

Major 20th century changes of water-soluble humic-like substances (HULIS_{WS}) aerosol over Europe inferred from Alpine ice cores

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[1] Using a newly developed method dedicated to measurements of water-soluble humic-like substances (HULIS_{WS}) in atmospheric aerosol samples, the carbon mass quantification of HULIS_{WS} in an Alpine ice core is achieved for the first time. The method is based on the extraction of HULIS_{WS} with a weak anion-exchanger resin and the subsequent quantification of the extracted carbon fraction with a total organic carbon (TOC) analyzer. Measurements were performed along a Col du Dôme (4250 m above sea level, French Alps) ice core covering the 1920–2004 time period. The HULIS_{WS} concentrations exhibit a well-marked seasonal cycle with winter minima close to 7 ppbC and summer maxima ranging between 10 and 50 ppbC. Whereas the winter HULIS_{WS} concentrations remained unchanged over the twentieth century, the summer concentrations increased from 20 ppbC prior to the Second World War to 35 ppbC in the 1970–1990s. These different trends reflect the different types of HULIS_{WS} sources in winter and summer. HULIS_{WS} are mainly primarily emitted by domestic wood burning in winter and secondary in summer being produced from biogenic precursors. For unknown reason, the HULIS_{WS} signal is found to be unusual in ice samples corresponding to World War II.

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1. Introduction

[2] Several recent studies have shown that over continents organic aerosols represent an important part of total atmospheric aerosols with a mass contribution close to 50% (see Putaud *et al.* [2004] and Pio *et al.* [2007] for Europe). Being mainly submicronic and hygroscopic, the organic aerosol is expected to play an important role in the radiative properties of the atmosphere [Fuzzi *et al.*, 2006; Kanakidou *et al.*, 2005].

[3] Studies performed on the organic speciation assigned only a minor fraction of the organic carbon (OC) present in aerosol to individual organic compounds [Turpin *et al.*, 2000; Goldstein and Galbally, 2007]. However, a more significant fraction of OC may be present as oligomeric or polymeric matter. Aside from plant debris and fungal spores, the largest contribution to OC is from substances that have chemical and physical similarities with terrestrial and

aquatic humic and fulvic acids [Graber and Rudich, 2006, and references therein]. These substances, commonly named HULIS (humic-like substances), are oligomeric material with strong polar, poly-acidic, and chromophoric properties. They consist mainly of aromatic compounds that have aliphatic chains with carboxyl, hydroxyl, or carbonyl polar functional groups [Decesari *et al.*, 2000; Kiss *et al.*, 2002; Krivácsy *et al.*, 2000].

[4] HULIS can be divided in two major fractions based on their solubility in water. Until now the water-insoluble fraction did not get much attention except in the 2-year climatology obtained by Feczko *et al.* [2007] in western/central Europe for what these authors called the alkali soluble HULIS. The authors showed that water-soluble and alkali soluble HULIS are present in similar proportion at all sites (in the boundary layer as well as in the free troposphere) and that the total of HULIS accounts for 15% to 30% of OC. More extensively investigated, water-soluble HULIS (HULIS_{WS}) were found to represent a significant fraction of the water-soluble organic carbon (WSOC) mass with up to 20–50% in rural, urban, marine, and biomass-burning aerosol [see Baduel *et al.*, 2009, 2010 and references therein]. It has been shown that HULIS_{WS} might decrease the surface tension and affect the formation of cloud condensation nuclei [Facchini *et al.*, 2000; Kiss *et al.*, 2005]. HULIS_{WS} represent a light absorbing material [Dinar *et al.*, 2008; Hoffer *et al.*, 2004].

[5] The main source of HULIS_{WS} is biomass burning [Decesari *et al.*, 2006; Mayol-Bracero *et al.*, 2002]. Several

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recent studies pointed out residential wood burning as a possible major source of HULIS_{WS} during the winter season in Europe [Baduel et al., 2010; Feczko et al., 2007]. Secondary formation processes such as heterogeneous reaction of dienes on sulfuric acid clusters [Limbeck et al., 2003] or aerosol-phase polymerization of semivolatile oxidation products [Gelencsér et al., 2002; Kalberer et al., 2004] can lead to HULIS_{WS} formation. In summer, even though many secondary processes may contribute to the HULIS_{WS} level, it is not yet known in which proportion their precursors originate from anthropogenic and biogenic sources.

[6] The study of aerosols trapped in solid precipitation accumulated over the past on cold glaciers represents a unique and powerful way to reconstruct our changing atmosphere from the pre-industrial era to present-day (see [Legrand and Mayewski, 1997] for a review). In this way, the ice core record of HULIS_{WS} may contain powerful information on their origins, in particular on the respective contribution of anthropogenic versus biogenic sources. Investigations on the overall potential of Alpine ice cores to derive information on past carbonaceous aerosol components were done by [Legrand et al., 2007a]. With the objective to reconstruct the long-term trend of atmospheric OC over Europe, the authors analyzed an extended array of carbonaceous species including elemental carbon, water-insoluble organic carbon as well as dissolved organic carbon, single organic compounds such as carboxylic acids, and cellulose in Alpine ice cores. Some preliminary HULIS_{WS} measurements were also done, but no information about the carbon content of HULIS_{WS} was derived due to the analytical method used. It also needs to be emphasized that this pioneering study focused on ice layers corresponding to the summer season.

[7] The aim of our study is to obtain the first Alpine ice core record of HULIS_{WS} in terms of carbon content, as operationally defined by [Baduel et al., 2009]. Our measurements allow the recovery of seasonally resolved (winter and summer) long-term changes of HULIS_{WS}, a major contributor to atmospheric organic carbon. In this paper, results are discussed with respect to the atmospheric budget of HULIS_{WS} and its change over most of the past century at the scale of the free troposphere over Europe. In addition, the data set allows to extend the chemical documentation of the dissolved organic carbon (DOC) fraction present in ice, which until now was restricted to mono- and dicarboxylic acids [Legrand et al., 2013].

2. Experimental Part

2.1. Extraction of the HULIS_{WS} Fraction

[8] Several methods to extract HULIS are available and described in the literature. The two main methods used either a diethylaminoethyl resin (DEAE) or a C18 resin + a strong anion-exchanger (SAX) and were compared by [Baduel et al., 2009]. The advantages of the DEAE method include a simple isolation of HULIS_{WS} without pre-acidification and a high recovery. Its disadvantage lies in the high ionic strength solution used for the final HULIS_{WS} extraction that makes the HULIS_{WS} quantification less sensitive. We used here the method described by [Baduel et al., 2009], which was initially developed for HULIS measurements in atmospheric samples. First developed by [Havers et al., 1998], the method was modified by [Decesari et al.

[2000] in order to separate water-soluble organic carbon (WSOC) aerosol into three classes of compounds: neutral and basic compounds, mono- and dicarboxylic acids, and polyacids (HULIS_{WS}).

[9] Ice core samples are first decontaminated (see section 2.3), then melted and processed for HULIS_{WS} extraction following the procedure described by [Baduel et al., 2009]. The first step of this procedure is the concentration of HULIS_{WS} on a DEAE-Sepharose resin (GE Healthcare[®], HiTrap[™] DEAE FF, 0.7 cm ID × 2.5 cm length). The sample is injected at a flow rate of 1 mL min⁻¹ without any pretreatment. The DEAE-Sepharose resin is a weak anion-exchanger with diethylaminoethyl functional groups bounded to an agarose insoluble matrix. At pH lower than the pK_a value of 9.5, as commonly encountered in rain or melted ice samples, the diethylaminoethyl functional groups are mainly present in an acidic state (i.e., the resin is positive charged) and the strong negative polar species such as HULIS_{WS} are retained in the resin (Figure 1). To have enough HULIS_{WS} trapped on the resin for a reliable quantification of the HULIS_{WS}, the sample volume was chosen with regard to the determination of the dissolved organic carbon (DOC) content of the samples [Legrand et al., 2013]. Typical melted ice sample volume (after the ice decontamination step, see section 2.3) is between 60 to 140 mL for summer samples and up to 180 mL for winter samples, compared to 2.5 mL for aerosol extracts. This much higher sample volume results in a much longer concentration step, which lies between 1 and 4 h for ice samples against a few minutes for atmospheric samples, but concentrates HULIS carbon by a factor of 25 to 100 in the extract compared to the samples, thus allowing the determination of very low concentrations.

[10] The second step is the elution of organic compounds trapped in the resin. The elution program is run in three steps: the organic matter is first washed with organic free ultrapure water (Elga[®]) in order to remove neutral compounds and hydrophobic bases. Then, 9 mL of a solution of 0.04 M NaOH (J.T. Baker[®], pro analysis) are injected to remove mono- and dicarboxylic acids and some inorganic anions from the resin. Finally, the HULIS_{WS} fraction (polyacids) is eluted with 7 mL of 1 M NaCl solution (Normapur[®]) [Baduel et al., 2009] (Figure 1). The HULIS_{WS} fraction (2.3 mL) is collected between 11.5 and 13.8 min and immediately frozen until quantification. Melted ice sample and eluants are injected onto the resin with a high-performance liquid chromatography (HPLC) pump (Dionex[®] P680 HPLC Pump), and all eluted fractions flow through an online diode array UV/VIS detector (Dionex[®] UVD 170U/340U) placed after the resin. Complete extraction of the different fractions is controlled by the spectroscopic signal, which also provides information on the absorbance properties of the eluted fraction. Extraction yield is determined with a Suwannee River Fulvic Acid (SRFA) standard from the international humic substance society (IHSS, product number 1R101F) and tested for a large range of volume (between 20 and 200 mL) and concentrations (5 to 70 ppbC). The long concentration step results in lower extraction yields with slightly higher variability (89.3 ± 4.5%) compared to [Baduel et al., 2009], who obtained 93.0 ± 1.1% with the same method for atmospheric samples. To accurately determine the low concentrations of HULIS_{WS}, one or two washings of the resin and one blank measurement are done before each sample analysis to avoid

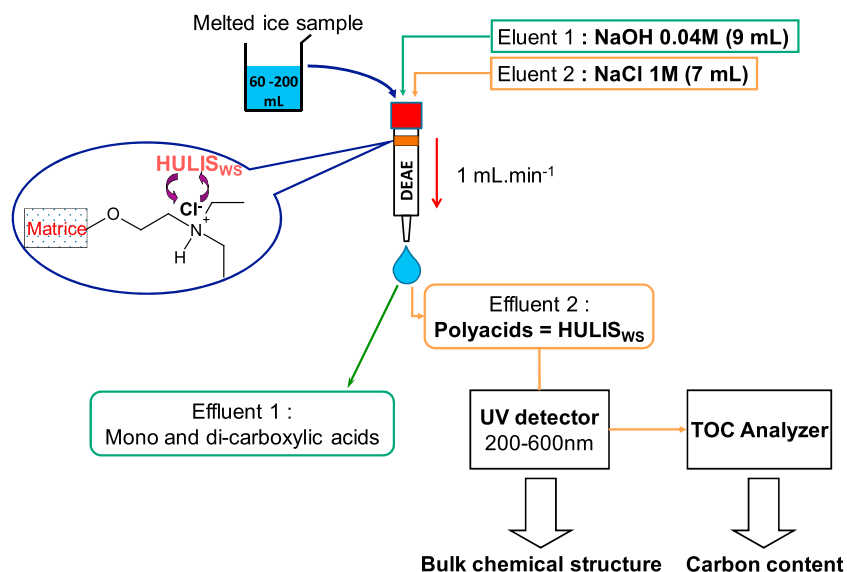


Figure 1. Schematic diagram of the extraction procedure used for the isolation of HULIS_{WS} from ice samples.

memory effect on the resin (washings and blank are being run with the elution program above-described). The blank value accounts for organic carbon released during the entire experimental procedure (i.e., eluant, pump system and resin leak) and is subtracted from the measured carbon amount of the sample.

2.2. Quantification of the HULIS Fraction

[11] Two different methods are used in literature for quantifying the extracted HULIS_{WS} fraction: a UV spectroscopic method and a measurement of the organic carbon content with a Total Organic Carbon analyzer (TOC). UV spectroscopy needs a standard whose optical properties are close enough to the actual optical properties of the measured HULIS_{WS}. The most commonly used standard for UV spectroscopic method calibration, SRFA, has optical properties that may differ largely from those of HULIS_{WS} [Graber and Rudich, 2006]. The absorbance can indeed be affected by pH, aromaticity, total carbon content, and molecular weight [Chen *et al.*, 1977]. Thus, quantifying aerosol HULIS using humic or fulvic standards can introduce large errors in the quantification of HULIS_{WS} [Baduel *et al.*, 2009]. Therefore, in this study we directly quantify the carbon content of the extracted HULIS_{WS} fraction with a TOC analyzer (Shimadzu[®] TOC-Vcsh). The extracted HULIS_{WS} fraction is sampled with a Teflon[®] tube and sucked into a syringe. Then, a solution of acid is added in the syringe (10% 2 M HCl, Sigma-Aldrich[®], ACS reagent), and the inorganic carbon is removed by bubbling N₂ through it during 1.5 min. After that, 50 μ L of the sample are injected in a combustion tube heated at 680°C. Here, the organic carbon of the HULIS_{WS} fraction is oxidized into CO₂ on a platinum catalyst. A carrier gas pushes the combustion products into an electronic dehumidifier, where the gas is cooled and dehydrated, and then into a halogen scrubber. Finally, the combusted sample is transported to a nondispersive infrared gas analyzer in order to quantify its CO₂ content. A calibration curve is performed with a sucrose solution (Merck[®]). Each sample is analyzed 3 times, and the first value is discarded

since it is regularly influenced by the rising of the tubes. Because of the presence of salt in the HULIS_{WS} extract, the TOC analyzer cannot be used in its high sensitivity mode. Under these conditions, the carbon detection limit is close to 100 ppbC. The blank value of the entire experimental process including the sample decontamination (see section 2.3), the concentration step, the extraction, and the quantification is 200 ± 50 ppbC in the extract, well above the carbon detection limit. The determination of the carbon content in the HULIS_{WS} extracted fraction is thus limited by blank variability. Thanks to the concentration factor introduced by the DEAE extraction (see section 2.1.), the ability to determine very low HULIS_{WS} concentrations is limited only by the volume of ice used for the concentration step. This volume is chosen so that the expected carbon concentration in the HULIS_{WS} fraction exceeds 5 times the carbon detection limit (500 ppbC). Because of this limit, there is no actual detection limit for HULIS in ice, the limiting factor being the available volume of sample.

2.3. Col du Dôme Ice Core

[12] HULIS_{WS} measurements were carried out on 250 ice core samples from a 124 m long ice core (denoted CDK) extracted at the Col du Dôme site located near the Mt Blanc summit. The dating of the CDK ice core is detailed by [Legrand *et al.*, 2013]. Briefly, the upper 114 m of the core span the 1921–2004 time period. However, as detailed in [Legrand *et al.*, 2013], the continuity of the ice core chronology was disturbed in ice corresponding to the 1951–1971 years, possibly due to the presence of a crevasse upstream to the borehole. Two hundred twenty samples of ice were cut along the well-dated and seasonally resolved parts of the CDK ice core (i.e., the 1921–1951 and 1971–1988 time periods). In order to investigate the 1955–1970 time period, we used additional ice samples from another Col du Dôme ice core (C11, 140 m long), drilled in 1994 virtually at the same place as CDK and in which the 1925–1994 time period is well preserved [Legrand *et al.*, 2007a]. 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. As detailed in [Legrand *et al.*, 2013], the dating of CDK and C11 cores was estimated to be close to ± 2 years after 1954, ± 4 years in the 40's, and 6 years around 1920. Based on examination of the ammonium profile, each annual layer was divided in two parts corresponding to winter and summer snow following the procedure detailed in [Preunkert *et al.*, 2000]. From that, the individual means of summer and winter half years were calculated for HULIS_{WS}.

[13] Ice samples were cut with a band saw. For decontamination, the outer parts of the ice samples, which had been in contact with plastic bags during storage, were rinsed with carbon-free ultrapure water (Elga®). Samples covering 2 years (1992 and 2000) in the firm part of the core, present from the surface down to 58 m depth, were also analyzed. Since firm is a porous material, the samples were not rinsed with water but decontaminated by shaving the external parts with a stainless steel lathe. Contamination tests made with frozen ultra pure water showed that HULIS_{WS} are rather insensitive to contamination during ice core storage in polyethylene bags and cutting. The contamination in HULIS_{WS} is lower than 1 ppbC and below 0.4 ppbC without and with the decontamination procedure, respectively.

[14] A total of 250 samples were analyzed with the aim to extract the reliable winter (50 samples) and summer (200 samples) long-term trends. The temporal resolution of the ice core sampling was adapted to preserve the amount needed for the analyses and to take into account the parameters inherent to the Col du Dôme ice archive (i.e., annual layer thinning with depth and better preservation of summer than winter snow, [Preunkert *et al.*, 2000]). Over the 1970–1988 time period, it was possible to analyze several samples per summer and 1 to 2 samples per winter. For the 1920–1950 years, winter samples were obtained by pooling successive winters, and the summer resolution was sometimes reduced to one sample per year.

3. Ancillary Data Set

[15] For ice core data discussions, we used two sets of atmospheric aerosol data. First, archived fractions of 21 high-volume filters collected during the CARBOSOL project (present and retrospective state of organic versus inorganic aerosol over Europe) [Legrand and Puxbaum, 2007] were used to measure HULIS_{WS} with the same method used for our ice core samples. [Pio *et al.*, 2007] already characterized these filters for major ions, including sulfate and various organic fractions, including WSOC. The set of selected filters is well representative of winter and summer conditions at the different European sites as seen in Table 1 where the levels of key chemical components including WSOC, sulfate, and fine potassium are reported.

[16] Second, we also used a set of daily filters collected over a week in June 2010 at the Puy de Dôme site (see analysis results in Table 2). The week's weather conditions at this site clearly favored a strengthening of WSOC aerosol biogenic sources (see details in [Legrand *et al.*, 2013]). This favorable situation helped us to apportion HULIS_{WS} in terms of biogenic and fossil fuel sources in summer at a European mountain site.

4. Results and Discussions

4.1. Seasonal Variations

[17] HULIS_{WS} concentrations in the Col du Dôme firn and ice range between 4 and 250 ppbC (Figure 2). Over the entire studied time period, a well-marked seasonal cycle characterized by lower winter values (between 4 and 13 ppbC) and enhanced summer values (between 5 and 140 ppbC) is observed (Figure 3). Summer concentrations are 4.5 and 2.5 times higher than winter ones over the 1951–1988 and the 1920–1950 periods, respectively (Table 3). Such seasonal changes with maxima in the ice layers are a common feature observed for various chemical species (see e.g.,

Table 1. Summer and Winter HULIS_{WS} Atmospheric Concentrations Measured on Filters Collected at Various European Sites During the CARBOSOL Project^a

Site (N)	Elevation	WSOC ^b	Sulfate ^b	Fine K ^b	HULIS _{WS} ^c
	(m asl)	(ngC m ⁻³)	(ng m ⁻³)	(ng m ⁻³)	(ngC m ⁻³)
Summer					
K-Pusztza (3)	130	3260 (3490)	3910 (3974)	101 (107)	890
Schauinsland (2)	1205	2850 (3040)	3380 (3460)	62 (85)	770
Puy de Dôme (8)	1450	1890 (2020)	2152 (2050)	51 (43)	390
Sonnblick (3)	3106	1190 (990)	1624 (1040)	<23	142
Winter					
K-Pusztza (2)	130	10220 (7400)	5461 (6060)	548 (380)	2145
Schauinsland (2)	1205	515 (780)	400 (1030)	12.5 (35)	55
Sonnblick (1)	3106	105 (140)	103 (212)	<1	10

^aN refers to the number of filters on which HULIS_{WS} measurements were done by using our DEAE method (see section 2). The levels of water-soluble organic carbon (WSOC), sulfate (its non-sea-salt and non-dust fraction), and fine potassium (i.e., its non-sea-salt and non-dust fraction) on these filters are compared to the corresponding values observed over the entire 2-years climatology gained during the CARBOSOL project (values in parenthesis) [Pio *et al.*, 2007].

^bData are from Pio *et al.* [2007].

^cThis work.

Table 2. Aerosol Composition at Puy de Dôme from 22 to 26 June 2010^a

	Day 1	Day 2	Day 3	Day 3 to Day 1
	(22 June 18:00 to 23 June 18:00)	(23 June 18:00 to 24 June 18:00)	(24 June 18:00 to 25 June 18:00)	
WSOC ^b (ngC m ⁻³)	1404	1730	2583	1179
F ¹⁴ C ^c	0.74	0.81	0.85	
HULIS ^b (ngC m ⁻³)	465	606	935	470
Biogenic WSOC (ngC m ⁻³)	999	1347	2111	1112
Anthropogenic WSOC (ngC m ⁻³)	405	383	472	
Biogenic HULIS (ngC m ⁻³)	398 (86%)	537 (89%)	842 (90%)	470
Anthropogenic HULIS (ngC m ⁻³)	67 (16%)	69 (18%)	93 (20%)	

^aThe increase of the WSOC level (denoted Δ (day 3 – day 1)) and of its ¹⁴C signature indicates an increase of predominantly biogenic origin (see section 4.3). We also report the WSOC fossil fuel fraction of days 1, 2, and 3. The fossil fuel and anthropogenic fractions of WSOC have been calculated assuming a two-source mix of biogenic (F¹⁴C = 1.04) and fossil (F¹⁴C = 0) contributions. The biogenic HULIS concentration is calculated as 40% of the biogenic WSOC (see text). In parenthesis is indicated the contribution of biogenic HULIS to the total HULIS, and the contribution of anthropogenic HULIS to anthropogenic WSOC.

^bThis work.

^cData are from Legrand *et al.* [this issue].

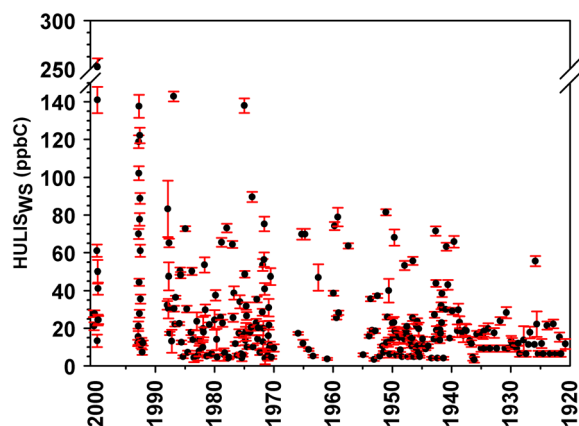


Figure 2. Temporal change of HULIS_{WS} concentrations in ice and firn covering the 1920–2000 time period. Vertical bars denote the analytical measurement error.

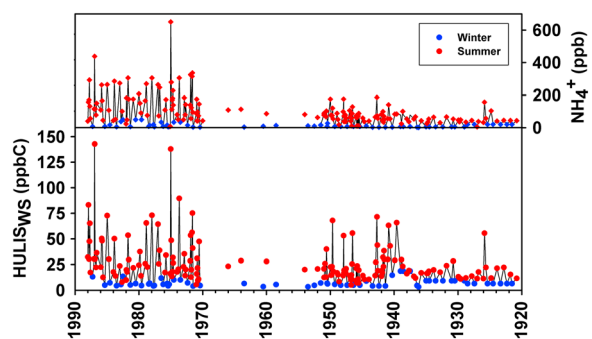


Figure 3. Temporal changes of HULIS_{WS} and ammonium concentrations in ice layers corresponding to the 1920–1950 and 1970–1988 periods. Red and blue dots represent HULIS_{WS} and ammonium concentrations in summer and winter samples, respectively (see details in Legrand *et al.* [2013] for the seasonal dissection).

[Preunkert *et al.*, 2000]). For instance, along the CDK ice core the summer to winter ratio for sulfate is close to 5.4 and 4.0 for the 1970–1988 and 1920–1950 periods, respectively [Legrand *et al.*, 2013]. Similar well-marked summer maxima have been

observed in aerosol components at elevated alpine sites and result from a more efficient upward transport of the air masses from the boundary layer in summer than winter [Baltensperger *et al.*, 1997; Hammer *et al.*, 2007; Pio *et al.*, 2007]. This common driver for seasonal variation of HULIS_{WS} and sulfate also results in summer to winter concentration ratios that are similar for sulfate and HULIS_{WS} in the aerosol at the high-elevation alpine site of Sonnblick and in the ice at the Col du Dôme (Table 1).

[18] Since this work reports the very first data on HULIS_{WS} concentrations in ice, we will discuss here that the extent of the Col du Dôme ice results are consistent with concentrations of HULIS found in the atmosphere. As seen in Table 1, a typical present-day atmospheric HULIS_{WS} concentration of 140 ngC m⁻³ is observed at the high-elevation Alpine site of Sonnblick in summer, and summer HULIS_{WS} concentrations (in ngC m⁻³) decrease with altitude (h in km) following an exponential function ($[HULIS_{WS}] = 1150 e^{-0.65h}$ with $R^2 = 0.9$). Applying this exponential law to the Col du Dôme site (4250 m asl) we would expect an atmospheric HULIS_{WS} level of 70 ngC m⁻³ in summer at this site. [Preunkert *et al.*, 2001] found under summer conditions at this site that atmospheric sulfate levels of 800 ng m⁻³ correspond to 650 ppb in corresponding snow layers. If we assume the same transfer of aerosols in firn for HULIS than for sulfate, we would expect a HULIS_{WS} level close to 50 ppbC in the Col du Dôme summer snow. This estimated value is very consistent with the range of values observed in ice layers corresponding to the recent summers (31 ± 11 ppbC over 1951–1988, see Table 3) (see also the 2000 levels in Figure 2). It has to be emphasized that the sources of atmospheric aerosol that are trapped in the Col du Dôme ice cores differ from winter to summer. For instance, using the regional European Monitoring and Evaluation Programme (EMEP) chemical transport model, [Fagerli *et al.*, 2007] performed source-receptor calculations for sulfate. It was shown that Spain, Italy, France, and Germany are the main contributors at the Col du Dôme in summer, whereas in winter more European wide and trans-Atlantic contributions were found. Therefore, as done in previous Col du Dôme ice core studies, we examine separately winter and summer long-term trends.

Table 3. DOC and HULIS_{WS} Concentrations in Winter and Summer Ice Layers Deposited over Recent (1951–1988) and Older (1920–1950) Time Periods

Time period	Winter		Summer	
	DOC ^a , ppbC	HULIS _{WS} , ppbC	DOC ^a , ppbC	HULIS _{WS} , ppbC
1951–1988	83.6 ± 26.7	6.5 ± 2.9	188.0 ± 28.1	30.6 ± 10.7
1920–1950	43.3 ± 12.9	8.1 ± 3.8	92.5 ± 7.5	21.2 ± 9.9
	(42.3 ± 13.6) ^b	(6.8 ± 1.9) ^b	(90.8 ± 27.4) ^b	(18.5 ± 6.5) ^b
WWII	46.7 ± 1.8	17.6 ± 1.5	104.7 ± 5.8	47.2 ± 1.2

^aData are from *Legrand et al.* [this issue].

^bDenotes values when samples from the beginning of World War II were not considered (see section 4).

4.2. Past Changes of HULIS_{WS} in Winter

[19] HULIS_{WS} concentrations in winter layers remain unchanged (8.1 ± 3.8 ppbC) from the first half of the twentieth century (1920–1950) to more recent times (6.5 ± 2.9 ppbC for 1951–1988, Table 3 and Figure 4). HULIS_{WS} concentrations were twice higher than the 1920–1950 mean in two exceptional samples. The first (18.6 ppbC) pools together winters 1937–1938, 1938–1939, and 1939–1940, and the second (15.7 ppbC) represents winter 1940–1941 (Figure 4). These unusually high winter values corresponding to the Second World War will be discussed in section 4.4. Even excluding these two values (Table 3), there is no detectable trend in winter from 1920 to the 1990s. However, the carbon contribution of HULIS_{WS} to the DOC concentration in ice was larger in the past ($17 \pm 6\%$, Table 3) than for recent time ($9 \pm 3\%$, Table 3). As discussed by [*Legrand et al.*, 2013], this change results from increased concentrations of other DOC contributors over the recent decades.

[20] In continental European regions, the most likely source of HULIS_{WS} in winter is biomass combustion for space heating [*Baduel et al.*, 2010; *Feczko et al.*, 2007; *Krivácsy et al.*, 2008]. Some formation processes were proposed involving the incomplete breakdown of polymeric plant matter or recombination and direct condensation of low-molecular-mass primary combustion products [*Mayol-Bracero et al.*, 2002; *Salma et al.*, 2010]. The primary origin of this source is consistent with the decrease of atmospheric concentrations with altitude reported in Table 1. Indeed, the HULIS_{WS} decreased in winter by a factor of 200 between the surface site of K-Pusztá and the high-elevated Alpine site

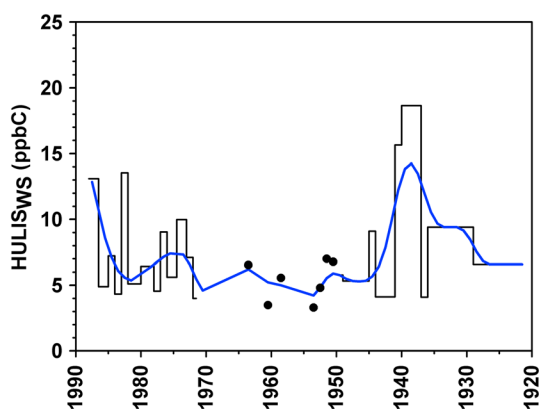


Figure 4. Winter half years HULIS_{WS} concentrations from 1920 to 1988, blue line refer to robust spline smoothing [*Bloomfield and Steiger*, 1983].

of Sonnblick (Table 1). Such a high factor is similarly observed for the non-sea-salt-non-dust potassium fraction (a factor of 400, Table 1) that is used as a referent species for submicronic primary emissions of aerosol in Europe [see *Legrand et al.*, 2007b], note that the decrease of concentrations with altitude is far weaker for sulfate (a factor of 30), indicating a secondary production from sulfur dioxide (SO₂) still acting above the boundary layer.

[21] Although wood burning is now well recognized as a large source of OC in winter, it is also the source with the highest uncertainty. Using the EMEP 3-D chemistry-transport model developed for elementary carbon (EC) and OC, [*Simpson et al.*, 2007] compared simulations with present-day observations in Europe. This exercise was done by comparing the model estimates for the different fractions of OC (primary versus secondary, fossil fuel versus biogenic) with values derived from observations that were apportioned by combining radiocarbon and levoglucosan data [*Gelencsér et al.*, 2007]. It was shown that present-day OC concentrations are underpredicted by a factor of 3 to 5 in winter, including mountain sites like Puy de Dôme, and that this underprediction results mainly from too low wood burning emissions in the model. European scale wood burning emissions today are poorly known, particularly because many households use fuel wood that is not recorded in official statistics (right of estovers in rural zone).

[22] The evolution of wood burning emissions over the twentieth century is also poorly constrained. At the global scale, [*Junker and Lioussé*, 2008] estimated that the biofuel consumption remained quasi-constant from 1920 to 1960 and doubled from 1960 to 1990. For the Northern Hemisphere, [*Ito and Penner*, 2005] calculated that the particulate organic matter emissions from biofuel were stable from 1920 to 1965 (around 4 Tg yr^{-1}) and increased after 1965 to reach 7 Tg yr^{-1} in 1990. Yet, the ice core signal in winter has been showed (see section 4.1.) to result mainly from European wide emissions plus some trans-Atlantic contributions, and the comparison of our measurements to emission scenario should thus focus on these areas in winter. In Europe, the global (annual) biofuel consumption is decreasing between 1920 and 1980, according to [*Fernandes et al.*, 2007]. The same decrease is observed in North America [*Fernandes et al.*, 2007], but the inventories of biofuel consumption are different according to studies.

[23] Emission inventories for wood burning at the scale of Europe remain, however, uncertain since many households use fuel wood that is not recorded in official statistics (right of estovers in rural zone). We thus argue that the absence of significant trend of HULIS_{WS} in winter ice deposited over

the twentieth century suggests that primary OC emissions in winter from domestic wood burning remained unchanged in Europe over this time period.

4.3. Past Change of HULIS_{WS} in Summer

[24] HULIS_{WS} concentrations in summer layers tend to increase over the last decades (Figure 5). The average concentration of HULIS was 18.5 ppbC from 1920 to 1950 (excluding the Second World War years) and reached 30.6 ppbC in recent times (1951–1988) (Table 3). The summers 1939 and 1940 reveal the same anomalies as in winter. As seen in Table 3, the summer ratio of HULIS_{WS}/DOC is higher in the past ($21 \pm 5\%$ for the 1920–1950 period, Table 3) than for recent time ($17 \pm 4\%$ for the 1951–1988 years, Table 3), as a result of a more pronounced increase over the recent decades of other DOC contributors including dicarboxylic acids [Legrand *et al.*, 2013]. In the following, we discuss the possible causes for the increase by 40% of HULIS_{WS} levels seen in summer ice deposited since 1920 in the Alps.

[25] The presence of HULIS_{WS} in the atmosphere in summer is very often attributed to secondary production. Laboratory studies have reported multiphase chemistry producing absorbing species of higher molecular weight or oligomers (e.g., [Limbeck *et al.*, 2003; Nozière *et al.*, 2007]; El Haddad *et al.*, 2009)) that are assumed to be HULIS or are able to produce HULIS through further aging. Although the diverse pathways producing HULIS_{WS} from biogenic and anthropogenic precursors are not yet quantified, some processes begin to emerge, as reviewed by [Ervens *et al.*, 2011] and by Lim *et al.* [2010] in the case of glyoxal. Some of these processes involve ionic mediated reactions such as aldol condensations, which can produce oligomers starting from any carbonyl compounds. Initially thought to be restricted to acidic aerosol [see Jang and Kamens, 2001], they are now known to be also catalyzed by amino acids [Nozière and Córdoba, 2008] and more common ions such as ammonium and carbonate [Nozière *et al.*, 2010]. Moreover, they have been especially studied for isoprene oxidation products such as glyoxal [Nozière *et al.*, 2009], methylglyoxal [Sareen *et al.*, 2010], and methylvinylketone [Nozière *et al.*, 2006]. Although important because of their ability to occur in dark conditions, these ionic mediated reactions appear less effective than photochemical reactions involving radicals. Such

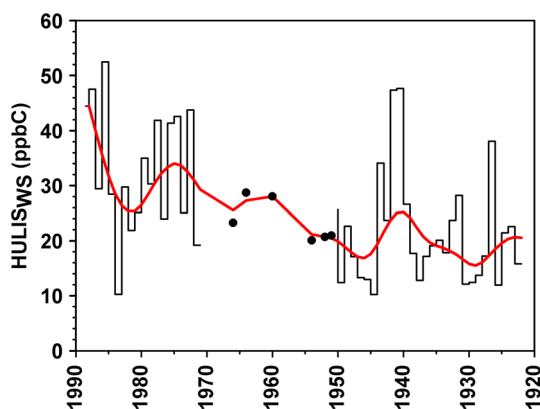


Figure 5. Summer half years HULIS_{WS} concentrations from 1920 to 1988, red line refer to robust spline smoothing [Bloomfield and Steiger, 1983].

reactions, initiated by OH radicals in the aqueous phase, have been evidenced for glyoxal [Carlton *et al.*, 2007; Tan *et al.*, 2010], methylglyoxal [Altieri *et al.*, 2008; Tan *et al.*, 2010], and methylvinylketone [Liu *et al.*, 2012], which are all oxidation products of isoprene. Oligomer production was also observed in OH initiated aqueous phase reactions of phenolic compounds [Sun *et al.*, 2010; Chang and Thompson, 2010], indicating that nonbiogenic precursors can also be involved in HULIS productions. At this time, several mechanisms able to produce HULIS_{WS} have been suggested, but it is yet impossible to evaluate the respective contribution of anthropogenic versus biogenic precursors.

[26] With the aim to apportion fossil fuel and biogenic sources of HULIS_{WS}, in the following we examine results of measurements made on atmospheric aerosol filters collected in June 2010 at the Puy de Dôme site including the ¹⁴C signature of WSOC aerosol (F¹⁴C, see Table 2). As discussed by [Legrand *et al.*, 2013], although based on three sampling days, this study was conducted under typical summer conditions taking place at a mountain site. It can thus provide useful information on the source apportionment of HULIS_{WS} (biogenic versus fossil fuel) in summer in Europe. As seen in Table 2, the regular increase of WSOC that took place from 22 to 26 June is almost exclusively from biogenic origin ($0.85 \times 2583 \text{ ngC m}^{-3} - 0.74 \times 1404 \text{ ngC m}^{-3} = 1158 \text{ ngC m}^{-3}$). Actually, as seen in Table 2, the anthropogenic WSOC concentration is almost constant during those 3 days, around 400 ngC m^{-3} . Assuming that both the anthropogenic and biogenic fractions of WSOC keep a homogenous chemical composition over those 3 days, then the HULIS_{WS} increase between day 1 and day 3 (470 ngC m^{-3}) has to be entirely biogenic, just as the increase in WSOC. This biogenic HULIS_{WS} increase (470 ngC m^{-3}) represents 40% of the observed biogenic WSOC increase (1179 ngC m^{-3}). As we assume this ratio to be constant over the 3 days, we can use it to estimate the biogenic HULIS_{WS} concentration from the measured biogenic WSOC: $999 \times 0.4 = 398 \text{ ngC m}^{-3}$ on day 1; 537 ngC m^{-3} on day 2; and 842 ngC m^{-3} on day 3. These concentrations represent respectively 86%, 89%, and 90% of the total HULIS_{WS} concentration. HULIS_{WS} in summer are thus mainly produced from the oxidation of biogenic precursors emitted by the living biosphere, which we will assume in the following also holds for the past.

[27] Among numerous environmental parameters, the strength of biogenic volatile organic compound (BVOC) emissions is strongly dependent on light, temperature, and atmospheric CO₂ concentration [Guenther, 1997; Liao *et al.*, 2006]. Increase in CO₂ concentration causes plants to grow [Ainsworth and Long, 2005] and increases the leaf area index [Constable *et al.*, 1999]. Isoprene is the most important BVOC, with a mass contribution between 30% and 50% of total BVOC emissions [Arneeth *et al.*, 2008; Guenther *et al.*, 1995]. Isoprene emissions are affected by the same parameters as BVOC, but recent studies revealed a more complex situation for this particular BVOC with the existence of a direct effect of emission inhibition by CO₂ [Arneeth *et al.*, 2007; Pacifico *et al.*, 2011; Young *et al.*, 2009]. The two opposite effects of increasing CO₂ concentration are currently the most important uncertainty about present and past isoprene emission inventories. The last and possibly the most important parameter for BVOC emissions is land use change. It is established that the forest

area in Europe and particularly in France has increased since the beginning of the twentieth century. In France, the area increased from $9 \times 10^4 \text{ km}^2$ in 1850 to $15 \times 10^4 \text{ km}^2$ in 1990 with a sharp increase between 1950 ($11 \times 10^4 \text{ km}^2$) and 1990 ($15 \times 10^4 \text{ km}^2$) [Cinotti, 1996]. This increase of the forested region area combined with the increasing CO_2 concentration and the rise of temperature over the last century might lead to enhanced BVOC emissions [Schurgers *et al.*, 2009].

[28] Finally, the enhanced oxidative properties of the European summer atmosphere over the twentieth century may also have contributed to enhanced secondary HULIS_{WS} production, as it was more generally proposed for secondary organic aerosol production by Kanakidou *et al.* [2000] that it increased from 17–28 Tg yr^{-1} for pre-industrial times to 61–79 Tg yr^{-1} at present.

4.4. HULIS During the Second World War

[29] As mentioned above, HULIS_{WS} measurements show unexpected high values at the beginning of the Second World War (i.e., in samples pooling together winters 1937–1938, 1938–1939, 1939–1940, and 1940–1941; and in samples corresponding to summers 1940 and 1941). Seven samples are concerned: two for winter and five for summer. These years are characterized by enhanced HULIS_{WS} concentrations as well as a HULIS_{WS}/DOC ratio twice higher than the average values over the 1920–1950 time period (Table 3). An experimental error or a contamination problem can be excluded since the seven corresponding samples were not analyzed at the same time. Interestingly, although the method used was very different, [Legrand *et al.*, 2007a] also reported unusually high values for the World War II period, 510 ppb over the 1939–1947 years against 183 ppb over 1952–1957 and 139 ppb over 1925–1936.

[30] No anomaly is detected in the record of other organic species or fractions including DOC [Legrand *et al.*, 2013]. Figure 6 compares the extraction chromatograms of two ice samples containing similar amount of HULIS_{WS}, a regular one and one of the samples corresponding to World War II. In the World War II sample, additional species are eluted at the same time as the mono- and dicarboxylic acids and a

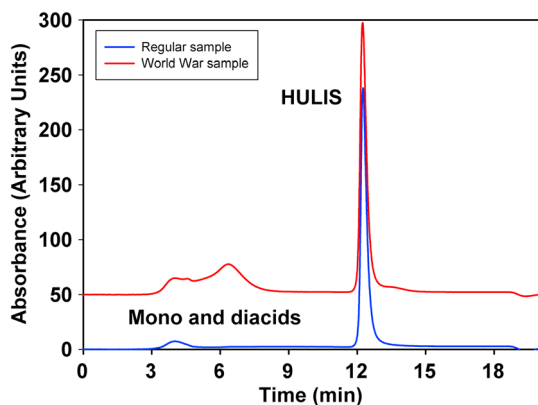


Figure 6. Extraction chromatograms of two different ice samples: in blue a regular sample and in red a sample with a high unusually HULIS_{WS} content corresponding to the beginning of World War II, an offset of 50 arbitrary units is applied to this sample for more visibility.

small hump is detected on the tail of the HULIS_{WS} peak (at 14 min).

[31] Examination of other ice archives from the Northern Hemisphere including those extracted at other Alpine sites and in Greenland may help here to highlight the origin of this possible additional (or unusual) source of HULIS that seems to have acted both in summer and winter at least over Europe during the beginning of World War II.

5. Conclusions

[32] This work represents the first attempt to quantify HULIS_{WS} on a carbon mass basis in Alpine ice cores. The HULIS_{WS} ice core record shows a well-preserved seasonality over the twentieth century, in agreement with corresponding atmospheric studies conducted at high-elevated European stations. The HULIS_{WS} ice record is characterized by winter minima remaining close to 7 ppbC over most of the last century. Moreover, an absence of a winter trend in Col du Dôme ice layers suggests that emissions from domestic wood combustion remained rather unchanged over the course of last century. The ice summer trend reveals an increase by 40% from 1920 to the recent decades (from an average of 18 ppbC over the 1920–1950 period to 30 ppbC over 1951–1988). Additional atmospheric measurements made at the mountain site of Puy de Dôme (center of France) strongly support the hypothesis of a dominant secondary production of HULIS_{WS} from biogenic precursors in summer. The summer trend extracted from summer ice layers may reflect either enhanced emissions of biogenic precursors or an effect of stronger oxidative capacity for the European atmosphere including an ozone increase. Furthermore, many environmental parameters may have contributed to a change of the strength of biogenic emissions including the changing use of land as well as the increase of temperature and CO_2 concentrations. Given the large existing uncertainties in emission inventories of the source of HULIS_{WS} (domestic wood burning in winter, secondary biogenic production in summer), our data extracted from high-elevated Alpine ice cores should be useful to better constrain them.

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