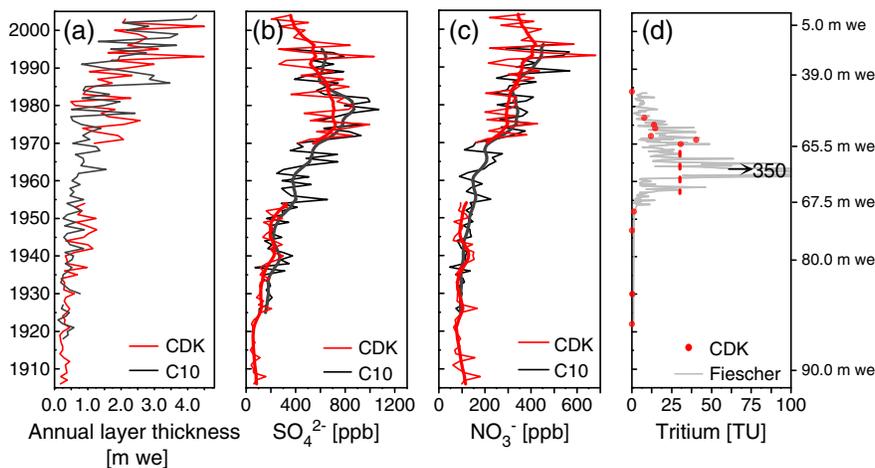


Figure 1. Dating of the CDK ice core: (a) annual layer thickness estimated via the ammonium stratigraphy along the CDK ice core and in comparison with the C10 ice core previously studied by Preunkert *et al.* [2000]; (b) comparison of sulfate summer half-year means along the CDK and the C10 ice cores, the thin solid lines refer to individual summer means, and the thick solid lines refer to the smoothed profile (single spectrum analyses, time window of 5 years); (c) same as Figure 1b for nitrate; and (d) tritium measurements made on CDK ice core samples (red dots and dashed line) compared with the tritium ice core record from the Fiescherhorn glacier (Swiss Alps) [Schotterer *et al.*, 1998]. All tritium data were converted to 2009 with regard to the half-life time of tritium ($T_{1/2} = 12.32$ year). The left scale refers to years, the right scale to depths of the CDK ice core in meter water equivalent (mwe).

major ions. As seen in Figure 1, from the surface down to 65.5 meters water equivalent (mwe), the annual layer thickness of the CDK ice core decreases from 3 to 1 mwe (i.e., a factor of 3) similarly to what was observed at corresponding depths along the C10 ice core. Along this upper part of the CDK ice core, summer half-year means of sulfate and nitrate are in very good agreement with the ones of the C10 ice core over the overlapping time period (1970–1994) (Figure 1).

[7] However, at 65.5 mwe, the ammonium seasonal cycle suddenly vanishes, and sulfate and nitrate exhibit unexpected low values (70 and 35 ppb, respectively) (not shown). These values are closer to typical winter values in the 1960s (75 ppb for sulfate [Preunkert *et al.*, 2001a] and 37 ppb for nitrate [Preunkert *et al.*, 2003]) than to summer values (400 ppb for sulfate and 150 ppb for nitrate; Figure 1). At approximately 68 mwe, the seasonal signature of ammonium recovers and remains easily detectable down to 91.5 mwe. As seen in Figure 1, the summer half-year means of sulfate and nitrate at approximately 68 mwe are significantly lower than those observed at 65.5 mwe and are similar to those found around 1950–1955 in the C10 ice core, respectively.

[8] To obtain further information on the age of CDK ice layers, we measured tritium, a species commonly used to identify the 1963 and 1954 time horizons corresponding to atmospheric nuclear tests. CDK tritium data are compared in Figure 1, with the tritium record of a well-dated ice core from the Fiescherhorn glacier Swiss Alps [Schotterer *et al.*, 1997]. The CDK ice located below 67.5 mwe contains less than one tritium unit (TU, 1 TU = 0.12 Bq L⁻¹), confirming that it was deposited before 1954. Between 65.5 and 67.5 mwe, tritium levels remained close to 30 TU, suggesting that these layers are younger than 1954 and older than 1970, but that ice layers corresponding to the main bomb peak were definitely missing (Figure 1). In addition, the expected annual layer thickness close to 0.7 mwe between 1954 and 1970 (as seen in the C10 ice core; Figure 1) is found to be approximately four times lower in the CDK core (0.16 mwe calculated if 16 years have been stored between 65.5 and 68 mwe). Therefore, it seems that the continuity of the ice layer chronology is disturbed in the CDK ice core between 65.5 and 68 mwe. That is also supported by comparison of the ²¹⁰Pb inventory of CDK (A. Waldner, 2011, personal communication) with the one of C10 [Vincent *et al.*, 1997]. To conclude, the detailed ion profiles as well as the ²¹⁰Pb inventories suggest in combination with glaciological evidence [Vincent *et al.*, 1997] that a crevasse system might have recently developed or changed upstream of the borehole just before the 1970s, having caused a hiatus in the stratigraphy of the CDK ice core which does not exist in the C10 ice core drilled 10 years before.

[9] As stated above, CDK ice located below 67.5 mwe was deposited before 1954 and shows annual variations down to 91.5 mwe. To achieve the dating for this part of the CDK core, the stratigraphies of various species (raw as well as smoothed data of ammonium, nitrate, sulfate, calcium, and others) were compared those of the C10 core. In this way, several common features in the shape of the seasonal signals and the appearance of Saharan dust events were recognized in the two cores permitting to scale down the CDK depth profile on the well-dated C10 one. It is found that the CDK layers deposited between 86.0 and 67.5 mwe cover the 1925–1954 time period with an uncertainty of ± 3

years. It has to be emphasized that we can exclude the occurrence of another hiatus over this time period. Indeed, the examination of fluoride in the CDK layers indicates a rapid increase of levels between 1930 and 1940 as already seen in the C10 core following the growing release of fluoride by aluminum smelters [Preunkert *et al.*, 2001b].

[10] The DOC content and its chemically identified fractions (HCHO, mono- and dicarboxylates, and HULIS) were investigated along the well-dated (from around 1920 to the recent decades) and seasonally resolved parts of the CDK ice core. As discussed in the next section, the cleaning of samples for DOC determinations can only be applied to ice material but not to firm, a porous material, present from the surface down to 58 m depth (i.e., 38.5 mwe).

[11] To investigate the 1955–1970 time period that is not well preserved in the CDK core, additional ice samples from the C11 core (140 m long), of which discontinuous sections are still available, were used to investigate the different organic species and DOC as well as for ¹⁴C investigations around the 1963 bomb peak [May *et al.*, this issue]. Drilled in 1994 as twin ice core of C10 less than 50 m away from the latter one, the C11 ice core was found as C10 to have well recorded the 1925–1994 years [Legrand *et al.*, 2007a]. For CDK as well as C11, the dating accuracy depends on depth and to the proximity of identified time markers. The dating of both ice cores is estimated to be better than ± 2 years after 1954, ± 4 years in the 1940s, and ± 6 years around 1920.

3. Methods

3.1. Ice Core Samplings and Analytical Methods

[12] The dissolved organic content (DOC) of ice samples was determined by using a commercial Phoenix 8000 device (Teledyne Tekmar company), which was modified by Preunkert *et al.* [2011] to allow DOC determinations at the level of a few ppbC. 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 a UV lamp together with the use of synthetic air as a carrier gas oxidizes organic carbon into CO₂ hereafter quantified in a nondispersive infrared detector. At least three to five device blanks were made per day showing typical mean ($\pm 1\sigma$) of 25 ± 1.5 ppbC. This mean blank value was subtracted from sample values. Taken as twice the variability of the blanks made over a day, the detection limit is ~ 5 ppbC. The typical uncertainty of the DOC determination calculated by considering uncertainty of the calibration curve and variability of the blank value is less than 10% for summer samples that contain more than 50 ppbC of DOC. Due to the blank variability the uncertainty of winter samples reaches 20% in samples containing around 20 ppbC of DOC. To remove contamination from ice before DOC analysis, we applied the procedure from Preunkert *et al.* [2011], who developed a special glass device in which pieces of ice are washed with ultrapure water and kept melting. During sample melting, an inert gas atmosphere is maintained inside the glass receptacle to prevent contact of sample with ambient air of the lab. DOC determinations were made on 524 pieces of ice covering winter (125 samples) and summer (396 samples) ice layers deposited over the two well-dated ice parts of the CDK core (i.e., from 1921 to

1951 and from 1971 to 1988). The length of individual pieces of ice range from 20 to 30 cm over the 1971–1988 time period and from 4 to 6 cm over the 1921–1951 one. Twenty-six additional ice samples from the C11 ice core were analyzed to cover winters 1952, 1953, 1958, 1960, and 1963 and summers 1954, 1960, 1962, and 1965.

[13] For cations, a Dionex ICS 1000 chromatograph equipped with a CS12 separator column was used. Anions were quantified with a Dionex DX600 chromatograph equipped with an AS11 separator column and a gradient pump system, allowing the determination of inorganic species such as sulfate and nitrate as well as short-chain carboxylates. Determined monocarboxylates include formate (HCOO^-), lactate ($\text{CH}_3\text{CHOHCOO}^-$), acetate (CH_3COO^-), glycolate ($\text{CH}_2\text{OHCOO}^-$), and glyoxylate (CHOCOO^-). Investigated dicarboxylates are oxalate ($^- \text{OOC} \text{COO}^-$), malate ($^- \text{OOC} \text{CH}_2\text{CHOHCOO}^-$), malonate ($^- \text{OOCCH}_2\text{COO}^-$), succinate ($^- \text{OOC}(\text{CH}_2)_2\text{COO}^-$), and glutarate ($^- \text{OOC}(\text{CH}_2)_3\text{COO}^-$). Detection limits are close to 0.1 ppb for most carboxylates. The blank of the ice decontamination procedure was less than 0.5 ppb for all carboxylates. The detection limits for major ions like ammonium, nitrate, and sulfate are close to 1 ppb. Ions were determined on 8–10 cm long pieces of snow and ice from the surface down to 83 m depth (i.e., the 1971–2004 time period). Further down, the length of ice pieces was reduced from 5 to 2.5 cm. A total of 1800 samples were analyzed, among which 800 samples that cover the two well-dated ice parts of the core (1921–1951 and 1971–1988) were cleaned under a clean air bench located in a cold room (-15°C) using an electric plane device. Ninety additional ice samples from the C11 ice core were analyzed to cover winters 1952, 1953, 1958, 1960, and 1963 and summers 1954, 1960, 1962, and 1965.

[14] Water-soluble HULIS were extracted by using a diethylaminoethyl resin, and the quantification of the organic carbon content of the HULIS fraction was made with a Shimadzu TOC analyzer. As detailed by *Guilhermet et al.* [this issue], the required sample volume ranges between 60 and 140 mL for summer and up to 180 mL for winter, respectively. Pieces of ice dedicated to HULIS determination were decontaminated in a clean room by washing them in three successive baths of ultrapure water produced by a Maxima HPLC system (Elga, High Wycombe Bucks, England) that was fed with ultrapure water from a Milli-Q 10 TS system (Millipore, Bedford, MA). During the cleaning procedure, around 20% of the outer ice layer was

removed. With a total of 220 samples, the resolution of the HULIS profile is lower than the ones of ions and DOC but still high enough to allow seasonal dissection. As for DOC, additional ice samples from the C11 ice core were analyzed to cover winters 1952, 1953, 1958, 1960, and 1963 and summers 1954, 1960, 1962, and 1965.

[15] HCHO was measured by a fluorimetric method based on the liquid phase reaction of formaldehyde with acetyl acetone and a $\text{CH}_3\text{COONH}_4\text{-CH}_3\text{COOH}$ mixture (Hantzsch reagent). The analyzer (Aerolaser AL4021) has a detection limit of 0.1 ppb. Blank values of the decontamination procedure were below 1 ppb. In contrast to all other investigated species, no seasonality was detected for HCHO, likely due to postdepositional diffusion of this volatile species. Therefore, HCHO was measured in a very low time resolution. The two well-dated ice parts of the core (1921–1951 and 1971–1988) were covered by 60 HCHO determinations in pooled aliquots of remaining sample liquid from ion chromatography analysis.

3.2. Ancillary Data Set

[16] Within the discussion of ice core data, we will refer to two sets of atmospheric aerosol data. First, with the aim to relate the obtained chemical speciation of DOC present in ice with the one of atmospheric organic carbon aerosol, we examined the chemical composition of WSOC aerosol on a selected set of 21 high volume filters collected in Europe during the CARBOSOL project [*Legrand and Puxbaum, 2007*] (Table 1). The filters were already well characterized by *Pio et al.* [2007] for WSOC and inorganic ions and by *Legrand et al.* [2007b] for $\text{C}_2\text{-C}_5$ diacids. Furthermore, water-soluble HULIS were measured on these filters with the same method (diethylaminoethyl) as the one used to measure water-soluble HULIS in the ice core (see section 3.1). This will allow comparing the chemical speciation of atmospheric WSOC over Europe directly with the one of the DOC content of Alpine ice.

[17] Second, we will use data from high volume aerosol filters (circular quartz filters, 15 cm diameter; Gelman Pallflex Tissuquartz 2500QAT-UP) collected in June 2010 at the Puy de Dôme (1450 m asl, centre of France) site. The sampling was achieved continuously with a flow rate of $1.1 \text{ m}^3 \text{ min}^{-1}$ during 3 days and 3 nights from the 22nd of June at 17:00 h to the 25th of June at 19:00 h. Weather conditions remained unusually cold and wet in France from 15 June to 21 June and the recovery of fine (sunny) weather

Table 1. Summer and Winter Atmospheric Levels of WSOC, Diacids, and HULIS_{WS} at Various European Sites

| Site (N) | Elevation (m asl) | WSOC (ng C m^{-3}) ^a | Diacids (ng C m^{-3}) ^a | HULIS (ng C m^{-3}) ^b | Unknown (ng C m^{-3}) |
|------------------|-------------------|--|---|---|----------------------------------|
| Summer | | | | | |
| K-Puszt (3) | 130 | 3260 (3490) | 125 (134) | 890 | 2226 |
| Schauinsland (2) | 1205 | 2850 (3040) | 119 (194) | 770 | 1960 |
| Puy de Dôme (8) | 1450 | 1890 (2020) | 111 (115) | 390 | 1500 |
| Sonnblick (3) | 3106 | 1190 (990) | 76 (51) | 142 | 972 |
| Winter | | | | | |
| K-Puszt (2) | 130 | 10,220 (7400) | 98 (149) | 2145 | 8,000 |
| Schauinsland (2) | 1205 | 515 (780) | 10 (31) | 55 | 450 |
| Sonnblick (1) | 3106 | 105 (140) | 2.3 (4) | 10 | 93 |

N refers to the number of filters collected during the CARBOSOL project on which HULIS were measured by *Guilhermet et al.* [this issue]. The WSOC and diacid levels of these filters are compared with the ones observed over the entire 2 year climatology gained during CARBOSOL (values in parentheses [*Pio et al., 2007*]). The notation “unknown” refers to the part of WSOC that remains chemically unidentified (see section 6).

^aData from *Pio et al.* [2007].

^bData from *Guilhermet et al.* [this issue].

conditions coincided with the start of the sampling period. As seen in Figure 2, the sampling period started with air masses arriving at the Puy de Dôme coming from the high latitudes of the North Atlantic Ocean rapidly replaced by air masses coming from Scandinavia/Denmark through Germany. At the same time, midday temperatures regularly rose in France, for instance from 18 °C on 22 June to 27 °C on 26 June at Clermont-Ferrand located in the centre of France, 5 km from the Puy de Dôme site. The filters were analyzed for sulfate, WSOC and its ^{14}C content (after removing the inorganic carbon fraction), $\text{C}_2\text{--C}_5$ diacids, and water-soluble HULIS (Table 2). As discussed in section 7.1, data clearly reveal that encountered weather conditions have favored a strengthening of WSOC aerosol biogenic sources. That permits to highlight the chemical composition

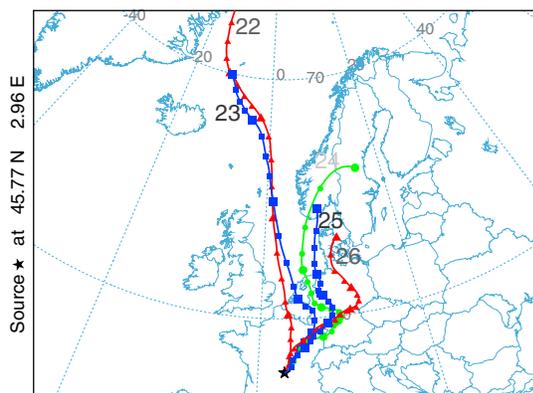


Figure 2. Five-day backward trajectories arriving at Puy de Dôme from 22 June to 26 June 2010 computed with the HYSPLIT (hybrid single-particle Lagrangian integrated trajectory) model (R. R. Draxler and G. D. Rolph, NOAA Air Resources Laboratory, Silver Spring, Maryland, 2003, available at <http://www.arl.noaa.gov/ready/hysplit4.html>). The numbers reported on the map correspond to dates.

of a pure biogenic WSOC aerosol present in the atmosphere in summer at a European mountain site.

4. Data Presentation

[18] For interpreting long-term chemical records extracted from a small-scale glacier like the Col du Dôme in terms of past atmospheric chemistry, special caution has to be paid to systematic changes in the snow deposition characteristics upstream to the drill site. As shown by *Preunkert et al.* [2000] along the C10 ice 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. This effect is due to the systematic change of the surface topography upstream to the borehole. Thus, and since numerous atmospheric studies carried out at elevated sites in Europe have revealed a well-marked summer maximum of concentrations of various species in relation to a more efficient upward advection of air masses from the boundary layer in summer than in winter [*Legrand et al.*, 2005; *Pio et al.*, 2007; *Hammer et al.*, 2007], such a glaciological forcing 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 ice core, we will try to examine separately winter and summer long-term trends, as done in previous studies dealing with the long-term trends of inorganic species.

[19] Figure 3 compares the CDK record of ammonium, i.e., the reference species of seasonal cycle, and those of organics. It appears that the DOC signal as well as its different subfractions defined section 5 remains seasonally resolved back to approximately 1920 (except, as discussed in section 2, between 1955 and 1970). Therefore, data were dissected in summer and winter snow sections and averaged in half-year means (Figure 4) on the basis of the ammonium record.

[20] As seen in Figure 4, investigated ice core samples cover the key periods of the history of the inorganic pollution over Europe. As already discussed by *Preunkert et al.* [2001a],

Table 2. Ozone Mixing Ratio and Aerosol Composition at Puy de Dôme From 22 June to 26 June 2010

| Date | O ₃ (ppbv) ^c | Sulfate (ng m ⁻³) ^b | WSOC (ng C m ⁻³) ^a | F ¹⁴ C ^b | Diacids (ng C m ⁻³) ^b | HULIS (ng C m ⁻³) ^a | Unknown (ng C m ⁻³) |
|---------------------|------------------------------------|--|---|--------------------------------|--|--|---------------------------------|
| Day 1 | 53.0 | 1567 | 1404 | 0.74 ± 0.03 | 99.6 | 465 | 840 |
| 22 June at 18:00 h | | | | | | | |
| 23 June at 18:00 h | | | | | | | |
| Day 2 | 63.6 | 1280 | 1730 | 0.81 ± 0.02 | 129.0 | 606 | 995 |
| 23 June at 18:00 h | | | | | | | |
| 24 June at 20:00 h | | | | | | | |
| Day 3 | 70.0 | 1750 | 2583 | 0.85 ± 0.02 | 163.0 | 935 | 1485 |
| 24 June at 20:00 h | | | | | | | |
| 25 June at 19:00 h | | | | | | | |
| Δ (day 3–day 1) | | | 1179 | | 63.4 (5.4%) | 470 (40%) | 645 (54.6%) |
| Day 1 (fossil fuel) | | | 405 | | 46 (11%) | 67 (17%) | 292 (72%) |
| Day 2 (fossil fuel) | | | 383 | | 56 (15%) | 69 (18%) | 256 (67%) |
| Day 3 (fossil fuel) | | | 472 | | 50 (10%) | 93 (20%) | 329 (70%) |

For aerosol, the increase of the WSOC level (denoted Δ [day 3–day 1]) and of its ^{14}C signature indicates an increase of predominantly biogenic origin (see section 6.1). We also report the WSOC fossil fuel fraction of days 1, 2, and 3. The fossil fuel fraction of WSOC is hereby calculated assuming a two-source mix of biogenic ($F^{14}\text{C}=1.04$ at the European background station of Jungfraujoch [3471 m asl] for the living biosphere in 2010; I. Levin, 2011, personal communication) and fossil ($F^{14}\text{C}=0$) contributions. For example, the fossil fuel fraction over day 1 is calculated as $(1-0.74/1.04) \times 1404 \text{ ng C m}^{-3}$ (i.e., 405 ng C m⁻³). For calculations of the fossil fuel contributions of diacids, HULIS, and the unknown fractions, see section 7.1. For example, the fossil fuel diacid fraction over day 1 is equal to $99.6-0.054 \times (1404-405) \text{ ng C m}^{-3}$ (i.e., 46 ng C m⁻³). Values in parentheses refer to the respective contribution of diacid, HULIS, and unknown fractions to the WSOC amount.

^aData from *Guilhermet et al.* [this issue].

^bThis work.

^cData available at <http://www.obs.univ-bpclermont.fr/SO/mesures/pdd.php>.

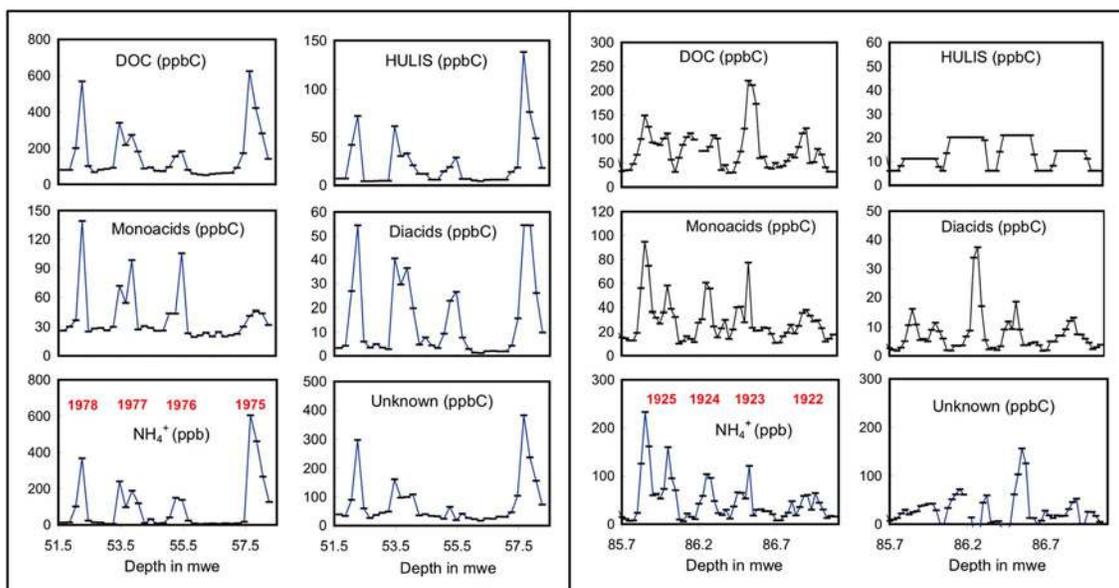


Figure 3. High-resolution depth profiles of ammonium and organic fractions in the CDK ice core over a recent (left) and a prior World War II (right) time period. The DOC fraction is reported together with the three chemically identified DOC fractions (denoted monoacids, diacids, and HULIS) and the chemically unidentified (denoted Unknown) one (see section 5). Note that the HCHO fraction that exhibits no seasonality and contributes only weakly to the DOC content (a few ppbC) is not reported.

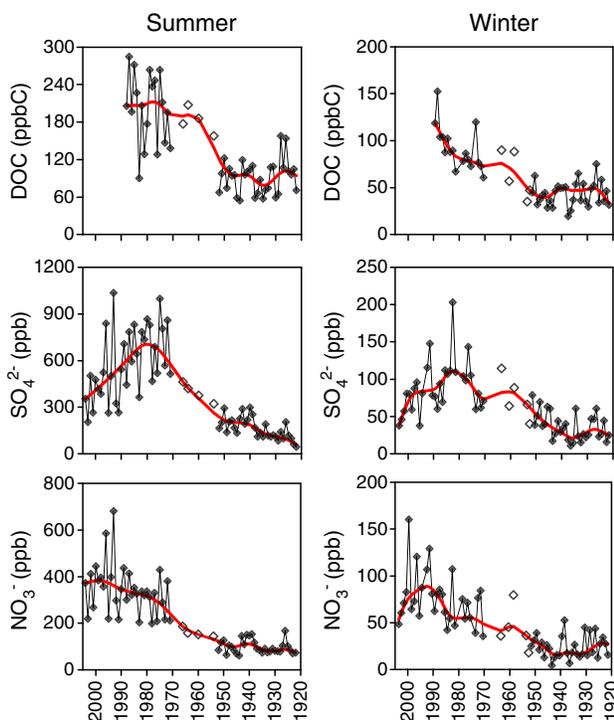


Figure 4. Summer (left) and winter (right) half-year means of DOC (top), sulfate (middle), and nitrate (bottom) along the well-dated part of the CDK ice core (solid points). The open points correspond to samples from the C11 ice core (see section 3.1). The red lines are robust spline smoothing [Bloomfield and Steiger, 1983].

the regular increase of both summer and winter sulfate levels from 1925 to 1980 followed by a decrease resulting from improvement in the quality of fuel and emission abatements [Mylona, 1996] can be seen in the Col du Dôme ice archives. Conversely, as discussed by Preunkert *et al.* [2003], the nitrate levels show a persistent increase until 1995. Interestingly, the CDK ice core data, which enlarge the covered time period with respect to the previous Col du Dôme ice core studies, indicate that sulfate continues to decrease from 1995 to 2004 in agreement with a lasting reduction of SO_2 in Western Europe until the beginning of the 20th century, whereas nitrate started to decrease after 1995 consistently with the decrease of NO emissions from vehicles [Vestring and Klein, 2002].

5. The Chemical Speciation of the Organic Carbon in Ice

[21] From our extended investigation of organic compounds, including for the first time water-soluble HULIS measurements, we first examine the contribution of these different organic compounds to the DOC amount present in the ice.

[22] As mentioned in section 4, the DOC content and the different organic fractions that were investigated exhibit a clear seasonal cycle (Figure 3). That is true for the sum of C_1 – C_3 monocarboxylates, the sum of C_2 – C_5 dicarboxylates, and HULIS. The only identified organic species that reveals no seasonal cycle is formaldehyde, but as discussed later, the contribution of this species to the DOC content remains among the weakest. The unidentified fraction of DOC, hereafter denoted “unknown,” calculated by subtracting from the DOC content the carbon levels corresponding to

monoacids, diacids, and HULIS, also exhibits a seasonal cycle. The respective contribution of the different organic fractions to the DOC content is reported on a seasonal basis in Figure 5 for the 1921–1951 and 1971–1988 time periods.

[23] Although HULIS are a class of compounds rather than a single species, to our knowledge, the chemical speciation of the DOC content in ice we report in Figure 5 represents the unique case for which more than half of the DOC content in a hydrometeor is chemically identified. Indeed, light mono- and dicarboxylates, HULIS, and formaldehyde account together for 53%–57% of the DOC content in ice corresponding to 1971–1988. This percentage becomes even higher (67%–73%) in ice corresponding to the first part of the 20th century (1921–1951).

[24] Monoacids together with diacids contribute 38% and 44% of the DOC in ice corresponding to the 1971–1988 and 1921–1951 years (annual mean values), respectively. The contribution of monocarboxylic acids is three times larger than that of dicarboxylic acids, formic acid alone representing on average half of monocarboxylic acids (i.e., 15% of DOC). As already pointed out by *Legrand et al.* [2007a], the contribution of these organic acids to the DOC content of ice is relatively large compared with what is generally seen in precipitation at lower-elevation sites in Europe. For example, in cloud water samples, monocarboxylates and dicarboxylates account together for 10% of DOC at Puy de Dôme [*Marinoni et al.*, 2004] located at 1450 m elevation and at Mount Rax (70 km southwest of Vienna, 2000 m asl, Austria) [*Löflund et al.*, 2002]. *Legrand et al.* [2007b] showed that the atmospheric abundance of C-diacids relative to WSOC aerosol increases from 4% in summer at surface continental sites to 12% at the Vallot Observatory (4360 m asl) located nearby the Col du Dôme site. In addition, gas phase samplings achieved at this site in summer 2004 indicate a mixing ratio of formic acid close to 0.3 ppbv [*Preunkert et al.*, 2007]. Compared with

levels observed by *Puxbaum et al.* [1988] at a semirural surface site in eastern Austria (~1 ppbv), the decrease of this species with elevation is far weaker than that of WSOC aerosol (~2500 ng m⁻³ STP in summer at surface sites [*Pio et al.*, 2007] compared with 150 ng m⁻³ STP at Vallot [*Legrand et al.*, 2007b]). Thus, the weaker decrease with elevation of both diacid aerosols and gaseous HCOOH with respect to the WSOC aerosol may account for the rather high contribution of carboxylic acids to the DOC content of ice at the Col du Dôme compared with those in precipitation at lower-elevation sites. Of course, the high fraction of identified species in the DOC of ice is also due to the fact that our study includes water-soluble HULIS, which represent from 9% to 21% of the DOC ice content (Figure 5) and which were rarely analyzed in European precipitation until now (for instance, see *Cerqueira et al.* [2010]).

6. The Fraction of DOC Related to WSOC

[25] As schematized in Figure 6, the DOC content of ice is related to WSOC aerosols as well as organic gases that have been solubilized in precipitation. To reconstruct relevant information on the long-term trend of WSOC, we examine in the following which fraction of DOC in ice can be attributed to atmospheric WSOC aerosol.

[26] Among identified species that contribute to the DOC ice content (Figure 5), formaldehyde and C₁–C₃ monocarboxylic acids are organic gases that have been solubilized in precipitation, whereas C₂–C₅ dicarboxylic acids and HULIS represent a part of WSOC aerosol. Among short-chain organic gases present in the atmosphere, those having a polar character like monocarboxylic acids, alcohols, aldehydes, and ketones can be incorporated in snow and ice and contribute to the DOC level in ice. Given their atmospheric abundance and solubility in water, formic and acetic acids, and to a lesser extent formaldehyde and methanol may significantly contribute to the DOC content of ice. Ketones and aldehydes other than HCHO, with effective Henry's law constants far below the one of HCHO (30 M

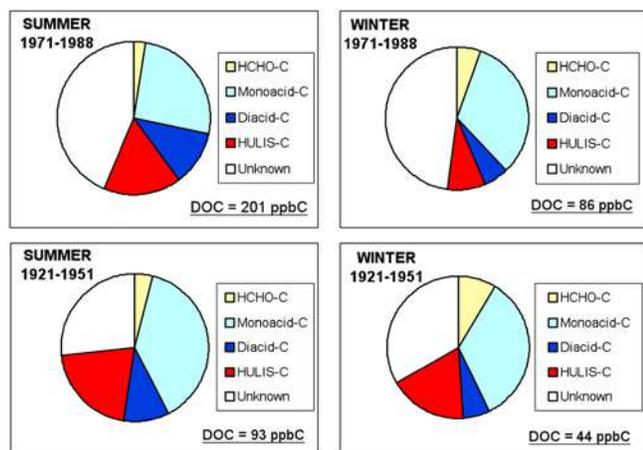


Figure 5. Chemical composition of DOC present in winter and summer ice layers corresponding to the first (1921–1951) and second (1971–1988) half of the 20th century. The identified organic species include formaldehyde, C₁–C₃ monocarboxylic (formic, lactic, acetic, glycolic, and glyoxylic) acids, C₂–C₅ dicarboxylic (oxalic, malic, malonic, succinic, and glutaric) acids, HULIS, and the unidentified fraction of DOC (see section 5).

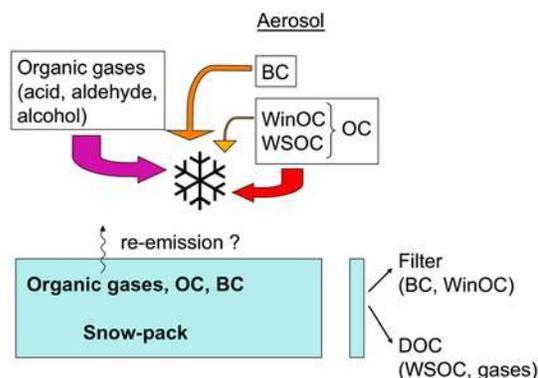


Figure 6. The different atmospheric organic fractions that are trapped by wet deposition in ice (see section 6). They include black carbon (BC), organic carbon (OC), and its two subfractions (water-soluble and water-insoluble organic carbon denoted WSOC and WinOC, respectively). The scheme only shows the wet deposition and the dry deposition of aerosols and gases that also contributes to the snowpack content is not schematized.

atm⁻¹ for acetone and 14 M atm⁻¹ for acetaldehyde against 3200 M atm⁻¹ for HCHO [Staudinger and Roberts 1996]) would not be trapped significantly by precipitation. Methanol (not measured in this study) is still relatively abundant (a few ppbv [Jacob *et al.*, 2005]) in the atmosphere. With a Henry's law constant of 220 M atm⁻¹ [Meylan and Howard, 1991], this organic gas is still relatively soluble in water, and its contribution to the DOC of precipitation can be questioned. Investigations of methanol in hydrometeors are very rare, especially those permitting to evaluate its contribution to the DOC content. With this respect, the study from Felix [2008] on rains collected in North Carolina is rather unique. The latter author reports a contribution of methanol to DOC of 1.5% compared with 2% for HCHO, 0.2% for acetaldehyde, and 8% for formic acid. Snider and Dawson [1985] reported an even lower abundance of methanol compared with that of formaldehyde in rains collected at the Santa Rita mountain (1300 m asl, southwestern United States). It is therefore very likely that the determination of light monocarboxylic acids together with that of HCHO in ice permits to quantify most water-soluble organic gases contributing to the DOC content of ice and that the unknown fraction of the DOC is mainly related to atmospheric WSOC aerosol.

[27] If the preceding assumption is correct (i.e., the unknown fraction of DOC in ice is related to atmospheric aerosol), the quantity WSOC* calculated as the sum of HULIS, diacids, and unknown in ice would correspond to WSOC atmospheric aerosol. As discussed later in section 7, WSOC* values remain close to 150 ppbC in summer ice layers corresponding to the 1960–1990 time period, whereas Legrand *et al.* [2007a] reported a mean concentration of 50 ppbC of water insoluble OC (WinOC) in summer ice layers covering the same period. This relative abundance of WSOC* and WinOC in ice (75% and 25%, respectively) can be compared with the relative abundance of water-soluble and water-insoluble organic aerosol present in the atmosphere in summer. At the high elevation site of Sonnblick (3106 m asl), Pio *et al.* [2007] found that 40% of atmospheric OC is water insoluble. Comparing air and snow precipitation at that site, Cerqueira *et al.* [2010] showed that sulfate is twice more efficiently removed from the atmosphere than WinOC. Given the affinity of species to water, it is legitimate to assume that WSOC is also twice more efficiently scavenged by precipitation than WinOC. If so, the contribution of WinOC to OC (40%) in the atmosphere would be reduced to 25% in ice by the scavenging process. This excellent consistency between the relative abundance of WSOC and WinOC in air and ice strongly supports our preceding conclusion that the WSOC* quantity corresponds to WSOC atmospheric aerosol and that the contribution of organic gases to the DOC content of ice mainly comes from monocarboxylic acids together with HCHO.

[28] The assumption that the unknown fraction of DOC in ice is related to atmospheric aerosol makes the unknown fraction the dominant part of WSOC* in ice. That is also seen in the atmospheric WSOC aerosol. The chemical speciation of WSOC aerosol in the present-day European atmosphere is reported in Table 1, showing that whatever the site, a very large fraction of WSOC remains chemically unidentified (from 68% to 82% in summer and from 78% to 88% in winter). Note that the percentage of the unidentified fraction

in the present-day WSOC aerosol at Sonnblick is higher (80% in summer 2003, for instance) than the one of the unknown DOC fraction related to WSOC in recent ice (60% in summer 1971–1988, see Table 3). However, as discussed in section 7, the increase in DOC between 1921 and 1988 is mainly due to the increase in the unknown fraction of DOC rather than to diacids and HULIS. If continuing after 1988, this feature of the DOC trend may increase the contribution of the unknown fraction to WSOC* in 2003 ice to become closer to that of the unknown fraction in atmospheric WSOC in 2003.

[29] In view to reconstruct the long-term change of atmospheric WSOC aerosol, we examine in section 7 the long-term winter and summer trends of WSOC*. Although the preceding discussion suggests that WSOC* may be related to WSOC atmospheric aerosol, it is possible that it slightly overestimates the importance of the unknown fraction.

7. Long-Term Trends of WSOC Inferred From DOC Ice Core Trends

[30] In Table 4, we report the change of the different fractions of DOC including WSOC* from the 1921–1951 to the 1971–1988 time period. Changes are examined separately for winter and summer. Figure 7 shows the summer

Table 3. Relative Contributions of the Chemically Unidentified Organic Species to the WSOC Aerosol Levels Observed at Sonnblick (calculated from data reported in Table 1) and of the Unknown Fraction (see section 5) to the WSOC* Content in the Col du Dôme Ice

| | WSOC Aerosol Sonnblick (2002–2003) (%) | WSOC* Ice (1971–1988) (%) | WSOC* Ice (1921–1951) (%) |
|--------|---|------------------------------|------------------------------|
| Summer | 82 | 62 | 49 |
| Winter | 88 | 76 | 61 |

Table 4. Concentrations of DOC, Formaldehyde (HCHO), Sum of Monocarboxylates (monoacids) and Dicarboxylates (diacids), HULIS_{WS}, the Unidentified Organic Carbon Fraction (denoted unknown, see Section 5), and Sulfate in Summer (S) and Winter (W) Ice Layers Covering Two Different Time Periods of the 20th Century

| Time Period | 1921–1951 | 1971–1988 | Enhancement Factor |
|----------------------|-------------|-------------|--------------------|
| DOC W | 44 ± 12 | 86 ± 15 | 1.95 |
| DOC S | 91 ± 28 | 201 ± 57 | 2.2 |
| HCHO W | 3.5 ± 1.6 | 4.4 ± 0.8 | 1.25 |
| HCHO S | 3.2 ± 1.2 | 5.0 ± 1.2 | 1.55 |
| Monoacids W | 14 ± 4 | 28 ± 8 | 2.0 |
| Monoacids S | 33.4 ± 9.2 | 49 ± 13 | 1.5 |
| Diacids W | 2.7 ± 1.3 | 4.8 ± 2.6 | 1.8 |
| Diacids S | 9.0 ± 2.9 | 22.9 ± 6.5 | 2.55 |
| HULIS ^a W | 6.8 ± 1.9 | 7.7 ± 3.4 | 1.1 |
| HULIS ^a S | 18.4 ± 6.4 | 33.0 ± 11.0 | 1.8 |
| Unknown W | 16.7 ± 11 | 41 ± 10.5 | 2.45 |
| Unknown S | 26.5 ± 18.7 | 91 ± 38 | 3.4 |
| WSOC* W | 26 ± 12 | 53.5 ± 14 | 2.06 |
| WSOC* S | 53 ± 23 | 147 ± 51 | 2.8 |
| Sulfate W | 37 ± 19 | 126 ± 67 | 3.4 |
| Sulfate S | 145 ± 62 | 683 ± 176 | 4.7 |

The last line refers to the fraction of DOC estimated to be related to WSOC aerosol (WSOC*, taken as the sum of diacids, HULIS, and the unknown fraction; see section 6). All concentrations are in ppbC. The third column indicates the enhancement factor of concentrations between the first and the second period.

^aData from Guilhermet *et al.* [this issue].

and winter long-term trend of WSOC* from 1921 to 1988 with the apportionment between the two identified fractions (C₂-C₅ diacids and HULIS) and the unknown fraction.

[31] In summer, the DOC levels increased from 91 ± 28 ppbC over the 1921–1951 years to 201 ± 57 ppbC over the 1971–1988 years. These values are consistent with the ones reported by *Legrand et al.* [2007a]. Indeed, this previous discontinuous study covering approximately 50% of the summer time reported blank corrected values of 100 ± 15 ppbC and 290 ± 106 ppbC over the 1925–1936 and 1970–1976 years, respectively. Summer WSOC* levels ranging between 30 and 80 ppbC before 1950 rapidly increased by a factor of 3 from 1950 to 1960 and then remained close to 150 ppbC in recent times (Table 4).

[32] In winter, DOC levels increased from 44 ± 12 ppbC over the 1921–1951 years to 86 ± 15 ppbC over the 1971–1988 years. As reported in Figure 7, the WSOC* levels were enhanced by a factor of 2 between the two time periods mainly as a result of an increase of the unknown fraction.

7.1. Origins of the WSOC* Summer Increase Over the 20th Century

[33] Possible causes for the DOC increase by some 110 ppbC (with WSOC* accounting for 94 ppbC) seen in the summer CDK ice between the 1920s and the late 1980s are highlighted by the ¹⁴C signature of the DOC ice content investigated by *May et al.* [this issue]. Indeed, taking advantage of the strong variation of atmospheric ¹⁴CO₂ following the bomb peak in 1963, it is possible to investigate potential changes of the sources contributing to the DOC level by distinguishing between fossil fuel combustion, living biosphere, or biomass burning [*May et al.*, 2009]. Although it is not straightforward to separate living biosphere from biomass

burning or soils, *May et al.* [this issue] clearly concluded by examining the time lag of the DO¹⁴C in ice with the ¹⁴CO₂ around the bomb peak that the main biogenic source contributing to the DOC in ice in summer is the living biosphere, whereas biomass burning represents a very weak source. Furthermore, the eight summer ice samples investigated for ¹⁴C in DOC showed a mean DO¹⁴C depletion relative to the atmospheric ¹⁴CO₂ value of $25\% \pm 9\%$ attributed to fossil fuel sources, deviation being slightly lower (12%–19%) in the two summer samples corresponding to the late 1940s compared to those in the two more recent summers (24%–31% in 1975 and 1990). However, based on a limited number of samples, this might suggest a slight increase of the DOC fossil fuel fraction from the late 1940s to the early 1990s.

[34] To relate these DO¹⁴C data to relevant information for discussing the long-term trend of WSOC*, we need to make assumptions on the sources (i.e., on the ¹⁴C signature) of organic gases, which also contribute to the DOC in ice. More than 75% of organic gases contributing to DOC in ice are related to the presence of formic and acetic acids. The present-day budgets of these two acids were recently established by *Paulot et al.* [2011], who pointed out the importance of secondary productions from biogenic volatile organic compounds. From the analysis of ¹⁴C content of formic and acetic acids in the atmospheric boundary layer at various European sites in 1997–1999, *Glasius et al.* [2001] suggested that more than 80% of these species originate from recent biogenic sources at semiurban and semirural sites. Consistent with that, examining the record of formate and acetate in the C10 ice core, *Legrand et al.* [2003] concluded that before 1950 and during the 1990s, the main origins of formate and acetate are natural. The same authors suggested that a different picture took place between 1965 and 1975 when anthropogenic sources became significant with respect to natural sources likely in relation with increased vehicle emissions of reactive volatile organic compounds (carboxylic acids and alkenes). The authors found that the acetate content of ice changed from 15 ppb (i.e., 6 ppbC) to 30 ppb (i.e., 12 ppbC) from 1921–1951 to 1971–1988. For formic acid, they showed that between 1971 and 1988, around a quarter to a third of formic acid present in the European atmosphere would have had a fossil fuel origin although the increase was not detected in ice in relation with the concomitant increase of the acidity of precipitation. From that, we estimate that of the 98 ppb of formate observed in ice deposited between 1971 and 1988 around 24–33 ppb (i.e., around 8 ppbC) would have a fossil fuel origin. Thus, as seen in Table 5, the fraction of fossil fuel WSOC* for the 1971–1988 time period was calculated by subtraction 14 ppbC (6 ppbC representing the change in acetate between 1921–1951 and 1971–1988 plus 8 ppbC representing the estimate of the fossil fuel contribution to formate related to fossil fuel emissions of mono-carboxylic acids) from the total fossil fuel DOC fraction. The biogenic fraction of WSOC* was then calculated as the difference between total and fossil fuel WSOC* for the 1921–1951 and 1971–1988 time periods (Table 5). One of the major results derived from these estimates is that of the 94 ppbC WSOC* increase between the two time periods, only 15% of the WSOC* increase are related to enhanced fossil fuel emissions whereas 85% of the increase relates to biogenic emissions. Note that the 15% of the WSOC* increase

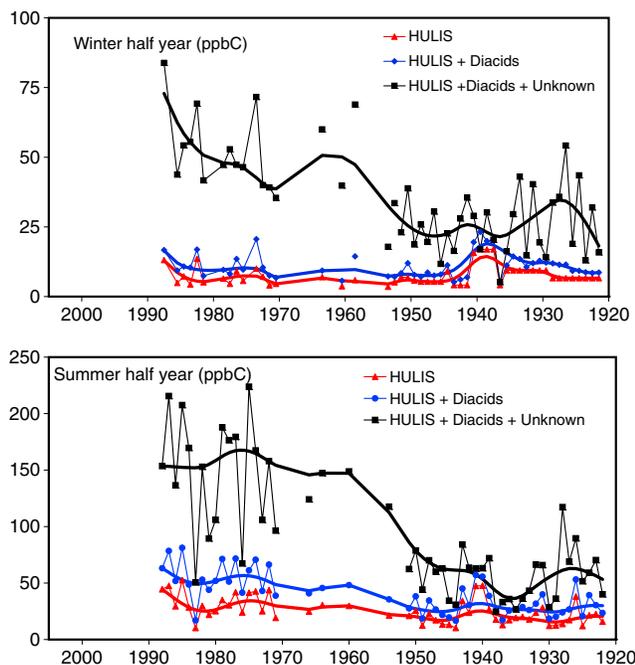


Figure 7. Long-term winter (top) and summer (bottom) trends in ice for HULIS, the sum of HULIS and diacids, and WSOC* (HULIS + diacids + unknown). Triangles refer to individual means, lines to robust spline smoothings.

Table 5. Apportionment (fossil fuel versus biogenic) of the Content of DOC, WSOC*, and Its Three Subfractions in Ice Over Two Time Periods in Summer

| Time Period | f_{bio} DOC (%) | | DOC (ppbC) | WSOC* (ppbC) | HULIS (ppbC) | Diacids (ppbC) | Unknown (ppbC) |
|----------------|--------------------------|-------------|------------|--------------|--------------|----------------|----------------|
| 1971–88 Summer | 75–83 | Total | 201 | 147 | 33 | 23 | 91 |
| | | Biogenic | 167–151 | 111–127 | 33 | 16 | 61–78 |
| | | Fossil Fuel | 34–50 | 20–36 | 0 | 7 | 13–29 |
| 1921–51 Summer | 81–88 | Total | 91 | 53 | 18 | 9 | 26 |
| | | Biogenic | 74–80 | 36–42 | 18 | 9 | 9–15 |
| | | Fossil Fuel | 11–17 | 11–17 | 0 | 0 | 11–17 |

The fossil fuel contribution to DOC is calculated from the amount of DOC and its biogenic fraction given as $f_{\text{bio}} = F^{14}\text{C}/F^{14}\text{C}(\text{CO}_2)$. Data on ^{14}C of DOC ($F^{14}\text{C}$) are presented in *May et al.* [this issue]. For the changes of $F^{14}\text{C}(\text{CO}_2)$ since 1940, we used values from *Stuiver and Quay* [1981] and *Levin et al.* [2010]. The fossil fuel contribution to WSOC* is calculated by assuming that 14 ppbC of monocarboxylic acids of fossil fuel origin contributed as organic gases to the DOC content of ice over the 1971–1988 time period (see section 7.1).

attributed to fossil fuel may be an upper limit since the DO^{14}C depletion relative to the atmospheric $^{14}\text{CO}_2$ range of 12%–19% applied for estimates over the 1921–1951 time period is an upper limit since it has been measured in ice deposited at the end of this period (in the late 1940s).

[35] In the following paragraphs, we make an attempt to apportion fossil fuel versus biogenic sources of the three WSOC* fractions (HULIS, diacids, and the unknown fraction) from 1921 to 1988. To do so, some assumptions need to be made on the partitioning (fossil fuel and biogenic) of each fraction. As discussed by *Guilhermet et al.* [this issue], HULIS essentially originate from biogenic emissions in summer. For C_2 – C_5 diacids, *Legrand et al.* [2007b] concluded on the basis of a 2 year aerosol climatology gained at several sites in Europe that, although a significant contribution of fossil fuel exists (e.g., through the formation of oxalic acid from aldehydes produced from toluene emitted by cars), the major contributions in summer seem to be of biogenic origin (i.e., isoprene and/or others precursors). In their modeling study of oxalate, *Myriokefalitakis et al.* [2011] concluded that the isoprene oxidation accounts for 80% of the budget of oxalate, the left part being related to anthropogenic precursors including toluene. Since the partitioning (fossil fuel/biogenic) of atmospheric WSOC aerosol is not documented yet, measurements were made on aerosol filters collected in June 2010 at the Puy de Dôme site (see section 3.2), including analyses of C_2 – C_5 diacids, water-soluble HULIS, WSOC, and of its ^{14}C signature. Over the sampling period of 3 days, the recovery of sunny conditions was accompanied by a regular increase of ozone (Table 2) and of temperature (see section 3.2). As expected for a species mainly related to anthropogenic sources, the level of sulfate showed no systematic change over the 3 days. Note also that the 3 day averaged sulfate value (1530 ng m^{-3}) is close to the typical summer value reported for that site (1530 ng m^{-3} over summers 2003 and 2004) by *Pio et al.* [2007]. Similarly, the level of WSOC over the 3 days (1900 ng C m^{-3}) is also very consistent with that observed in summer 2003 and 2004 (1540 ng C m^{-3} , *Pio et al.* [2007]). Finally, the dominant biogenic signature of WSOC suggested by radiocarbon measurements (Table 2) is expected given the previous studies from *May et al.* [2009] and *Gelencsér et al.* [2007], showing that around three quarters of OC aerosol originates from biogenic sources at that site in summer. Whereas no systematic change of the sulfate level is observed, a regular increase of the WSOC concentrations took place. Interestingly, the increase of WSOC is accompanied by an increase of the percentage

of modern carbon. Indeed, calculations indicate that the additional amount of WSOC present at the end with respect to the beginning of the period (1179 ng C m^{-3}) is almost exclusively of biogenic origin ($0.85 \times 2583 \text{ ng C m}^{-3} - 0.74 \times 1404 \text{ ng C m}^{-3} = 1158 \text{ ng C m}^{-3}$). The composition of this biogenic fraction with respect to C_2 – C_5 diacids, HULIS, and the unidentified fraction is reported also in Table 2 (denoted Δ ; day 3–day 1). Assuming that this chemical composition of the biogenic WSOC fraction remained unchanged over the 3 days of sampling and using the ^{14}C signature, we can also calculate the composition of the fossil fuel fraction of WSOC for each day (see Table 2). For HULIS, it clearly appears that they are mainly biogenic in origin (see details in *Guilhermet et al.* [this issue]). Table 2 confirms the existence of a fossil fuel contribution for diacids although the biogenic contribution still dominates. Although based on a limited number of sampling days, this study, conducted at a mountain site under typical summer conditions, permits to conclude that the unknown fraction of WSOC appears to be significantly present in both the fossil fuel and the biogenic fraction, accounting for half of the biogenic fraction and dominating the fossil fuel fraction (70%) of WSOC well above HULIS and diacids. This first attempt to apportion WSOC atmospheric aerosol and its different chemical fractions into fossil fuel and biogenic sources by using ^{14}C measurements appears very powerful and would motivate further studies in view to increase the data representativeness and to confirm conclusions drawn above.

[36] On the basis of the previous discussions, we assume for the WSOC* in ice that (1) HULIS are only biogenic in origin and (2) around two thirds of diacids are biogenic and one third fossil fuel in origin. As a consequence (see Table 5), the increase of WSOC* related to biogenic sources, which represents 75% of the total increase of WSOC*, is made up to 70% by the unknown fraction, to 19% by HULIS and by 9% by diacids. Although uncertain, the assumption we made on the partitioning of diacids between biogenic and anthropogenic sources does not significantly impact our major conclusion, namely, that most the WSOC* increase is related to enhanced biogenic emissions and primarily of the unknown fraction. The small increase of WSOC* that is related to fossil fuel is dominated by the unidentified fraction and the diacids.

[37] Several environmental factors may have modified biogenic emissions, including summer temperatures and CO_2 atmospheric levels [*Guenther, 1997*]. Furthermore, the production of organic aerosol from biogenic precursors may have been enhanced following the change of the

oxidative capacity of the atmosphere as previously suggested by model simulations [Kanakidou *et al.*, 2000]. Although, among others, the oxidation of terpenes by ozone may represent an important source of WSOC, any further discussions are limited by the fact that a large part of the biogenic summer increase of WSOC* from 1921 to 1988 is related to its unknown fraction.

7.2. The WSOC* Winter Trend

[38] In winter, the WSOC* levels increased by a factor of 2 between 1921–1951 and 1971–1988, mainly as a result of an increase by a factor of 2.5 (Table 4) of the unknown fraction. The winter levels of HULIS remained rather constant, this absence of trend having been attributed by Guilhermet *et al.* [this issue] to rather unchanged wood burning emissions in Europe since 1920. Finally, with a contribution remaining close to 10% (see Figure 7), the diacids do not contribute to the overall increase of WSOC*.

[39] Since only one DO¹⁴C value is available for winter ice [May *et al.*, this issue] and due to the potential significant role of domestic wood burning on the OC level over Europe at that season [Gelencsér *et al.*, 2007; May *et al.*, 2009], it is not possible to discuss the origin of the winter trend of WSOC* by interpreting the DO¹⁴C depletion relative to the atmospheric ¹⁴CO₂ value in terms of fossil fuel versus wood burning sources. Note also that the nature of the unknown fraction is not necessarily the same as the summer one.

8. Conclusions

[40] The investigation of the content and chemical speciation of DOC present in Alpine ice layers is powerful to reconstruct past water-soluble organic aerosol changes over Europe since 1920. It is shown that light mono- and dicarboxylates, HULIS, and formaldehyde account together for 55% of the DOC content of ice layers corresponding to the recent decades (1971–1988). This percentage becomes even higher (70%) in ice corresponding to the first part of the 20th century (1921–1951). The extended knowledge of the chemical speciation of DOC was successfully used to estimate the fraction that can be attributed to atmospheric WSOC aerosol. This fraction (WSOC*) was found to increase by a factor of 3 and 2 from 1920 to 1990 in summer and winter, respectively. Concerning the summer trend, the results are highlighted by the ¹⁴C signature of the DOC content of ice presented in the companion paper from May *et al.* [this issue]. One of the major derived results is that only approximately 15% of the WSOC* increase is related to enhanced fossil fuel emissions whereas approximately 85% of the increase relate to the living biosphere. There are many possible causes that may have strengthened either biogenic precursors of WSOC or the gas-particle conversion rate. However, since a large part of the increase of WSOC* in summer is found to be related to the chemically unidentified fraction, it remains difficult to discuss this summer trend in terms of possible involved precursors (isoprene and monoterpenes). The winter trend of WSOC* is discussed in less detail since no information on the ¹⁴C signature of the DOC content in winter is yet available.

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