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Major 20th century changes of carbonaceous aerosol components (EC, WinOC, DOC, HULIS, carboxylic acids, and cellulose) derived from Alpine ice cores

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[1] An extended array of carbonaceous species including elemental carbon (EC), water insoluble organic carbon (WinOC) as well as dissolved organic carbon (DOC), humic-like substances (HULIS), and single organic compounds like carboxylic acids, levoglucosan, and cellulose was investigated for the first time in Alpine snow deposits. These investigations were done on selected discrete ice cores sections extracted from Mount Rosa and Mount Blanc glaciers covering the 20th century and extending back to previous centuries. Here we focus on major changes in summer ice layers. Among carbonaceous components, EC reveals an outstanding increase with a sharp summer increase after World War II. This result is discussed against available past EC emission inventories in Europe which are thought to be mainly driven by emissions from road transport and residential sector. The long-term trend of organic carbon (OC) aerosol preserved in ice, WinOC as well as water soluble organic carbon (WSOC), was successfully reconstructed using the suitable array of organic compounds we investigated in this study. It is shown that the level of OC preserved in ice has increased by a factor of 2 after 1950 likely as a result of the enhancement of the oxidative capacity of the atmosphere over the last decades producing more secondary organic atmospheric aerosol from biogenic gaseous precursors.

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1. Introduction

[2] It is now well recognized that the present (and future) climate change is not only related to change of long-lived greenhouses gases but through complex processes also to aerosols, particularly on regional scales. A recent study has suggested that aerosols may have weakened the rate of the global warming during the last century [*Andreae et al.*, 2005].

[3] Until now, most efforts dedicated to the aerosol/climate coupling were focused on sulfate aerosol for which source apportionment (natural versus anthropogenic) has been established and past anthropogenic emission inventories exist. Although the carbonaceous matter seems to be a major constituent of present-day fine continental aerosol, there are still major gaps with respect to its sources as well as its climate forcing effects. For instance, the relative contributions of natural against anthropogenic (fossil fuel combustion, biosphere) sources are not well known even for the present-day atmosphere. On the basis of EC emission inventories, model simulations either overestimate [*Liousse et al.*, 1996; *Cooke and Wilson*, 1996] or underestimate [*Dentener et al.*, 2006] present-day atmospheric EC concentrations, depending on assumptions made on emission factors in the inventories. Even more uncertain are estimates of historical changes in EC emissions due to large changes of past emission factors [*Novakov et al.*, 2003]. The situation is worst for OC since its atmospheric budget is at many places dominated by secondary productions from biogenic precursors [*Tsigaridis and Kanakidou*, 2003] for which recent reviews have highlighted the complexity of involved formation mechanisms [*Donahue et al.*, 2005; *Fuzzi et al.*, 2006]. The degree to which the fragile equilibrium of our atmosphere has been disturbed thus remains very poorly understood. The reconstruction of the changing atmospheric aerosol load and composition from the present polluted atmosphere back to the preindustrial era and an

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Table 1. Summary of Subsampling Carried Out on Alpine Firn and Ice Cores From Col du Dôme (CDD) and Colle Gnifetti (CG)[a]

Ice Core Material	Time Period	Number of Samples	Fraction of the Time Period Covered by Subsampling	Remarks
		Summer		
CDD firn	1989–1991	2	13%	firn
CDD ice	1970–1976	9	50%	ice
CDD ice	1962–1967	10	74%	ice
CDD ice	1952–1957	7	75%	ice
CDD ice	1939–1947	3	36%	ice
CDD ice	1925–1936	4	56%	ice
CDD ice	1906–1911	4	70%	ice
CDD ice	prior 1890	2	100%	no seasonality detected
CG ice	~10 years	1	Close to 100%	mid-19th century
CG ice	~20 years	1	Close to 100%	second half of 18th century
CG ice	~30 years	1	Close to 100%	late 16th century
		Winter		
CDD firn	1982–1984	2	18%	firn
CDD ice	1973–1976	1	10%	ice
CDD ice	1954–1957	1	22%	ice
CDD ice	1937–1939	1	60%	ice

[a] Samples were carefully selected with respect to summer and winter time deposition (section 2).

evaluation of the subsequent radiative impact are thus needed to improve our understanding and to forecast future climate.

[4] The high-elevated glaciers present in Europe offer the possibility to derive information on past changes of aerosol (load and composition). The potential of Alpine ice cores to provide relevant environmental records was previously evaluated in the framework of the EU-ALPCLIM project (Environment and Climate Records from High Elevation Alpine Glaciers, 1999–2001) [see, e.g., *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 using ice cores extracted at two different drill sites (Mount Rosa and Mount Blanc glaciers located above 4000 m elevation) and on site year-round atmospheric sampling [*Preunkert et al.*, 2002]. Furthermore, within the CARBOSOL project it was shown that a regional chemistry-transport model, using past emission inventories of SO_2 in Europe, reproduces fairly well the long-term trends of sulfate extracted from Alpine ice cores [*Fagerli et al.*, 2007], suggesting that these archives can indeed help to reduce uncertainties in past emission inventories.

[5] A first attempt to extract information on past carbonaceous aerosol levels from preindustrial time to the 1970s was made in an ice core extracted at the Mount Rosa glacier [*Lavanchy et al.*, 1999]. Although incomplete, since this study only refers to water insoluble and filterable OC (WinOC) and EC fractions, these pioneering data stimulate further studies because the EC and WinOC trends over the 20th century appear far less pronounced than that of sulfate (a factor close to 2 instead of a factor of 5), suggesting the importance of natural and/or nonindustrial carbonaceous aerosol emissions. Water insoluble OC and EC fractions were also investigated in an ice core extracted at the Fiescherhorn glacier (3900 m elevation, Switzerland) but the record only extends to the first part of the 20th century (1650–1940) [*Jenk et al.*, 2006].

[6] This work represents a first attempt to determine an extended array of carbonaceous species, which were also investigated in present-day aerosol at several places in Europe [*Legrand and Puxbaum*, 2007], in Alpine ice cores. The investigations include the water insoluble carbonaceous fractions (EC, and WinOC) as well as dissolved organic carbon (DOC), humic-like substances (HULIS), and single organic compounds like carboxylic acids, levoglucosan, and cellulose. Measurements were done on well characterized and selected ice core samples to gain at first representative information on possible anthropogenic long-term changes and typical seasonal effects. This would help to draft future more detailed ice core studies in this field. Here we report on major results of these first dedicated analysis and on inherent implications in view to gain better understanding of the impact of carbonaceous compounds on the past aerosol composition and load over Europe.

2. Ice Core Dating and Sampling

[7] Most of measurements were achieved on pieces of ice cores selected along a 140 m long ice core drilled to bedrock in 1994 at the Col du Dôme (CDD, 4250 m asl) site, located nearby the Mount Blanc summit (Table 1). The dating of this ice core was estimated by scaling down the dating previously established by *Preunkert et al.* [2000] along another 126 m long ice core extracted 50 m away. The comparison between the two ice cores includes examination of time horizons of 1954 and 1963 (atmospheric nuclear tests) identified from ^{137}Cs measurements. The precise dating of the 126 m long ice core based on the well-preserved seasonality of ammonium indicated an ice age of 75 ± 5 years at 117 m depth. At 125 m depth the age of ice is more uncertain but likely close to 1905.

[8] Since the well-dated part of the CDD ice cores extends back to ~1925 only, the preindustrial levels were investigated in ice cores extracted at Colle Gnifetti (CG), another high-elevation Alpine glacier located at 4450 m elevation in the Mount Rosa region (Switzerland). These ice

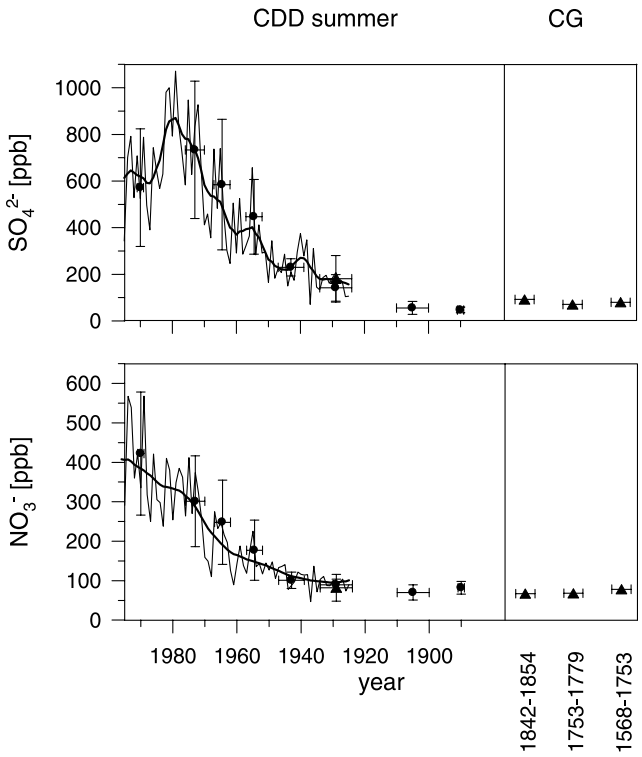

Figure 1. Summer sulfate and nitrate levels in the 140 m long CDD ice core (solid circles) and in CG (solid triangles) ice samples used in this work for determination of carbonaceous fractions and species. For CDD the discontinuous sampling is compared to the respective continuous profiles obtained in the 126 m long CDD ice core by *Preunkert et al.* [2001] for sulfate and *Preunkert et al.* [2003] for nitrate. The thin solid line refers to individual summer means, and the thick solid line refers to the smoothed profile with a 5 year time window. Vertical bars refer to the standard deviations related to sample content variability, and horizontal bars refer to the covered time periods.

samples span several decades of the last centuries (Table 1). Although the dating of these CG ice cores is less accurate than the more recent CDD ice layers, the covered time periods are clearly relevant to investigate the preindustrial levels of carbonaceous components.

[9] As discussed in previous alpine ice studies of inorganic species, summer ice layers generally exhibit a well-marked maximum of concentrations in relation to distinct seasonal atmospheric conditions prevailing there due to the presence or absence of upward advection of air masses from the boundary layer in summer and winter, respectively (see for instance the case of sulfate discussed by *Preunkert et al.* [2001]). Therefore an accurate identification of summer and winter ice layers is needed for a reliable interpretation of these ice data in terms of atmospheric changes. Following *Preunkert et al.* [2000] the dissection between summer and winter layers along the 140 m long CDD ice core sections was done after having performed high-resolution ammonium measurements. The CG ice cores selected to investigate preindustrial levels of carbonaceous components contain summer ice layers, because of the preferential loss of winter snow by wind erosion at this site [*Wagenbach et al.*, 1988]. That is confirmed by the good agreement observed for sulfate and nitrate levels between CG and summer CDD ice layers spanning the 1925–1936 time period (Figure 1).

[10] Except for the most recent layers (1989–1991), the discontinuous sampling of CDD summer ice core sections covers from 36% of the 1939–1947 time period to 75% of the 1952–1957 time period (Table 1). In order to examine how representative is such a discontinuous sampling, we compare in Figure 1 the temporal change of sulfate and nitrate in the discrete samples with the corresponding continuous profiles previously obtained along the 126 m long CDD ice core. The major patterns of temporal changes appear to be well depicted by the discontinuous sampling. The increase of sulfate started around the turn of the 19th century, remaining moderate until World War II and accelerates after 1960. Although the sampled fraction of the CDD firn layers (1989–1991) is weak (13%, Table 1) the post-1980 sulfate decrease is also captured by the discontinuous sampling. For nitrate the increase which becomes significant after World War II and continues until the very recent years is also well depicted by the discontinuous sampling.

[11] Because of high amount of material needed to investigate carbonaceous compounds in low-level winter layers only a few samples have been investigated. In spite of this limited number of winter data an increase of sulfate from 1937–1939 to 1982–1984 is detected (Table 2), and the sulfate levels in the four investigated wintertime periods are generally consistent with the continuous winter record (departure of less than 20 ppb) previously obtained at this site by *Preunkert et al.* [2001]. The relatively high sulfate level seen in the 1937–1939 discrete winter layer (65 ppb instead of 38 ppb in the corresponding continuous record), is likely due to a small overlap with summer layers when selecting pieces of ice. That will be considered when discussing the trends of carbonaceous compounds in winter.

3. Analytical Methods

[12] The general challenge for analytical methods deployed here to determine carbonaceous species in ice core extracted from very high elevated Alpine sites was to get reliable data on such very low content samples. Often, this required the use of analytical devices down to their detection capabilities, in combination with careful sample handling and preparation steps to avoid sample contamination or losses.

Table 2. Averaged Sulfate Levels in Winter CDD Layers Corresponding to Various Time Periods

Time Period	SO_4, ppb	EC, ppbC	WinOC, ppbC
1982–1984	101[a]–90[b]	2.4	20
1973–1976	125[a]–106[b]	6.5	32
1954–1957	74[a]–70[b]	<4.0	<13
1937–1939	65[a]–38[b]	3.8	22

[a] Discontinuous sampling achieved for investigation of carbonaceous fractions. For the discontinuous sampling we also report the levels of water insoluble carbonaceous fractions (EC and WinOC).
[b] Corresponding continuous sampling from *Preunkert et al.* [2001].

[13] All pieces of ice were decontaminated at Grenoble in a clean room by washing them in three successive baths of ultrapure water produced by a Maxima HPLC system (Elga, High Wycome Bucks, England) which was fed with ultrapure water from a Milli-Q 10 TS system (Millipore, Bedford, MA). The Elga system provides water with a dissolved organic carbon content lower than 5 ppbC. During the cleaning procedure around 20% of the outer ice layer was removed. Additional samplings were carried out on firn material whose decontamination was done under a clean air bench located in a cold room (−15°C) using an electric plane device. After the washing procedure, remaining pieces of ice were pulled and melted in a 2 L airtight glass bottle (Schott, Mainz, Germany) previously cleaned with Elga water.

[14] After the melting step the vial was carefully shaken in order to minimize loss of carbonaceous material onto the glass wall. Water samples dedicated to analysis of the different carbonaceous components were then put into precleaned airtight glass bottles and immediately sent by express mail to Hungary for HULIS, Germany for DOC, and Austria for cellulose and levoglucosan determinations. The glass bottles used for HULIS analysis were washed with ammonia after the water cleaning procedure. This is a common pretreatment to avoid adsorption of terrestrial and aquatic humic and fulvic acids. Samples dedicated to analysis of ions were stored frozen until analysis at Grenoble. For analysis of EC and water insoluble OC the liquid sample was filtered through a quartz fiber filter, which was thereafter dried and sent by express mail to Portugal.

[15] The validity of the decontamination procedure was tested by checking blank values obtained on pieces of ultrapure Elga water frozen into a large Schott bottle, and subsequently decontaminated similarly to ice cores. Obtained blank values are reported in the following paragraphs.

3.1. WinOC and EC

[16] For analysis of water insoluble OC and EC a liquid aliquot of 70 to 300 mL was filtered through a quartz fiber filter (Whatman QMA, 25 mm diameter) previously ignited at 550°C for 4 hours. The efficiency of quartz fiber filtration was previously found to be better than 80% for water insoluble OC and EC [*Cachier and Pertuisot*, 1994]. The separation of water insoluble matter was achieved by using a stainless steel filter unit equipped with a mask in order to concentrate particles onto a circular spot of 10 mm diameter. The filter was then dried in a desiccator for about 24 hours and preserved at −15°C until analysis.

[17] Organic and elemental carbon amounts accumulated in filters were measured by using the thermal-optical method detailed by *Pio et al.* [2007] to quantify carbonaceous matter in aerosols. Filter samples were first exposed to HCl vapors for several hours to remove carbonates. The heating steps of the thermal-optical method include the following: under N_2 at 150°C for 4 min, 350°C for 4 min, 600°C for 5 min, and from 600 to 250°C within 3 min; under N_2 with 4% of O_2 at 350°C for 1 min, from 350 to 500°C within 7 min, and at 850°C for 6 min. Correction for the pyrolysis contribution to EC from OC is accomplished by monitoring the transmission of light through the filter with a laser beam. The blank of the decontamination procedure was below detection limit for EC and lower than 10 ppbC for OC. A filtration of 100 mL of liquid leads to detection limits of 14 ppbC (related to the variability of filter blanks) for OC and of 1 ppbC for EC (related to noise of the analyzer). The precision of measurements, derived from several measurements made on the same filter, was below 10% for OC and below 25% for EC.

3.2. HULIS

[18] Humic-like substances (HULIS) are not a single chemical species but an ill-defined collective class which shares the general properties of natural humic matter. Since the properties of natural humic matter themselves may considerably vary, determination of HULIS is highly dependent on the specific property selected as a basis for the analytical method. We here used a method which relies on the spectral properties of HULIS, which are probably the most general and characteristic features of humic matter. This standardized method allows the determination of HULIS in water extract of aerosol, as well as in low concentration samples of precipitation and ice cores. The method involves an adjustable preconcentration step with freeze-drying which makes the detection limit linearly dependent on sample volume. As detailed by *Lukács et al.* [2007] HULIS concentrations were determined by measuring the absorbance of the extracts with a UV-VIS spectrophotometer at the wavelengths of 250 and 350 nm. For calibration not an arbitrarily selected reference humic or fulvic acid is used but the method is calibrated against HULIS isolated from a limited set of modern atmospheric aerosol samples following the method of *Varga et al.* [2001]. Most of the uncertainty results from the fact that the specific absorption of HULIS from different origins may vary significantly, even if the ratio of absorption at the two wavelengths does not change. This variation of specific absorption has been tested during the calibration step and found to be less than a factor of 2. For a typical sample of 100 mL, detection limit was close to 20 ppb. The blank of the decontamination procedure was close to 50 ± 30 ppb.

[19] The organic matter to organic carbon mass ratio of HULIS was investigated by elemental analysis following the HULIS isolation [*Kiss et al.*, 2002]. Overall, the organic mass to carbon mass ratio of HULIS was found to remain close to 0.5 in various locations and time of the year. The uncertainty accompanying this ratio is certainly less than 10% for HULIS in various environments, being a negligible contribution to the overall uncertainty of HULIS measurements.

3.3. DOC

[20] Meltwater samples were injected in an ultrapure water stream acidified with H_3PO_4 to remove dissolved inorganic carbon. The liquid passes through a first degassing unit to remove dissolved inorganic carbon and is then exposed to UV radiation for oxidation of dissolved organic carbon (DOC) and finally to a second degassing unit to remove the produced CO_2 hereafter quantified with a NDIR detector. With this procedure suspended organic micron particles are believed not to be oxidized and hence not to be detected. On the basis of numerous comparisons with a high temperature combustion device using various high concentration samples, it was shown that the detection efficiency of the UV method is close to 90%. As discussed by *Schock et al.* [2005] the detection limit is less than

1.5 ppbC for a sample volume of 20 mL. The blank of the decontamination of the ice was close to 30 ± 5 ppbC. Since firn is a porous material which is rapidly contaminated during storage in plastic bags by numerous volatile organic species (HCHO for instance, see section 3.7) no measurements were done on the firn CDD layers.

3.4. Cellulose

[21] Cellulose measurements of liquid samples (200 mL) were achieved by filtering them through a precleaned (combusted at 450°C for 24 hours) quartz fiber filter. The filtration efficiency, evaluated with a double filtration, was found to be close to 95%. Filters were extracted in PE-tubes with 3 ml of citric acid/thymol buffer at pH 4.8 during 15 minutes in an ultrasonic bath. The method used to quantify cellulose in aerosols by *Sánchez-Ochoa et al.* [2007] was applied for analyzing the filters. In brief, cellulose is enzymatically hydrolyzed into D-glucose hereafter determined using a UV-VIS spectrophotometer. A certain part of cellulose of plant debris particles is encapsulated by lignin and thus not hydrolyzed by enzymes. Therefore, following *Puxbaum and Tenze-Kunit* [2003], we multiplied the measured ''free cellulose'' value by a factor of 1.4 to estimate the total cellulose concentration. The blank of the decontamination procedure was below detection limit. The detection limit of the method, calculated as three times the standard deviation of filter blanks, is close 1.5 ppb for a sample volume of 200 mL.

3.5. Levoglucosan

[22] Determination of levoglucosan was performed using the method initially deployed for aerosol analysis [see *Puxbaum et al.*, 2007]. The method uses liquid chromatography on a Dionex CarboPAC PA1 Analytical Column equipped with a PA1 guard column with subsequent electrochemical detection (pulsed amperometry, gold electrode and pH-Ag/AgCl reference electrode). The eluent was a NaOH-gradient arising from 0.5 mM to 20 mM. A final gradient up to 250 mM was applied to clean the column after every sample run. Eluent flow was 1 mL min^{-1}.

[23] Since levoglucosan concentrations of the melted ice samples were below detection limit of the chromatographic system (30 ppb), samples were preconcentrated by evaporation (at ~70°C and reduced pressure) by a factor of 50. Higher preconcentrations led to a deterioration of the chromatographic resolution due to high background noise. With the preconcentration by a factor 50 a detection limit of 0.6 ppb was achieved for a 100 mL sample. The blank of the ice decontamination procedure was below detection limit.

3.6. Ions Including Monocarboxylic and Dicarboxylic Acids

[24] Ions were quantified with a Dionex DX600 chromatograph equipped with an AS11 separator column and a gradient pump system permitting the use of a quaternary gradient of eluents (H_2O, NaOH at 2.5 and 100 mM, and CH_3OH) as detailed by *Ricard et al.* [2002]. These working conditions allow the determination of inorganic species such as sulfate and nitrate in addition to short-chain carboxylates. Determined monocarboxylates here include formate ($HCOO^-$), lactate ($CH_3CHOHCOO^-$), acetate (CH_3COO^-), glycolate (CH_2OHCOO^-), propionate ($CH_3CH_2COO^-$), and glyoxylate ($CHOCOO^-$). Investigated dicarboxylates are oxalate ($^-OOCCOO^-$), malate ($^-OOCCH_2CHOHCOO^-$), malonate ($^-OOCCH_2COO^-$), succinate ($^-OOC(CH_2)_2COO^-$), and glutarate ($^-OOC(CH_2)_3COO^-$). Detection limits are close to 0.1 ppb for all carboxylates with the exception of malonate for which the detection limit is higher (0.5 to 1 ppb). The blank of the ice decontamination procedure was 0.5 ppb for formate and acetate, 0.4 ppb for propionate, 0.2 ppb for glutarate and oxalate. For other carboxylates blank were below the detection limits. The detection limits for major ions like nitrate and sulfate are close to 1 ppb.

3.7. Formaldehyde

[25] HCHO was measured by a fluorimetric method based on the liquid phase reaction of formaldehyde with acetylacetone and CH_3COONH_4-CH_3COOH mixture (Hantzsch reagent). The produced dimethyl-diacetyl-pyridine is excited at 400 nm and the fluorescence is detected at 510 nm. The analyzer (Aerolaser AL4011/21) has a detection limit of 0.1 ppb. Blank values of the decontamination procedure were below 1 ppb. The comparison of HCHO levels measured in near surface CDD snow layers collected under clean conditions directly in Schott bottles, and in firn cores stored frozen in sealed polyethylene bags for more than 5 years, indicates that the firn material had been severely contaminated (up to 10–20 ppb depending of the storage time) by the polyethylene bags. Therefore no HCHO data are available on investigated firn core sections.

4. Presentation of Discussions

[26] The major aim of this work is to investigate in what extent relevant information can be derived from the ice records of various carbonaceous fractions and species in view to investigate past atmospheric changes of carbonaceous aerosols. Therefore we first discuss the long-term ice record of EC, a water insoluble and rather inert species expected to be well preserved in snow and ice which is directly relevant to highlight past atmospheric changes of this water insoluble carbonaceous particle type.

[27] The extraction of the long-term trend of OC in ice core records is a challenge. Indeed, whereas past atmospheric WinOC can be investigated by examining filterable OC of melted ice samples, the dominant fraction of atmospheric OC (WSOC) cannot be directly investigated in ice. In a first step we will examine the ice records of (1) WinOC and one of its identified fraction (cellulose) and (2) identified species contributing to the WSOC fraction (short-chain dicarboxylic acids and HULIS). Then we will examine in what extent the amount of DOC present in ice, which is related to WSOC aerosol as well as to organic gases which have been solubilized in the precipitation, can be used to derive the long-term trend of the WSOC aerosol fraction preserved in ice cores. This requires the knowledge of the contribution of organic gases to the DOC level in ice what will be discussed on the basis of the ice core records of HCHO and light monocarboxylic acids. Whereas it is likely that similarly to EC WinOC is well preserved in snow and ice, more questionable is the preservation quality of the WSOC aerosol fraction since it cannot be excluded that some WSOC species may be exchanged between the snowpack and the atmosphere. Therefore, to avoid a mis-

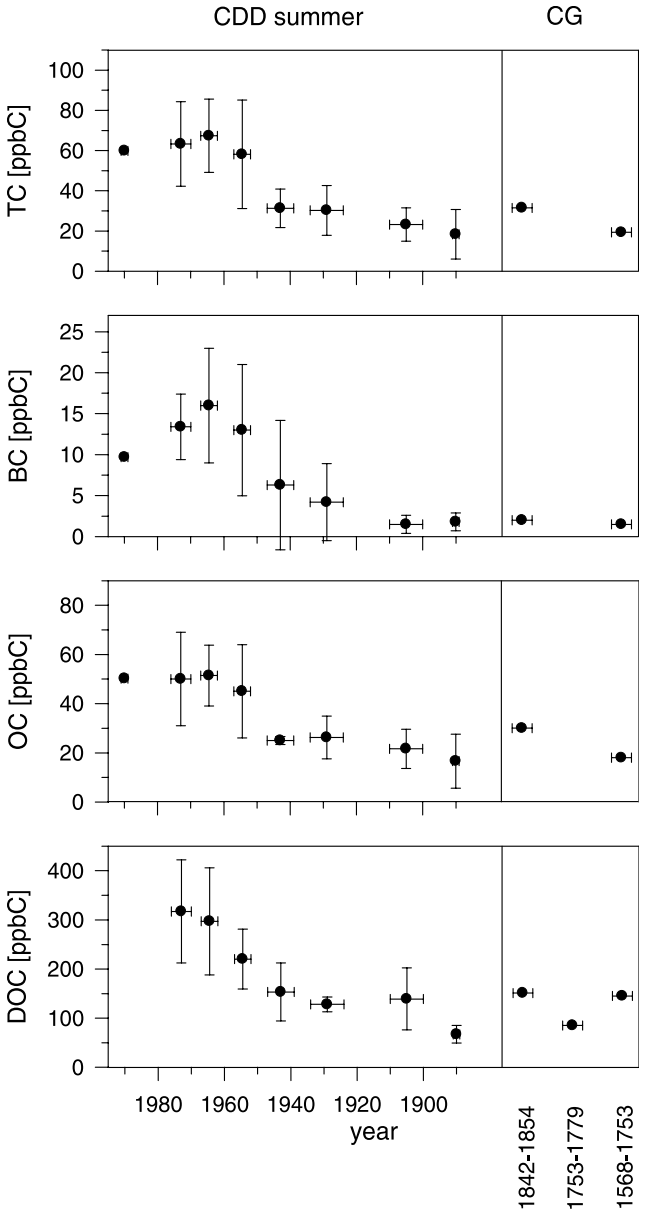

Figure 2. Temporal changes of concentrations of water insoluble carbonaceous material (TC), its two fractions (EC and WinOC), and dissolved organic carbon (DOC) in summer layers at CDD and CG. Vertical bars of circles refer to the standard deviations related to sample content variability, and horizontal bars refer to the covered time periods.

leading interpretation caused by possible processes taking place in snow and firn, the discussion of the long-term trend of organic carbon was restricted to the time period documented by ice only (from 1970 back to late 16th century). In the following the reader has to keep in mind that the OC ice record only refers to OC that was preserved in ice.

[28] Note that the ice records of monocarboxylic acids and HCHO, which are very volatile species, are quite complex because of possible postdepositional effects, past changing pH of precipitation, etc. Thus the interpretation of these records in terms of past atmospheric changes is a difficult task and is out of scope of this paper. The reader can find more details on these difficulties in the work by *Legrand et al.* [2003] for the records of formic and acetic acids in Alpine ice cores and in the work by *Hutterli et al.* [2003] for the one of HCHO. In our study these volatile species were only investigated to evaluate their contribution to the DOC level of ice.

5. EC Record

[29] The summer CDD trend of EC shows unchanged levels (1.6 ± 0.2 ppbC) from the end of the 16th century to 1910 (Figure 2). After World War II levels were rapidly enhanced up to 16 ± 7 ppbC in 1962–1967 and subsequently started to decrease again.

[30] *Lavanchy et al.* [1999] investigated EC in an Alpine ice core extracted at CG covering the 1755–1982 time period. Their EC values (42 ± 22 ppbC from 1890 to 1949 and 72 ± 35 ppbC from 1950 to 1975) are far higher than those at CDD. The thermal method used by *Lavanchy et al.* [1999] to determine EC totally differs from the thermal-optical method deployed here in separating EC and OC (see for this purpose *Schmid et al.* [2001] for intercomparison of various measurements methods), and does not account for pyrolytic conversion of OC to EC. The thermal method therefore may give higher EC values than our own method which evaluates the interference between pyrolyzed carbon and EC by continuous monitoring of the blackening of filter. However, it is unlikely that such a large difference between CG and CDD data is only related to the two different deployed methodologies. An alternative possibility is that higher EC emissions impact CG compared to CDD. This possibility is supported by model simulations made by *Fagerli et al.* [2007] showing that, whereas similar atmospheric levels of sulfate are simulated at the two Alpine sites, in agreement with ice core data [*Preunkert et al.*, 2000], the present-day level of EC is 5 times higher at CG than at CDD, because of the proximity of CG to the large EC emissions from the area of Milan in Italy.

[31] At the scale of Europe, *Fagerli et al.* [2007] estimated that annual EC emissions have increased by 50%, from 650 Gg in 1920 to over 1400 Gg in the 1970s, decreasing again to 950 Gg in 1985. Such moderate changes in annual EC emissions over the 20th century are due to a sharp decrease of coal burning use in the residential sector after 1960 accompanied by a fast increase of liquid fuel consumption at the same time. However, these past changes in total annual EC emissions are not directly relevant to discuss the long-term CDD summer trend since road traffic emits at a rather similar rate throughout the year whereas the residential sector emissions are much stronger in winter.

[32] On the basis of their estimates of past emission inventories *Fagerli et al.* [2007] simulated for summer at CDD rather unchanged EC atmospheric levels from 1920 to 1950 followed by a marked increase (around a factor of 3) up to 1970, and declining thereafter to become in 1985 twice as high than they were in 1920. These summer changes are mainly driven by enhanced road traffic emissions after 1950, combined with a decrease in the emission factor (assumed to decrease from 1965 to 1985). It was observed that the results are very sensitive to assumptions made on past emission factors from road traffic emissions. For instance, if the emission factors from road transport

from 1985 backward were considered constant in time, no peak in emissions or concentrations was seen around 1970. However, changes with variable emission factors are in far better agreement with summer CDD ice core data showing an increase by a factor of 3 from 1925–1936 to the second part of the 20th century and a recent decrease (Figure 2).

[33] The simulated change of winter concentrations at CDD strongly differs from the summer one with a weaker increase (less than a factor of 2 from 1920 to 1970) and an almost identical value in 1985 with respect to 1920 [*Fagerli et al.*, 2007]. That results from decreasing emissions from residential sector which counterbalanced the increase of road transport emissions in the recent decades. Although available winter EC ice core data are very limited, they are consistent with these simulations. Indeed, though the 1937–1939 level may be slightly overestimated (see section 2), no change of EC is seen between 1937–1939 and 1982–1984, while the 1973–1976 level is the highest observed over the 4 investigated time periods (Table 2).

[34] In conclusion, the long-term changes of EC in CDD ice cores are in agreement with model simulations done by assuming that road transport emission factors have decreased significantly between 1965 and 1985. The dominance of fuel combustion sources in EC emissions is also consistent with aerosol source apportionment made within CARBOSOL for present-day aerosol. In this latter study it was shown that at present-day at Sonnblick the fraction of EC related to fossil fuel is almost 20 times higher than that of biomass burning in summer [*Gelencsér et al.*, 2007]. Note however that preceding model simulations have not considered a possible change of atmospheric lifetime of EC particles from the first to the second part of the century because of the fact that EC particles emitted by coal burning have a totally different morphology compared to those emitted by diesel powered engines [*Bond et al.*, 2002].

6. WinOC and Cellulose Records

[35] With an unchanged level (21 ± 4 ppbC) from the end of the 16th century to prior World War II, and an increase hereafter by a factor of 2 to 3, the summer trend of water insoluble OC (Figure 2) shows a far less dramatic change than the EC trend. Whatever the ice samples, during analysis 80% of OC evolves at temperatures between 150°C and 600°C under N_2 and the contribution of pyrolytic carbon was low (less than 10%). Such a difference in the nature of WinOC of ice samples with respect to that of atmospheric OC aerosol, where pyrolytic carbon (PC) represents a large fraction (30% of OC at Sonnblick [*Pio et al.*, 2007]), is simply due to the fact that during filtration of melted ice sample polar oxygenated species constituting the PC fraction were removed because of their high water solubility. In return such an absence of pyrolytic PC in filtered ice samples suggests that interference of charring on EC determination was weak.

[36] As for EC, the WinOC levels in CDD ice are far lower than those obtained at CG by *Lavanchy et al.* [1999] (180 ± 110 ppbC from 1890 to 1949 and 290 ± 105 ppbC from 1950 to 1975). In contrast to the case of EC the discrepancy for WinOC between CDD and CG data cannot be explained by the different method deployed for the two data sets. A larger impact of the Milan region emissions, as argued for EC, is a possibility. However, the CG values are also far higher than those recently obtained in ice from the Fiescherhorn glacier (3900 m asl, Switzerland) (36 ppbC from 1900 to 1940 [*Jenk et al.*, 2006]), ever considering that these latest values are, in contrast to CG ones, related to winter and summer snow deposition. Instead of melting ice into glass vial, the ice core sections from CG were melted in polyethylene bags and that may be one cause for the unexpectedly high values of WinOC derived from the CG study.

[37] In the following we examine in what extent CDD summer data are consistent with aerosol observations done in the framework of the CARBOSOL project. As reported by *Legrand et al.* [2007], the typical present-day atmospheric level of organic carbon (OC) in summer aerosol at the CDD site is close to 250 ngC m^{-3} STP. Relevant to the discussion here is the filterable fraction of OC. At the high-elevation site of Sonnblick measurements indicate that 40% of OC is water insoluble in summer [*Pio et al.*, 2007]. Assuming a similar partitioning between water soluble and insoluble OC at CDD we may expect ~100 ngC m^{-3} of WinOC in summer at this site. *Preunkert et al.* [2002] found for summer at the CDD site that atmospheric sulfate levels of 800 ng m^{-3} STP in summer correspond to 650 ppb in corresponding snow layers. If a similar firn-air relationship is assumed for WinOC we would expect a WinOC level close to 80 ppbC in CDD summer snow. This is likely an overestimation since WinOC would be less efficiently scavenged than sulfate by clouds. For instance the scavenging efficiencies of water soluble plus water insoluble carbonaceous material was found to be some 60% weaker than the one of sulfate at Sonnblick [*Hitzenberger et al.*, 2000]. Therefore the level of WinOC in recent CDD snow deposit of 50 ppbC is consistent with atmospheric observations done at high-elevation sites in the Alps.

[38] The weaker increase of WinOC with respect to EC over the 20th century in CDD summer ice layers (Figure 2) is consistent with the finding from *Jenk et al.* [2006]. On the basis of the fraction of modern carbon derived from ^{14}C analysis, it was shown in this later study that WinOC in ice was less impacted than EC by combustion of fossil fuels at the Fiescherhorn glacier in 1950. Finally, concerning the differences between the summer and winter trends, we observed that similarly to what was found for EC, past changes of WinOC in CDD ice are far less pronounced in winter than in summer (Table 2).

[39] Cellulose constitutes one chemically identified component of WinOC. Mean mass concentrations of free cellulose range from 8 ± 5 ppb prior World War II to 12 ± 8 ppb after 1950 in summer CDD snow layers. This absence of detectable long-term trend is expected since cellulose is a major biopolymer emitted in the atmosphere by leaves from spring to fall [*Sánchez-Ochoa et al.*, 2007]. On a carbon mass basis, total cellulose represents on average ~20% of the WinOC (Table 3).

7. Diacids and HULIS Records

[40] C2–C5 diacids represent together a significant contribution to the DOC level of ice which however never exceeds 10% (Table 3). Whereas the sum of C2–C5 diacids is enhanced from 23 ± 6 ppb prior to World War II to

Table 3. Concentration of DOC and of Its Identified Aerosol Components (C2–C5 Diacids and HULIS) and Water Insoluble Organic Carbon and of Its Identified Aerosol Component (Total Cellulose) in the Different Summer Ice Layers[a]

Time Period	DOC, ppbC	Total Diacid-C, ppbC	WinOC, ppbC	Total Cellulose-C, ppbC	HULIS, ppb
1989–1991	ND	20 ± 10	50	···	860 ± 90
1970–1976	317 ± 106	22 ± 11	50 ± 19	3	310 ± 100
1962–1967	272 ± 84	22 ± 12	51 ± 12	10 ± 6	330 ± 50
1952–1957	220 ± 61	20 ± 11	45 ± 19	10 ± 4	183 ± 47
1939–1947	153 ± 59	15 ± 7	25 ± 2	9	510 ± 90
1925–1936	128 ± 15	9 ± 2	26 ± 9	7	139 ± 16
1906–1911	150 ± 72	5 ± 2	18 ± 4	3	130 ± 10
Prior 1850	127 ± 40	10 ± 2	24 ± 9	···	110 ± 90

[a] Standard deviations refer to sample content variabilities. The contribution of HULIS to DOC on a mass carbon basis is highly uncertain (see section 3) and not reported. ND, not determined in this porous firn material (see section 3).

60 ± 4 ppb after 1950, large differences appear when individual diacids are considered (Figure 3). For instance the trend of C3 to C5 diacids is quite large (from a factor of 4 for glutaric and succinic to a factor 10 for malic and malonic) whereas, if exists, the long-term trend of oxalic acid is weaker. On the basis of the present-day climatology of diacids gained at the CARBOSOL sites, *Legrand et al.* [2007] concluded that in summer glutaric, succinic, malic, and malonic acids probably arise mainly from the ozonolysis of biogenic species emitted by vegetation (unsaturated fatty acids, oxygenated volatile organic compounds, and eventually monoterpenes). The long-term trend of these species revealed in summer ice cores is thus a good example of the effect of the enhanced level of ozone in producing more secondary organic aerosols after World War II (see further discussions in section 8). Concerning oxalic acid, *Legrand et al.* [2007] concluded that, in addition to the oxidation of malonic acid, isoprene would be the main precursor of glyoxylic acid thereafter oxidized in the aqueous phase by OH into oxalic acid. The aqueous phase oxidation of glyoxylic acid into oxalic acid is less efficient at low pH because the rate constant of the reaction of glyoxylic acid with OH is an order of magnitude lower than that of glyoxylate [*Ervens et al.*, 2004; *Sorooshian et al.*, 2006]. Thus the absence of significant trend of oxalic acid (Figure 3), may be due to the large acidification of precipitation having occurred over the last decades.

[41] Summer mass concentrations of HULIS in CDD snow deposits are generally below 150 ppb prior to World War II whereas they tend to be higher (from 200 to 800 ppb) after 1945 (Table 3). Whereas the large presence of HULIS in winter aerosol in Europe can be clearly attributed to wood burning, their origin in summer is more unclear and it is suggested that there are secondarily produced [*Lukács et al.*, 2007]. The precursors that yield HULIS in summer are currently not yet known, but aqueous phase reactions of H_2O_2 or O_3 with soot, isoprene, carbonyl compounds, aromatics, or lignin pyrolysis products have recently been pointed out. If correct, there are many causes that can lead to enhanced summer levels of HULIS after 1940. First, the growing emissions of anthropogenic precursors like soot, carbonyl compounds or aromatics over the last decades may be the cause of the enhancement of HULIS. Second, even if the biogenic isoprene species is assumed to be the main precursor of HULIS, the more efficient secondary production in response to increased concentrations of atmospheric oxidants, in particular over the last decades, may also explain the trend of HULIS. However, since the chemical

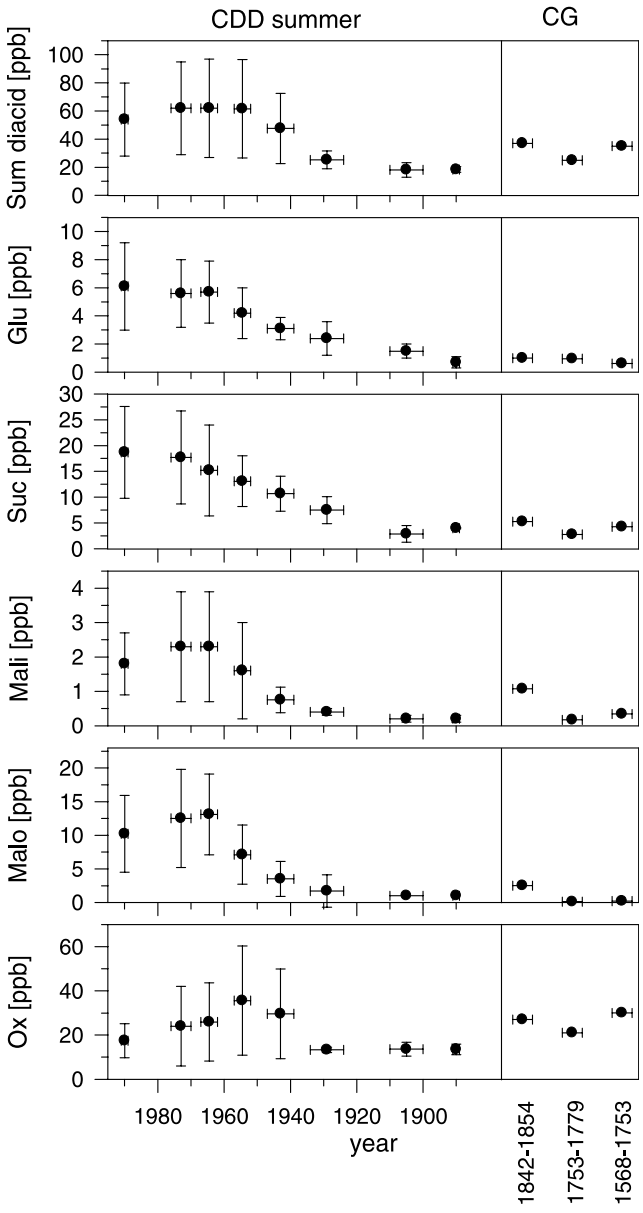

Figure 3. Temporal changes of total C2–C5 diacids and of individual diacids in summer layers at CDD and CG. Glu, glutaric; Suc, succinic; Mali, malic; Malo, malonic; and Ox, oxalic acid. Vertical bars of circles refer to the standard deviations related to sample content variability, and horizontal bars refer to the covered time periods.

and physical properties of HULIS may have changed over the past, which in turn may affect their specific UV-VIS absorptions and thus derived concentrations, further work is here needed before drawing sound conclusions.

[42] In contrast to most species for which levels are generally lower in winter than in summer, HULIS stand out with winter levels which remain in the order of magnitude (310 ± 170 ppb, not shown) of the summer ones (Table 3). That is consistent with the very pronounced seasonal cycle of HULIS seen at surface sites in Europe, with levels more than 4 times higher in winter than in summer (compared to 1.3 for sulfate) at the rural K-Puszta site in Hungary, for instance [*Pio et al.*, 2007].

[43] Considering the factor of 0.5 to convert HULIS mass in carbon mass and assuming that the uncertainty in measuring HULIS in modern aerosol samples, a factor of 2 (section 3.2), remains similar for recent snow deposits, it can be concluded from Table 3 that HULIS represent a major contribution to DOC at least for recent time (from 33% to 65% over the 1970–1976 time period, for instance). The contribution of HULIS to DOC becomes more uncertain in snow deposited prior 1940 because of possible change of chemical and physical properties of HULIS leading to uncertainties of analysis possibly higher than a factor of two.

8. DOC and Its Identified Chemical Components in Ice Cores: Can We Use DOC as a Proxy of WSOC Preserved in Ice?

[44] As seen in Figure 2, DOC concentrations in summer ice remain close to 120 ± 35 ppbC prior to World War II and reached values close to 300 ppbC in the 1970s. All together carboxylic acids represent a significant part (32 ± 7%) of DOC. The contribution of monocarboxylic acids dominates (25 ± 7% of DOC) that of dicarboxylic acids (less than 10%, Table 3). Formic acid alone represents a half of the monocarboxylic acid contribution, and succinic together with oxalic acid account for the main contribution of diacids to DOC. The contribution of these species to DOC in summer CDD ice is relatively large compared to what is generally seen in precipitation at lower-elevation sites. For example in cloud water samples monocarboxylates and dicarboxylates account together for 10% of DOC at Puy de Dome (1465 m elevation, center of France) [*Marinoni et al.*, 2004] and at Mount Rax (70 km southwest of Vienna, Austria) [*Löflund et al.*, 2002]. In precipitations collected during the CARBOSOL project at the K-Puszta site (Hungarian plain) we also found that monocarboxylates and dicarboxylates account together for 10% of DOC. *Legrand et al.* [2007] showed that the atmospheric abundance of C-diacids relative to WSOC aerosol increases from 4% at surface continental sites to 12% at the Vallot Observatory in summer. In addition, gas phase samplings achieved at this site in summer 2004 indicate a mixing ratio of formic acid which is close to 0.3 ppbv [*Preunkert et al.*, 2007]. Compared to 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 to ~150 ng m^{-3} STP at Vallot [*Legrand et al.*, 2007]). Thus the weaker decrease with elevation of both diacid aerosols and gaseous HCOOH with respect to the WSOC aerosol may account for the relatively high contribution of carboxylic acids to DOC at CDD compared to precipitation at lower-elevation sites.

[45] Because of their polar character, short-chain carbonyl compounds (aldehydes and ketones) present in the gas phase can also be incorporated in snow and ice and contribute to the DOC level in ice. With a mean level in CDD ice close to 4 ppb prior 1940 and 14 ppb after World War II (not shown), HCHO represents a minor part of DOC (less than 2%). A few measurements of some other carbonyl compounds including acetaldehyde, propionaldehyde and acetone were achieved in CDD surface snow as well as in ice covering the 1940s [*Houdier et al.*, 2000]. Only acetaldehyde was detected at a significant level (~4 ppb). From that it can be concluded that aldehydes and ketones do not significantly contribute to the DOC load of alpine ice. Methanol, the most abundant alcohol present in the atmospheric gas phase, may also contribute to the DOC level of precipitation. Though, investigation of methanol in atmospheric condensates are very rare, the study from *Snider and Dawson* [1985] suggested that the contribution of methanol to DOC in precipitation is low. Within this study, only 22 ppb of methanol compared to 220 ppb of HCHO and 66 ppb of acetaldehyde were observed in rain collected at the Santa Rita mountain (1300 m elevation) in a rural area of southwestern United States.

[46] With the aim to estimate the long-term change of OC aerosol preserved in summer ice, we calculated the DOC fraction in ice from which the identified part of organics related to gas solubilization in precipitation was subtracted. Thereby we have assumed that most of these gases have been identified by investigating monocarboxylic acids and HCHO. The remaining fraction of DOC ([DOC]-[Monocarboxylic-C]) would be related to WSOC aerosol preserved in ice. This estimate of WSOC aerosol preserved in ice can be examined in the light of aerosol data gained for the present-day atmosphere during the CARBOSOL project. *Pio et al.* [2007] observed 1.5 to 2 times more WSOC than WinOC in the European continental atmosphere, and if we assume a scavenging efficiency by cloud 2 times higher for WSOC than for WinOC, a crude estimate of WSOC aerosol trapped in ice would be obtained by multiplying the measured WinOC in ice by a factor of 4. As seen in Table 4 the two independent estimates of the fraction of DOC in ice related to atmospheric WSOC provide consistent values whatever the time period considered. Adding the fraction of DOC in ice attributed to WSOC aerosol to the WinOC ice level, we get a crude estimate of total OC related to aerosol preserved in ice. From that, we observed that the change from prior World War II to the 1950–1970s is an increase by a factor of 2 (from 115 ± 37 to 256 ± 50 ppbC), mainly caused by the increase of WSOC (Table 4).

[47] Finally we try to evaluate the part of OC present in ice which is related to secondary aerosol production. Since EC present in summer CDD ice mainly comes from fossil fuel combustion (section 5) we can estimate the corresponding amount of OC primarily emitted by this source. Using the factor of 0.58 proposed by *Gelencsér et al.* [2007] for the present-day OC to EC ratio of fossil fuel emissions, and assuming a scavenging efficiency 2 times

Table 4. Concentration Changes in Summer Ice Layers: DOC, Monocarboxylic-C Acids, Estimates of the DOC Fraction Related to WSOC Aerosol Preserved in Ice Obtained by Subtracting the Contribution of Monocarboxylic Acids to Total DOC, Four Times the WinOC Level, and an Estimate of OC Preserved in Ice Calculated as the Sum of WinOC and DOC Related to WSOC[a]

Time Period	DOC	Monocarboxylic-C	DOC Related to WSOC Aerosol	Four Times WinOC	Estimated OC
1970–1976	317	61	256	200	306
1962–1967	272	64	208	202	259
1952–1957	220	61	159	180	204
1939–1947	153	39	114	100	139
1925–1936	128	39	89	105	115
1906–1911	150	23	127	72	145
Prior 1850	127	25	102	96	126

[a] All values are in ppbC.

higher for OC than for EC, the increase of EC from 2 to 15 ppb from the first to the second part of the 20th century would have led to a corresponding change of OC related to primary fossil fuel emission of ~15 ppb (Table 5). It is however likely an overestimation since the OC/EC ratio was likely higher back in time as a result of older technology (i.e., lower temperature for combustion). It therefore clearly appears that, in contrast to EC, primary emissions of OC related to fossil fuel burning are not accounting very much for past OC changes in ice cores. Another part of primary OC aerosol would come from biomass burning. These emissions, although poorly documented are thought to be rather unchanged over the course of the 20th century. The lack of accurate statistic on biomass burning over the past motivates the investigation of wood burning tracers such as levoglucosan. Unfortunately, all investigated ice samples were found to contain levoglucosan levels which are lower than the detection limit (1 ppb). Thus we have here assumed that OC related to biomass burning is two times less abundant than OC related to fuel burning as concluded from source apportionment made for present-day summer aerosol at Sonnblick [*Gelencsér et al.*, 2007]. Assuming that this amount of primary OC from biomass burning remained unchanged over the past, and neglecting biogenic primary OC on the basis of cellulose data (section 6), it appears that secondary OC preserved in ice has increased by more than a factor of 2 from the first to the second part of the 20th century. Since it was shown that secondary organic atmospheric aerosol at Sonnblick in summer mainly originates from non fossil fuel precursors [*Gelencsér et al.*, 2007], it may be concluded that the past change of OC preserved in ice is related to change of secondary production from biogenic precursors. That is consistent with model simulations made by *Kanakidou et al.* [2000] who suggested that the changed oxidative capacity of the atmosphere has enhanced the production of organic aerosol (mainly from biogenic emissions) by a factor of 2 to 4 over the 20th century.

9. Conclusions

[48] This work represents the first attempt to analyze an extended array of carbonaceous species including elemental carbon, water insoluble organic carbon as well as dissolved organic carbon, humic-like substances, and single organic compounds like carboxylic acids, levoglucosan, and cellulose in Alpine ice cores.

[49] Among carbonaceous components, EC reveals an outstanding increase in Alpine ice cores with a sharp increase (a factor of 6) after World War II in summer. This observation is fairly consistent with historical emission inventories of EC established at the scale of Europe during the CARBOSOL project if it is assumed that emission factors from road transport have increased backward from 1985 to 1965.

[50] The reconstruction of past changes of OC preserved in ice was a challenge since only the water insoluble organic carbon fraction is measured in ice, and, conversely, the DOC content of ice accounts for water soluble organic aerosol as well as water soluble organic gases. In spite of these difficulties, we demonstrated that the DOC ice record together with the ones of light carboxylates and WinOC allows to reconstruct past OC changes with a rather good degree of confidence. It is suggested that the level of OC preserved in ice has been enhanced by a factor of 2 after World War II, possibly related to due the enhanced oxida-

Table 5. Summer Ice Levels of Estimated OC Preserved in Ice (see Table 4), Measured EC, Estimated Fractions of OC Related to Fossil Fuel (OC_{FF}) and Biomass Burning (OC_{BB}) (See Section 8), and Estimated Levels of Secondary Organic Carbon Aerosol Preserved in Ice[a]

Time Period	Estimated OC	EC	Primary OC_{FF}	Primary OC_{BB}	Secondary OC
1970–1976	306	13.4	16	~8	282
1962–1967	259	16	19	~8	232
1952–1957	204	13	15	~8	181
1939–1947	139	6.3	7	~8	124
1925–1936	115	4.2	5	~8	109
1906–1911	145	1.5	2	~8	135
Prior 1850	126	1.5	2	~8	116

[a] All values are in ppbC.

tive capacity of the atmosphere which had led to an enhanced production of secondary organic aerosol.

[51] Inherent to their analyses, HULIS data have large uncertainties but definitely their levels indicate that these water soluble organic aerosols contribute far more to the OC content of ice cores than dicarboxylic acids. Further work is here clearly needed to conclude if the HULIS levels have changed or not over the past.

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References

Andreae, M. O., C. D. Jones, and P. M. Cox (2005), Strong present-day aerosol cooling implies a hot future, *Nature*, *435*, 1187–1190.

Bond, T. C., D. S. Covert, J. C. Kramlich, T. V. Larson, and R. J. Charlson (2002), Primary particle emissions from residential coal burning: Optical properties and size distributions, *J. Geophys. Res.*, *107*(D21), 8347, doi:10.1029/2001JD000571.

Cachier, H., and M. H. Pertuisot (1994), Particulate carbon in Arctic ice, *Analusis*, *22*, M34–M37.

Cooke, W. F., and J. J. N. Wilson (1996), A global black carbon aerosol model, *J. Geophys. Res.*, *101*, 19,395–19,409.

Dentener, F., et al. (2006), Emissions of primary aerosol and precursor gases in the year 2000 and 1750-prescribed data-sets for aeroCom, *Atmos. Chem. Phys. Disc.*, *6*, 2703–2763.

Donahue, N., K. Hartz, B. Chuong, A. Presto, C. Stanier, T. Rosenhorn, A. Robinson, and S. Pandis (2005), Critical factors determining the variation in SOA yields from terpene ozonolysis: A combined experimental and computational study, *Faraday Disc.*, *130*, 295–309.

Ervens, B., G. Feingold, G. J. Frost, and S. M. Kreidenweis (2004), A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production, *J. Geophys. Res.*, *109*, D15205, doi:10.1029/2003JD004387.

Fagerli, H., M. Legrand, S. Preunkert, D. Simpson, V. Vestreng, and M. Cerqueira (2007), Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps, *J. Geophys. Res.*, doi:10.1029/2006JD008044, in press.

Fuzzi, S., et al. (2006), Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, *Atmos. Chem. Phys.*, *6*, 2017–2038.

Gelencsér, A., B. May, D. Simpson, A. Sánchez-Ochoa, A. Kasper-Giebl, H. Puxbaum, A. Caseiro, C. Pio, and M. Legrand (2007), Source apportionment of PM2.5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin, *J. Geophys. Res.*, doi:10.1029/2006JD008094, in press.

Hitzenberger, R., A. Berner, R. Kromp, A. Kasper-Giebl, A. Limbeck, W. Tscherwenka, and H. Puxbaum (2000), Black carbon and other species at a high-elevation European site (Mount Sonnblick, 3106 m, Austria): Concentrations and scavenging efficiencies, *J. Geophys. Res.*, *105*, 24,637–24,645.

Houdier, S., S. Perrier, E. Defrancq, and M. Legrand (2000), A new fluorescent probe for sensitive detection of carbonyl compounds: Sensitivity improvement and application to environmental natural waters, *Anal. Chem. Acta*, *412*, 221–233.

Hutterli, M., J. R. McConnell, R. Bales, and R. Steward (2003), Sensitivity of hydrogen peroxide (H_2O_2) and formaldehyde (HCHO) preservation in snow to changing environmental conditions: Implications for ice core records, *J. Geophys. Res.*, *108*(D1), 4023, doi:10.1029/2002JD002528.

Jenk, T. M., S. Szidat, M. Schwikowski, H. W. Gäggeler, S. Brütsch, L. Wacker, H. A. Synal, and M. Saurer (2006), Radiocarbon analysis in an Alpine ice: Record of anthropogenic and biogenic contributions to carbonaceous aerosols in the past (1650–1940), *Atmos. Chem. Phys.*, *6*, 5381–5390.

Kanakidou, M., K. Tsigaridis, F. J. Dentener, and P. J. Crutzen (2000), Human-activity-enhanced formation of organic aerosols by biogenic hydrocarbon oxidation, *J. Geophys. Res.*, *105*(D7), 9243–9254.

Kiss, G., B. Varga, I. Galambos, and I. Ganszky (2002), Characterization of water-soluble organic matter isolated from atmospheric fine aerosol, *J. Geophys. Res.*, *107*(D21), 8339, doi:10.1029/2001JD000603.

Lavanchy, V. M. H., H. W. Gäggeler, U. Schotterer, M. Schwikowski, and U. Baltensperger (1999), Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland), *J. Geophys. Res.*, *104*, 21,227–21,236.

Legrand, M., and H. Puxbaum (2007), Summary of the CARBOSOL project: Present and retrospective state of organic versus inorganic aerosol over Europe, *J. Geophys. Res.*, doi:10.1029/2006JD008271, in press.

Legrand, M., S. Preunkert, D. Wagenbach, H. Cachier, and H. Puxbaum (2003), A historical record of formate and acetate from a high elevation Alpine glacier: Implications for their natural versus anthropogenic budgets at the European scale, *J. Geophys. Res.*, *108*(D24), 4788, doi:10.1029/2003JD003594.

Legrand, M., S. Preunkert, T. Oliveira, C. A. Pio, S. Hammer, A. Gelencsér, A. Kasper-Giebl, and P. Laj (2007), Origin of C_2–C_5 dicarboxylic acids in the European atmosphere inferred from year-round aerosol study conducted at a west-east transect, *J. Geophys. Res.*, doi:10.1029/2006JD008019, in press.

Liousse, C., J. E. Penner, C. C. Chuang, J. J. Walton, and H. Edelman (1996), A global three-dimensional model study of carbonaceous aerosols, *J. Geophys. Res.*, *101*, 19,411–19,432.

Löflund, M., A. Kasper-Giebl, B. Schuster, H. Giebl, R. Hitzenberger, and H. Puxbaum (2002), Formic, acetic, oxalic, malonic and succinic concentrations and their contribution to organic carbon in cloud water, *Atmos. Environ.*, *36*, 1553–1558.

Lukács, H., A. Gelencsér, H. Puxbaum, C. Pio, M. Legrand, A. Kasper-Giebl, M. Handler, A. Limbeck, D. Simpson, and S. Preunkert (2007), Seasonal trends and possible sources of brown carbon based on 2-year aerosol measurements at six sites in Europe, *J. Geophys. Res.*, doi:10.1029/2006JD008151, in press.

Marinoni, A., P. Laj, K. Sellegri, and G. Mailhot (2004), Cloud chemistry at Puy de Dôme: Variability and relationships with environmental factors, *Atmos. Chem. Phys.*, *4*, 715–728.

Novakov, T., V. Ramanathan, J. E. Hansen, T. W. Kirchstetter, M. Sato, J. E. Sinton, and J. A. Sathaye (2003), Large historical changes of fossil-fuel black carbon aerosols, *Geophys. Res. Lett.*, *30*(6), 1324, doi:10.1029/2002GL016345.

Pio, C., et al. (2007), Climatology of aerosol composition (organic versus inorganic) at non-urban areas on a west-east transect across Europe, *J. Geophys. Res.*, doi:10.1029/2006JD008038, in press.

Preunkert, S., D. Wagenbach, M. Legrand, and C. Vincent (2000), Col du Dôme (Mt Blanc Massif, French Alps) suitability for ice core studies in relation with past atmospheric chemistry over Europe, *Tellus*, *59*, 993–1012.

Preunkert, S., M. Legrand, and D. Wagenbach (2001), Sulfate trends in a Col du Dôme (French Alps) ice core: A record of anthropogenic sulfate levels in the European mid-troposphere over the 20th century, *J. Geophys. Res.*, *106*, 31,991–32,004.

Preunkert, S., D. Wagenbach, and M. Legrand (2002), Improvement and characterization of an automatic aerosol sampler at high-Alpine drilling sites, *Atmos. Environ.*, *36*, 1221–1232.

Preunkert, S., D. Wagenbach, and M. Legrand (2003), A seasonally resolved Alpine ice core record of nitrate: Comparison with anthropogenic inventories and estimation of pre-industrial emissions of NO from Europe, *J. Geophys. Res.*, *108*(D21), 4681, doi:10.1029/2003JD003475.

Preunkert, S., M. Legrand, B. Jourdain, and I. Dombrowski-Etchevers (2007), Acidic gases (HCOOH, CH_3COOH, HNO_3, HCl, and SO_2) and related aerosols at a high Alpine site (4360 m elevation) in Europe, *J. Geophys. Res.*, doi:10.1029/2006JD008225, in press.

Puxbaum, H., and M. Tenze-Kunit (2003), Size distribution and seasonal variations of atmospheric cellulose, *Atmos. Environ.*, *37*, 3693–3699.

Puxbaum, H., C. Rosenberg, M. Gregori, C. Lanzerstorfer, E. Ober, and W. Winiwarter (1988), Atmospheric concentrations of formic and acetic acid and related compounds in eastern and northern Austria, *Atmos. Environ.*, *22*, 2841–2850.

Puxbaum, H., A. Caseiro, A. Sánchez-Ochoa, A. Kasper-Giebl, M. Claeys, A. Gelencsér, M. Legrand, S. Preunkert, and C. Pio (2007), Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background, *J. Geophys. Res.*, doi:10.1029/2006JD008114, in press.

Ricard, V., J.-L. Jaffrezo, V.-M. Kerminen, R. E. Hillamo, M. Sillanpaa, S. Ruellan, C. Liousse, and H. Cachier (2002), Two years of continuous aerosol measurements in northern Finland, *J. Geophys. Res.*, *107*(D11), 4129, doi:10.1029/2001JD000952.

Sánchez-Ochoa, A., A. Kasper-Giebl, H. Puxbaum, A. Gelencser, M. Legrand, C. Pio, and D. Wagenbach (2007), Concentration of atmospheric cellulose: A proxy for plant debris across a west-east transect over Europe, *J. Geophys. Res.*, doi:10.1029/2006JD008180, in press.

Schmid, H., et al. (2001), Results of the "carbon conference" international aerosol carbon round robin test stage I, *Atmos. Environ.*, *35*, 2111–2121.

Schock, M., S. Greilich, D. Wagenbach, S. Preunkert, M. Legrand, J. R. Petit, J. Flückiger, M. Leuenberger, W. Haeberli, and R. Psenner (2005), Dissolved organic carbon (DOC) in ice samples from non-temperate, polar and Alpine glaciers, *Geophys. Res. Abstr.*, *7*, 08671, SRef-ID:1607-7962/gra/EGU05-A-08671.

Snider, J., and G. A. Dawson (1985), Tropospheric light alcohols, carbonyls, and acetonitrile: Concentrations in the southwestern United States and Henry's law data, *J. Geophys. Res.*, *90*, 3797–3805.

Sorooshian, A., et al. (2006), Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation, *J. Geophys. Res.*, *111*, D23S45, 4681, doi:10.1029/2005JD006880.

Tsigaridis, K., and M. Kanakidou (2003), Global mopdelling of secondary organic aerosol in the troposphere: A sensitivity analysis, *Atmos. Chem. Phys.*, *3*, 1849–1869.

Varga, B., G. Kiss, I. Ganszky, A. Gelencsér, and Z. Krivácsy (2001), Isolation of water-soluble organic matter from atmospheric aerosol, *Talanta*, *55*(3), 561–572.

Wagenbach, D., K. O. Muennich, U. Schotterer, and H. Oeschger (1988), The anthropogenic impact on snow chemistry at Colle Gnifetti, Swiss Alps, *Ann. Glaciol.*, *10*, 183–187.

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