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Michel Legrand, Hans Puxbaum. Summary of the CARBOSOL project: Present and retrospective state of organic versus inorganic aerosol over Europe. *Journal of Geophysical Research: Atmospheres*, American Geophysical Union, 2007, 112 (D23S01), 1 à 7 p. 10.1029/2006JD008271 . insu-00377149

**HAL Id: insu-00377149**

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Submitted on 10 May 2021

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## Summary of the CARBOSOL project: Present and retrospective state of organic versus inorganic aerosol over Europe

M. Legrand<sup>1</sup> and H. Puxbaum<sup>2</sup>

Received 21 November 2006; revised 18 June 2007; accepted 4 September 2007; published 17 November 2007.

[1] Aerosol is an important source of uncertainty concerning the role of the atmosphere in climate forcing. In particular, major gaps exist with respect to its carbonaceous fraction in terms of composition, source apportionment (natural versus anthropogenic), change over the past, and radiative impact. The CARBOSOL project contributes to reduce these uncertainties. CARBOSOL combines a 2-year study of present-day carbonaceous aerosol in air and precipitation in western/central Europe with the trends of climatically relevant species in Alpine ice cores. Comparisons between observed atmospheric distributions (present and proxy of past) and transport/chemistry model simulations allow to test the accuracy of present and past anthropogenic emission inventories and enable for the first time a comparison of the model results for individual components (primary, secondary, fossil fuel, and biogenic) against data derived from measurements. The net radiative effect of the aerosol load and composition (inorganic/organic) in Europe is evaluated using radiative/chemistry/transport models. This summary paper gives an overview of the CARBOSOL goals, and reports on the key findings as a guide to the results detailed in the papers that follow.

**Citation:** 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.*, 112, D23S01, doi:10.1029/2006JD008271.

### 1. Introduction and CARBOSOL Goals

[2] Two of the most crucial environmental problems dealing with our changing atmosphere are health issues associated with air pollution, and climate change resulting from man-made activities. In both aspects aerosol plays a crucial role, particularly its carbonaceous fraction which now turns out to be the major constituent of fine continental aerosol [Heintzenberg, 1989; Zappoli *et al.*, 1999]. However, our knowledge of carbonaceous aerosol remains limited with respect to speciation, and spatiotemporal distribution.

[3] Until recently, organic speciation studies have failed to assign more than 15% of the carbon in aerosol to individual organic compound classes [Turpin *et al.*, 2000], and it seems now that most OC is contained in oligomeric or polymeric matter for which very sparse data are presently available [Simoneit and Mazurek, 1982; Puxbaum and Tenze-Kunit, 2003]. Considerable efforts to investigate the complex nature of the aerosol have been performed in North America, Amazonia, Africa, and Asia [e.g., Novakov *et al.*, 1997; Lelieveld *et al.*, 2001; Mayol-Bracero *et al.*, 2002; Kirchstetter *et al.*, 2003]. In these studies the particulate emissions based on anthropogenic activities, including

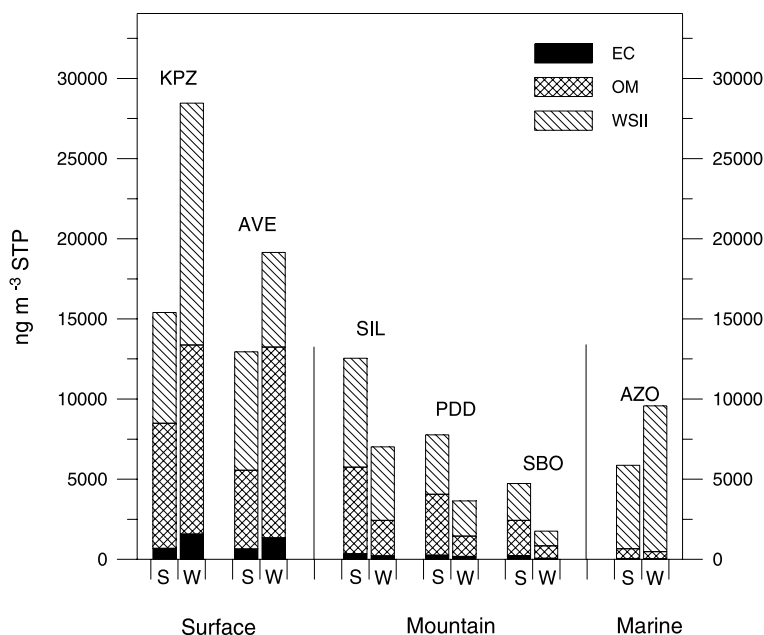
biomass burning and fossil fuel combustion, were in the center of the investigations. Much sparse are studies which investigated remote and rural environments, and most of them were restricted to short-time campaigns (see Putaud *et al.* [2004] for a recent review focused on Europe). The present-day source apportionment (natural/anthropogenic, primary/secondary) of the two major groups of carbonaceous species, elemental carbon (EC) and organic carbon (OC), is on the European scale, and in particular on a seasonal basis, poorly known.

[4] The temporal evolution in the past century is practically unknown. Two attempts to extract information on past carbonaceous aerosol levels (EC and water insoluble organic carbon (WinOC)) were made in ice cores extracted at two Alpine glacier sites [Lavanchy *et al.*, 1999; Jenk *et al.*, 2006]. However, these investigations did not document the water soluble organic material and were not accompanied by an aerosol study to invert ice core signals into relevant atmospheric information.

[5] The lack of historical data of carbonaceous material in the atmosphere, either from the emission inventory side, or from field data, led to the foundation for the current project: A Study of the Present and Retrospective State of the Organic Versus Inorganic Aerosol over Europe. CARBOSOL activities are divided into three linked work tasks addressing (1) the present-day state of aerosol in Europe, (2) its long-term changes, and (3) the assimilation of observations in model simulations to provide estimates of source emission change and the resulting changes of the radiative balance over Europe.

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**Figure 1.** Mean summer (S) and winter (W) levels of elemental carbon (EC), total mass of particulate organic matter (OM), and total water soluble inorganic ions (WSII) at the six CARBOSOL sites. A value of 1.6 was applied to convert OC into OM. Adapted from *Pio et al.* [2007].

[6] Given the aerosol lifetime of a few days, the spatial and temporal distributions of aerosols are highly variable and investigations need to be carried out at numerous places (marine and continental, boundary layer and free troposphere) and over long-enough time periods (including winter and summer). The present-day aerosol and precipitation was studied over a time span of 2 years at a set of 6 sites arranged over a west-east transect from the Azores (Atlantic Ocean) to Hungary. They include a marine background site at Azores (denoted AZO), two rural surface background sites (Aveiro in Portugal, AVE, and K-Puszt in Hungary, KPZ), and three mountain sites (Puy de Dome in France (PDD), Schauinsland in Germany (SIL), and Sonnblick in Austria (SBO)). Components under investigation were inorganic ions, EC/OC, water soluble/water insoluble organic carbon (WSOC/WinOC), cellulose, humic-like substances (HULIS), levoglucosan, dicarboxylic acids, <sup>210</sup>Pb, and selected organic trace compounds. A subset of samples was analyzed for <sup>14</sup>C in order to determine the fraction of modern carbon versus C from fossil fuel.

[7] With the objective to reconstruct changes from pre-industrial time to the present of the atmospheric load of carbonaceous aerosol over Europe, an extended array of organic species was investigated in Alpine ice cores. In addition, year-round routine automatic aerosol sampling and intensive summer campaigns were achieved at the Vallot observatory (4260 m elevation, near the Mt Blanc summit, France) in order to highlight the relationship between air composition and snow deposits. This secondary objective is required to evaluate ice core data in terms of past atmospheric concentrations.

[8] To reconstruct the past evolution of aerosol emissions, air concentrations and radiative forcing in Europe, a regional circulation model coupled with a radiative transfer model, in which aerosols are treated online, was deployed. In a first

step, the observed present-day spatial distributions of EC and OC are related to simulations of models which use present-day EC and OC direct emission inventories and estimated secondary OC production. Comparisons between simulations and past atmospheric concentrations derived from ice core records were foreseen to highlight estimates of the EC and OC emission inventories in Europe over the last century. The net radiative effect of the present-day aerosol load and composition (inorganic/organic) in Europe is evaluated using radiative/chemistry/transport models. Finally, as far as the comparison between simulations and observations are good enough for present-day, simulations dealing with predictions of the temporal changes of radiative impacts of aerosol over Europe were foreseen.

## 2. Key Findings of CARBOSOL

[9] This section briefly highlights some key results and may guide the reader through the different CARBOSOL papers.

[10] 1. Atmospheric aerosol studies conducted during the CARBOSOL project provide an overview of the present-day climatology of aerosol over Europe. The main characteristics of the sampling sites, the collected samples and measurements are detailed by *Pio et al.* [2007]. It is shown that, except at the Azores where inorganic material (sea-salt and non-sea-salt-sulfate) dominates, similar amounts of organic and inorganic matter are present in the nonurban European atmosphere in the boundary layer as well as at elevations up to around 3000 m (Figure 1). Carbonaceous aerosol concentrations show a gradient of more than 20 times between the Azores and the lowland continental sites of Aveiro in Portugal and K-Puszt in Hungary, with intermediate levels at continental mountain sites. With exception of the Azores, seasonal cycles are observed in

**Table 1.** Seasonal Variations of Elemental Carbon (EC), Organic Carbon (OC), Water Soluble Organic Carbon (WSOC), Brown Carbon, Sum of Dicarboxylic Acids, Total Cellulose and Levoglucosan, at the Six CARBOSOL Sites<sup>a</sup>

Sites	EC, ng C m <sup>-3</sup>	OC, ng C m <sup>-3</sup>	WSOC, ng C m <sup>-3</sup>	Brown Carbon, ng C m <sup>-3</sup>	Diacids, ng C m <sup>-3</sup>	Total Cellulose, ng C m <sup>-3</sup>	Levoglucosan, ng C m <sup>-3</sup>
AZO S	47	380	211	105	28	9	1
AZO W	39	270	181	87	12	6	4
AVE S	650	3100	1800	940	109	23	34
AVE W	1340	7500	3700	2900	94	41	430
PDD S	260	2400	1540	480	93	50	5
PDD W	185	790	610	370	34	16	10
SIL S	350	3400	2700	680	159	84	8
SIL W	220	1370	1020	570	51	27	14
SBO S	230	1380	840	360	49	24	2
SBO W	66	480	350	179	nd	15	4
KPZ S	690	4900	3400	950	111	107	29
KPZ W	1570	7400	5800	4400	123	66	260

<sup>a</sup>Summer (S) and winter (W) refer to months from April to September and October to March, respectively. Adapted from *Pio et al.* [2007]. nd, not determined.

the concentration of carbonaceous matter with clear maxima in winter for lowland conditions and maxima in summer at mountain sites. To investigate changes driven by air mass transport processes from those tied to variations of the various involved source and sink strengths, the present-day aerosol climatology is backed up by <sup>210</sup>Pb observations [Hammer *et al.*, 2007]. With this approach, transport related variations of the aerosol could be well spotted. The aerosol data set gained during CARBOSOL for nonurban environment also permits characterization of the OC aerosol with regard to its water solubility, showing that most (50–80%) of OC is water-soluble, both in summer and winter (Table 1).

[11] 2. Source apportionment of present-day aerosol combining measurements of radiocarbon with those of OC, EC, and of two organic tracers (levoglucosan for primary OC from biomass burning, and cellulose for primary OC from vegetation) is successfully done with an uncertainty analysis [Gelencsér *et al.*, 2007]. Source types are lumped into primary emissions from fossil fuel combustion and biomass burning, plant-derived bioaerosol, and secondary productions from precursors emitted by fossil and nonfossil sources. As seen in Table 2, while fossil-related sources dominate EC throughout the year at all sites, the sources of OC are mainly biogenic. In winter, biomass burning is the main OC source, with primary emission at surface sites and secondary production (condensation of directly emitted semivolatile organic compounds at low ambient temperatures) at mountain sites. Given the OC/levoglucosan emission factors for biomass burning reported in the literature (from 6 to 12.5, see *Puxbaum et al.* [2007]), the importance of biomass burning as a primary source of OC at surface sites in winter is clearly seen in the levoglucosan data reported in Table 1. More detailed calculations indicate that in winter biomass smoke represents 50–70% of the organic matter at surface continental European sites, not including secondary organic aerosol related to biomass combustion sources [*Puxbaum et al.*, 2007]. Source apportionment reported in Table 2 indicates that in summer secondary organic aerosol from non-fossil sources becomes predominant.

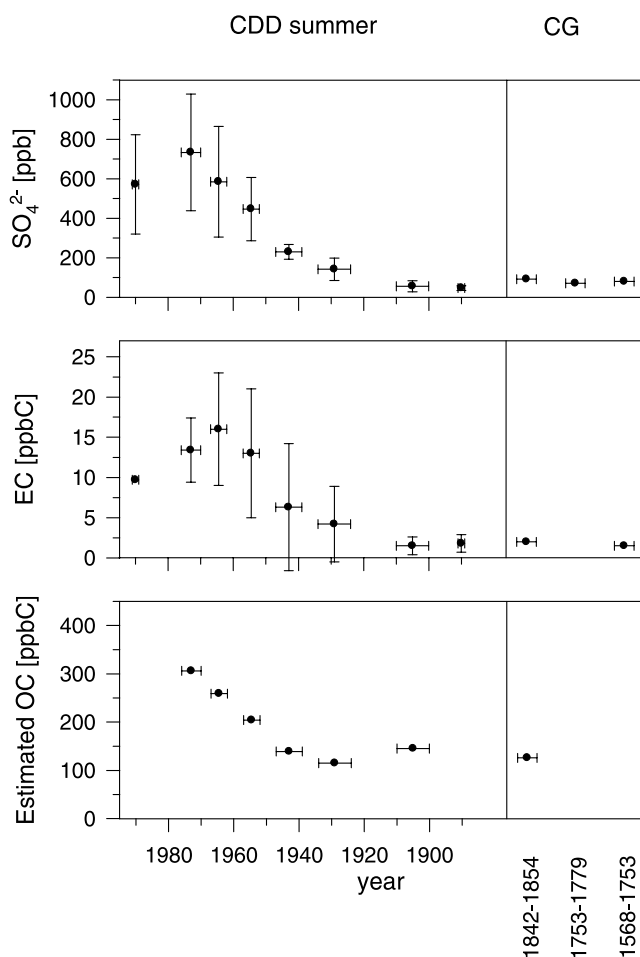
[12] 3. More than 200 compounds were identified and quantified by GC/MS, including alkanes, polyaromatic hydrocarbons, aldehydes, ketones, alcohols, sterols and organic acids in CARBOSOL aerosol samples. The amount of

OC identified by such organic speciation is weak (only 2–4% of the organic matter). Specific discussions and interpretations of the results are given by *Oliveira et al.* [2007] and we just emphasize here that the GC/MS results confirm the strong impact of biomass burning during winter at lowland sites. Short-chain dicarboxylic acids (C2–C5), not analyzed with the GM/MS method, were investigated by using ion chromatography. As seen in Table 1, they are significant contributors to WSOC, from ~5% at continental sites to 14% at Azores in summer. Observations are discussed to highlight the poorly known atmospheric budget of dicarboxylic acids in Europe. Since it was recently found that, among secondary productions of diacids, some pathways also form oligomers [*Altieri et al.*, 2006], the knowledge of the sources of diacids is of importance for the understanding of secondary organic aerosol formation. Observed correlations between the diacids and the fine fraction of potassium suggest that continental surface sites are influenced in winter by fast production of C2–C5 diacids in wood burning plumes, and secondary aqueous phase production of oxalic acid from aldehydes, formed by the rapid oxidation of toluene and ethene emitted by cars [*Legrand et al.*, 2007a]. In summer, the presence of

**Table 2.** Relative Share of EC and OC Source Categories Within Total Carbon (TC)<sup>a</sup>

Site	EC <sub>BB</sub> , %	EC <sub>FF</sub> , %	OC <sub>BB</sub> , %	OC <sub>FF</sub> , %	OC <sub>bio</sub> , %	SOA <sub>nonfossil</sub> , %	SOA <sub>FF</sub> , %
AVE W	11	2	64	1	1	5	16
AVE S	1	13	7	7	2	63	7
PDD W	2	23	9	13	3	44	7
PDD S	0	6	1	3	4	76	10
SIL W	2	15	14	8	2	54	4
SIL S	0	6	2	3	5	70	13
SBO W	2	8	11	5	8	46	22
SBO S	0	7	2	4	3	72	11
KPZ W	7	10	40	6	1	21	15
KPZ S	1	9	6	5	5	69	4

<sup>a</sup>Index BB refers to biomass burning, FF refers to fossil fuel, and bio refers to biogenic. Secondary organic aerosol (SOA) is divided into subcategories related to fossil fuel (index FF) and non-fossil fuel (index nonfossil). Bulk concentration ratios used to estimate the primary source types (BB, FF, and bio) are discussed by *Gelencsér et al.* [2007]. The two SOA subcategories are constrained by measured radiocarbon measurements. Adapted from *Gelencsér et al.* [2007].



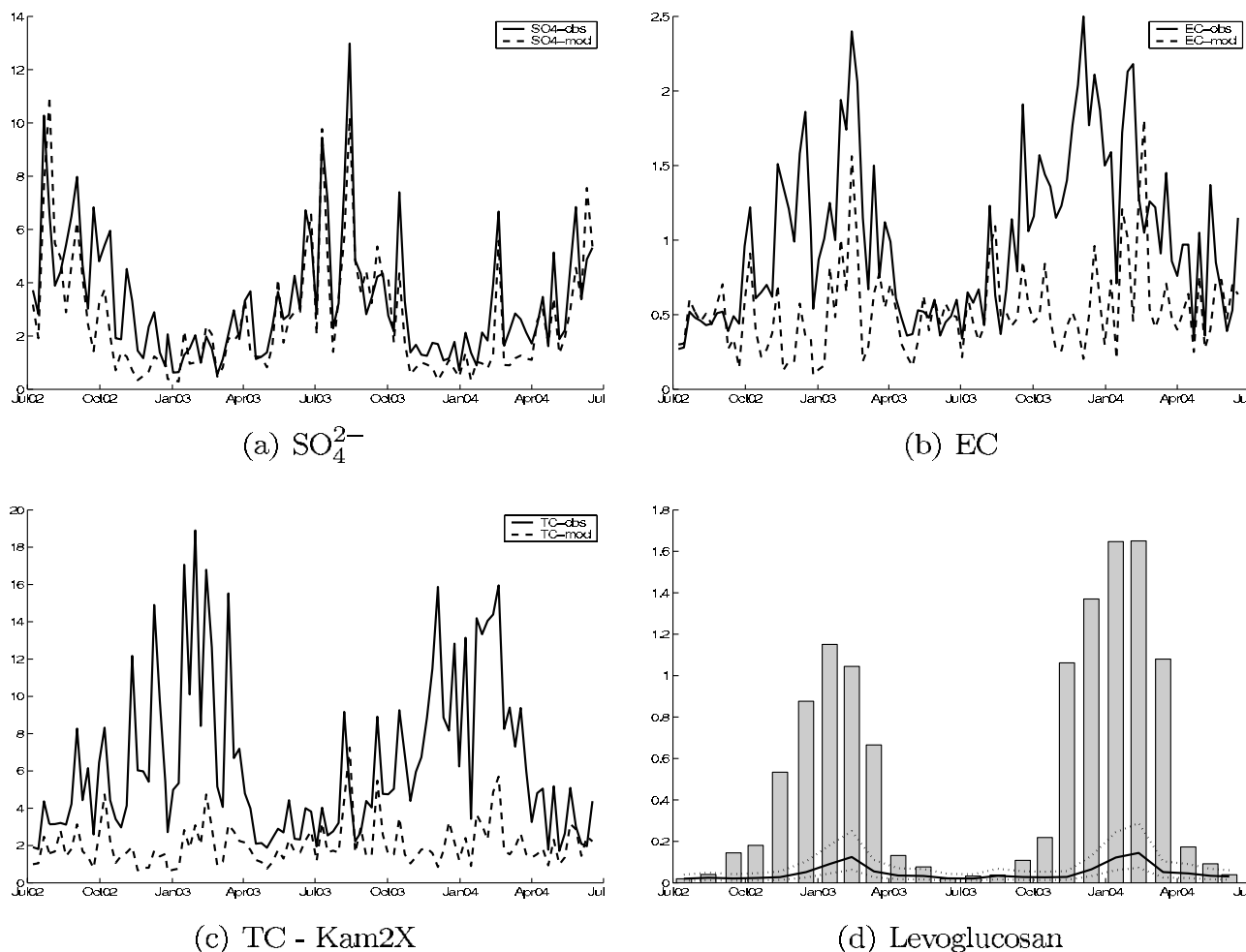
**Figure 2.** Temporal changes of concentrations of sulfate, elemental carbon (EC), and an estimate of atmospheric OC preserved in Alpine summer snow and ice layers. The concentration of atmospheric OC is calculated as the sum of measured WinOC and DOC related to WSOC (obtained by subtracting the measured contribution of monocarboxylic acids to total DOC). Vertical bars refer to the standard deviations related to sample content variability, and horizontal bars refer to the covered time periods. CDD refers to samples from Col du Dome, and CG refers to samples from Colle Gnifetti. Adapted from *Legrand et al.* [2007b].

diacids is related to aqueous production from biogenic precursors (isoprene, unsaturated fatty acids and oxygenated volatile organic compounds). The importance of biogenic emissions for the budget of diacids in summer can be seen in Table 1, with the highest concentration of diacids recorded at SIL, a site located in the dense forested area of the Black Forest.

[13] The rather weak amount of OC identified by the above mentioned investigations (those quantified by GC/MS, C2-C5 diacids, and levoglucosan) stimulated the study of the oligomeric or polymeric matter. This was done for cellulose which, as expected, reveals higher concentrations in the growing season than in winter at continental surface sites. The relative contribution of plant debris to organic matter ranges from  $\sim 2\%$  at AVE to 10% at SBO [*Sánchez-*

*Ochoa et al., 2007*]. With the aim to establish the climatology of humic-like substances (HULIS) that are omnipresent in atmospheric aerosol, two different analytical methods were used. *Lukács et al.* [2007] investigated HULIS by measuring absorbance of the water extract of filters with a UV-VIS spectrophotometer at the wavelength of 350 nm. This method was used for all CARBOSOL aerosol filters collected over 2 years (data presented by *Pio et al.* [2007] and *Lukács et al.* [2007]) as well as in ice cores (data presented by *Legrand et al.* [2007b]). *Feczko et al.* [2007] deployed a newly developed method based on the combination of two separation steps (by polarity and by acidity) with a universal detector for organic carbon. With this method half of the CARBOSOL aerosol filters were analyzed. There are large differences in the two data sets, particularly for winter samples. As an example, in winter 2002/2003 samples collected at Aveiro measurements made with the UV-VIS method give a value of  $3060 \pm 1850 \text{ ng m}^{-3}$ , while those made with the OC detector a value of  $690 \pm 460 \text{ ng m}^{-3}$ . On this basis, measurements made with the UV-VIS method are recalled brown carbon, defined as light-absorbing organic matter, that include HULIS as well as other colored substances. With the help of codetermined concentrations of levoglucosan a tentative source apportionment of brown carbon is done. It is shown that biomass burning is the major source for brown carbon, with domestic wood burning as a predominant source in winter. In summer brown carbon seems to be secondarily produced but its precursors are not yet clearly identified [*Lukács et al., 2007*].

[14] 4. An extended array of carbonaceous species including filterable elemental and organic fractions (EC and WinOC), dissolved organic carbon (DOC), cellulose, brown carbon, and single organic compounds like carboxylic acids were investigated together for the first time in Alpine snow deposits [*Legrand et al., 2007b*]. Related to this ice core task, it is shown that a regional chemistry-transport model using past emission inventories of  $\text{SO}_2$  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. Among organics, EC reveals an outstanding increase with a sharp summer increase after World War II (Figure 2). This observation is fairly consistent with the historical emission inventories of EC at the scale of Europe established during the CARBOSOL project which assumes that emission factors from road transport have increased backward in time, by a factor of 5 from 1985 to 1965 [*Fagerli et al., 2007*]. The reconstruction of past changes of atmospheric OC load from ice core record is a challenge since only the filterable organic carbon fraction was measured in ice, and conversely the DOC content of ice accounts for water soluble organic aerosol as well as organic gases which are water soluble. *Legrand et al.* [2007b] demonstrate that the ice record of DOC together with those of light monocarboxylates (see also *Preunkert et al.* [2007] for these species) and WinOC permit to reconstruct past OC aerosol changes with a rather good degree of confidence. The atmospheric load of OC in summer has been enhanced by a factor of 2 after World War II (Figure 2), likely because of the effect of an enhanced oxidative capacity of the atmosphere producing more secondary organic aerosol.



**Figure 3.** Modeled and observed concentrations of sulfate, elemental carbon (EC), total carbon (EC plus OC), and levoglucosan at AVE. Units are  $\mu\text{g C m}^{-3}$  for TC and EC and  $\mu\text{g m}^{-3}$  for sulfate and levoglucosan. For levoglucosan, bars refer to observations, the solid line refers to the central value of model results, and dotted lines indicate the factor of two ranges around this central value. For other species, observations are drawn as solid lines, and the modeled are drawn as dashed. Adapted from *Simpson et al.* [2007].

[15] 5. An extended version of the EMEP 3-D chemistry-transport model was developed toward EC and OC and simulations were compared with present-day observations in Europe. In addition to primary emissions from fossil fuel and wood burning, the model includes secondary production of anthropogenic and biogenic organic aerosol [*Simpson et al.*, 2007]. The EMEP model reproduces well pollutants with well-known emissions and chemistry like sulfate but significantly underpredicts EC, especially in winter (Figure 3). For EC a companion paper [*Tsyro et al.*, 2007] focuses on how uncertainties in scavenging processes, emission factors and atmospheric measurements affect the comparison between observations and simulations. It is shown that the largest uncertainties lie in EC emissions from residential wood/fossil combustion. For OC the performance of the EMEP model is evaluated not only with respect to observed OC but also for the first time against the levoglucosan analysis of *Puxbaum et al.* [2007] (see Figure 3) and the source apportionment calculations from *Gelencsér et al.* [2007]. This powerful exercise indicates

that present-day under predicted OC concentrations in winter (a factor of 3 to 5) mainly result from too low wood burning contribution in the model whereas in summer most of the departure (an underestimation by a factor of 2 to 3) is related to secondary production mainly from non-fossil-fuel precursors.

[16] 6. Using a regional atmosphere-chemistry model coupled with an off-line radiative transfer model (RE-MOTE), the aerosol (sulfate, elemental and organic carbon) distribution over Europe [*Marmier and Langmann*, 2007] is investigated. The direct aerosol forcing resulting from the simulated aerosol burden is studied by *Marmier et al.* [2007a]. Since the model captures only 50% of EC and 10% of OC, a sensitivity run is done by doubling the atmospheric concentration of EC and multiplying that of OC by a factor of 10. On this basis and assuming that aerosols are externally mixed, the mean direct forcing over Europe reaches  $-0.3 \text{ W m}^{-2}$  in winter,  $-2.5 \text{ W m}^{-2}$  in summer. Investigations of the changes in the direct aerosol forcing over Europe over the past century were carried out

**Table 3.** Mean Seasonal Values of the Direct Radiative Forcing of Different Aerosol Types, Total Aerosol Assuming External and Internal Mixing, and a Sensitivity Test (Achieved by Multiplying Atmospheric EC Concentrations by a Factor of 2 and OC by a Factor of 10) to Account for Discrepancies Between Observations and Simulations<sup>a</sup>

	SO <sub>4</sub>	EC	OC	Externally Mixed	Internally Mixed	Internally Mixed(Sensitivity Test)
JJA 2002	-1.4	+0.15	-0.07	-1.4	-1.5	-2.4
DJF 2002/2003	-0.2	+0.08	-0.03	-0.2	-0.1	-0.3

<sup>a</sup>JJA refers to June–July–August, and DJF refers to December–January–February. Unit is W m<sup>-2</sup>. Adapted from *Marmier et al.* [2007a].

for sulfate aerosol [*Marmier et al.*, 2007b] showing that the direct radiative forcing by sulfate alone was higher ( $-2.7$  W m<sup>-2</sup>) in the 80s than in 2002 ( $-1.4$  W m<sup>-2</sup>, Table 3). Difficulties of transport and chemistry models to reproduce present-day observations for organic matter, particularly OC, have hampered any attempt to investigate the past change of the radiative forcing of organic aerosol over the past.

### 3. Conclusions

[17] CARBOSOL contributes to the field of researches dealing with the global aerosol climatology. A comprehensive aerosol data set is now available for various conditions in Europe (marine versus continental, rural versus forested, boundary layer versus free troposphere, and winter versus summer).

[18] The integrated approach deployed in CARBOSOL, which combines radiocarbon measurements with bulk measurements of organic carbon and elemental carbon as well as levoglucosan and cellulose tracers to provide a bulk source apportionment of carbonaceous aerosol, is found to be successful. As discussed by *Simpson et al.* [2007] results are very valuable as validation data for atmospheric models for which the understanding behind some aspects is still in its infancy, particularly secondary production of organic aerosol. Regional chemistry-transport model simulations using past SO<sub>2</sub> emission inventories are for the first time compared to long-term sulfate trends extracted from Alpine ice cores suggesting that these archives can indeed help to reduce uncertainties in past emission inventories [*Fagerli et al.*, 2007].

[19] Major findings include the surprising high contribution of wood smoke to organic matter in winter, a finding based on levoglucosan data [*Puxbaum et al.*, 2007], which is confirmed by the source apportionment of present-day aerosol constrained by measurements of radiocarbon [*Gelencsér et al.*, 2007]. This statement has not been evidenced earlier in Europe. In contrast, the source apportionment of present-day aerosol indicates that in summer secondary organic aerosol (SOA) from nonfossil sources becomes largely predominant. It should be recalled that even if most of the SOA is biogenic and forms from VOCs emitted by vegetation, its formation involves photo oxidants whose levels have been strongly enhanced by human activities. Such a change over the past has been detected in Alpine ice cores [*Legrand et al.*, 2007b]. Therefore it appears that most of the biogenic SOA can be considered as anthropogenic in origin.

[20] **Acknowledgments.** The authors acknowledge the members of the CARBOSOL team. The project was funded by EU contract EVK2

CT2001-00113. We would like to thank the anonymous reviewer for valuable comments.

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