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Modeling historical long-term trends of sulfate, ammonium, and elemental carbon over Europe: A comparison with ice core records in the Alps

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[1] The regional EMEP chemical transport model has been run for the 1920–2003 period and the simulations compared to the long-term seasonally resolved trends of major inorganic aerosols (sulfate and ammonium) derived from ice cores extracted at Col du Dôme (CDD, 4250 m above sea level, French Alps). Source-receptor calculations have been performed in order to allocate the sources of air pollution arriving over the Alps. Spain, Italy, France, and Germany are found to be the main contributors at CDD in summer, accounting for 50% of sulfate and 75% of ammonium. In winter more European wide and trans-Atlantic contributions are found. The relative impact of these sources remains similar over the whole Alpine massif although transport from US and emissions from Spain contribute less as we move eastward from CDD, toward other alpine ice core drill sites like Colle Gnifetti (CG) in the Swiss Alps. For sulfate, the CDD ice core records and the simulated trends match very well. For ammonium, the trend simulated by the model and the summer ice core record are in reasonable agreement, both showing greater changes in ammonium concentrations than would be suggested by historical ammonia emissions. Motivated by a such good agreement between simulations of past atmospheric concentrations and ice core records for inorganic aerosol species, we also use the model to simulate trends in elemental carbon for which less information on past emission inventories are available.

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1. Introduction

[2] Human activities have greatly increased the inputs of sulfur, nitrogen and carbonaceous compounds to terrestrial and aquatic ecosystems since preindustrial times. It is well established that sulfur and nitrogen deposition affects ecosystems, directly or indirectly via chemical changes induced in soils, ground waters and surface waters. The effects tend to result from deposition accumulated over decades, thus it is important to know the long-term loads. In addition, inorganic aerosols (especially sulfate) and carbonaceous aerosols (especially black or elemental carbon) are very important components of the Earth's radiation balance [*Intergovernmental Panel on Climate Change*, 2001]. Today, several historical emission inventories exist for SO_2, NO_x, NH_3, CO, VOCs and carbonaceous aerosols [e.g., *Mylona*, 1996; *Lefohn et al.*, 1999; *van Aardenne et al.*, 2001; *Asman et al.*, 1988; *Ito and Penner*, 2005]. These inventories can be used as inputs to chemical transport models, thereby estimating historical concentrations and depositions of anthropogenic species. However, there are several uncertainties involved in this approach and the outcome of models needs to be validated against observations. Historic records of nitrogen and sulfur compounds in the European atmosphere are scarce and restricted to the most recent decades. SO_2 and sulfate background concentrations have been monitored in Europe at several sites since around 1980, for instance through the EMEP Programme (Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air pollutants in Europe). At a few European sites, total nitrate (nitrate aerosol plus nitric acid) and NHx (ammonia plus ammonium aerosols) have been sampled since 1990 but, even today, the spatial locations of such sites are mainly restricted to areas in central-west and north Europe. Only a few continuous short-term deposition data sets are available [*Oden*, 1976; *Brimblecombe and Stedham*, 1982], but from 1955 to 1979, sulfate, ammonium and nitrate wet deposition data were collected within the European air chemistry network

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[*Söderlund and Granat*, 1982; *Rodhe et al.*, 1984; *Söderlund et al.*, 1985].

[3] In addition to these atmospheric data covering the recent decades, numerous long-term trends of sulfate, nitrate and ammonium have been extracted from Alpine ice cores. The first advantage of such records is that they extend back to the preindustrial era. Second, the vertical distribution of pollutants in the atmosphere is an important constraint for chemical transport models and atmospheric data gained at such high-elevation continental sites are useful for analysis of model dynamics. Alpine ice cores are well suited for the purpose of reconstructing past atmospheric concentrations as they are surrounded by highly populated and industrial European areas. Unfortunately, several studies have shown that for such small areas the snow accumulation characteristics of glaciers, and their changes upstream to the drill sites, can affect the quality of the ice records in view of reconstructing past atmospheric changes [*Preunkert et al.*, 2000]. For instance a key point is the separation of winter and summer trends that are representative of different air masses (tropospheric background in winter versus boundary layer in summer). One of the aims within the CARBOSOL project [*Legrand and Puxbaum*, 2007] is to evaluate the extent to which ice core records obtained at a high-elevated Alpine site can help to constrain poorly known past emission inventories of carbonaceous aerosols. In this paper we examine ice core trends of major inorganic aerosols at the Alpine site Col du Dôme (CDD, 4250 m above sea level, French Alps) in the light of model simulations. We simulate summer and winter atmospheric concentrations of sulfate and ammonium over the 1920–2003 time period by using the regional EMEP model and past emissions inventories of SO_2 and NH_3. Here summer is defined as April-September in the modeling and winter as October to March. The summer/winter criteria for observations are discussed in section 2.1. The ammonium in the ice cores originates both from gas phase ammonia and particle ammonium (NHx), and the sum of the species have been extracted from the model calculations in the comparison of model results and inverted ice core concentrations. However, the fraction of ammonia is very low (model calculations give around 5%), thus it is basically a comparison of ammonium aerosol concentrations.

[4] The model calculations also consider past changes of NO_x, CO and VOCs. Simulated concentrations are first compared to present-day atmospheric observations made in recent years at the Vallot Observatory (VO), located nearby the CDD ice core drill site. Thereafter, simulated trends of atmospheric concentrations are compared to winter and summer ice core records which were inverted into historical atmospheric concentrations by using local firn to air (FAR) relationships established by *Preunkert et al.* [2001] for present-day summer and winter conditions. Further, the influence of the variability in meteorological conditions on atmospheric concentrations is investigated. By establishing so-called source-receptor relationships from model calculations, source apportionment is achieved at CDD as well as at another alpine drill sites located further east, CG, where ice records are also available but far less seasonally resolved than at CDD. Finally, an attempt is made to investigate the accuracy of past emission inventories of elemental carbon in the light of the long-term trend of this carbonaceous aerosol component extracted by *Legrand et al.* [2007] in the CDD ice cores.

2. Observations

2.1. Ice Core Records

[5] The main characteristics of the CDD ice core records we use here have been presented by *Preunkert et al.* [2000]. The dating of the CDD ice core was established by counting annual layers along the ammonium profile and using various time horizons. Time horizons are gained from ^{137}Cs measurements which permit identification of the 1986 (Tchernobyl event) and those of 1954 and 1963 (atmospheric nuclear tests) layers as well as the calcium record of Saharan dust horizons (1997, 1947, and 1936/1937). The annual layer counting was found to be in good agreement with the three ^{137}Cs horizons suggesting a precise dating (±1 year) over the 1954–1994 time period. On the basis of Saharan dusts events, it was shown that the uncertainty in snow deposits from 1925 to 1954 is ±5 years. Each annual snow layer was divided in two parts corresponding to winter and summer snow accumulation. The dissection cutting has been based on the ammonium profile [*Preunkert et al.*, 2000]. The frequency distribution of ammonium concentrations in the upper part of the CDD ice core (covering the 1981–1994 time period) indicates a bimodal distribution with a low concentration mode below 10 ppb and a second mode centered on 200–300 ppb. The boundaries of the winter half year snow pack have been identified by requiring at least 3 consecutive samples to significantly exceed the 10 ppb level.

[6] At CG, no seasonal dissection was attempted but CG snow deposits are usually made by summer layers, because of the preferential loss of winter snow by wind erosion at this site [*Wagenbach et al.*, 1988].

2.2. Present-Day Measurements

[7] In order to gain reliable year-round data on the chemical aerosol composition above 4000 m elevation, an automatic aerosol sampler was developed and deployed since 1999 at VO (4360 m a.s.l., French Alps) located close to Col du Dôme [*Preunkert et al.*, 2002]. The flow rate of the device is 3 L STP per minute and each aerosol sample covers 7–10 days in summer and 20 days in winter.

[8] These atmospheric data were also useful to investigate FAR relationship needed to invert ice core data in terms of atmospheric concentrations (see section 8).

3. Emissions

3.1. Anthropogenic Inorganic Emissions

[9] Anthropogenic emission data of SO_2, NO_x, NH_3, CO and VOCs from 1980 to 2003 used in the model simulations are based, as far as possible, upon emissions officially reported per emission sector and grid by Parties to the Convention on Long-Range Transboundary Air Pollution [e.g., *Vestreng et al.*, 2004]. For the period prior to 1980, we have used three different sources of information. For CO, NH_3 and VOCs, historic emissions estimated by *van Aardenne et al.* [2001] were available globally per sector on a $1 \times 1^\circ$ resolution. The EDGAR-HYDE sectors used by *van Aardenne et al.* [2001] were converted to emissions per

country and to the emission sectors used by EMEP, the so-called SNAP system (Selected Nomenclature for Air Pollution [*Vestreng and Klein*, 2002]). Scaling factors per country and sector were used to scale the EMEP 1980 emissions backward in time, but ensuring that the country totals are kept. In this way, the better resolution ($\sim$50 $\times$ 50 km^2) of EMEP data could be kept along with the evolution of the historic emissions. In the data from *van Aardenne et al.* [2001], spatial distribution over the years are only different when the relative amount within the sectors change. Thus we lose no information when applying only the scaling factors as the sector information is kept. For SO_2 and NO_x we used the emissions from *Mylona* [1996] and V. Vestreng and A. Semb (Nitrogen oxides emission inventories over Europe since the pre-industial era, manuscript in preparation, 2007), respectively. Emission scaling factors were defined in the same way as for NH_3, VOCs and CO. The historical emissions for NO_x and SO_2 were available from 1880 to 1985, for the countries with country borders as they were historically. For instance, emissions are not available separately for the countries within the former Soviet Union. Therefore the countries in the former Soviet Union are scaled with the same factor. East and West Germany are scaled separately back to 1950, but as the sum before. The areas corresponding to Czech Republic and Slovakia are scaled with emissions for former Czechoslovakia. Slovenia, Croatia, Bosnia and Herzegovina, Serbia and Montenegro and the Former Yugoslav Republic of Macedonia are scaled by using the historic emissions of former Yugoslavia. 5% of the SO_2 emissions were assumed to be primary sulfate emissions based on measurements of primary emissions of particulate sulfate in the mid-70s [*Shannon et al.*, 1980]. The different sources of sulfur emissions show large variability in emitted fraction of sulfate, thus the fraction has probably changed somewhat over the years. However, since there is not enough data to give a description of the changes in the primary sulfate emission fraction during the last hundred years, we have kept this estimate for the full period.

[10] Emissions are distributed temporally according to monthly and daily (Sunday to Saturday) factors derived from data provided by the University of Stuttgart (IER). These factors are specific for each pollutant, SNAP sector and country, and thus account for, e.g., the very different climates and hence energy use patterns in different parts of Europe. For instance, SO_2 emissions from combustion in energy and transformation industries (stationary sources), which are the largest sector for SO_2, are typically a factor 2–3 higher in winter than in summer for northern European countries, and typically more uniform over the year for southern European countries. In contrast, ammonia emissions, which predominantly originate from agriculture activities, peak in early spring, with an additional peak in autumn for countries that have two sowing seasons.

[11] The heights of the stacks have changed significantly during the last century, which we have taken into account by defining a "tall stack" period (from 1955 to present-day) and a "low stack" period (prior to 1955). In the "tall stack" period, the power plant emissions are assumed to have effective emission heights between 180–1100 m, with the peak of the distribution of effective emission heights of about 400 m. In the "low-stack" period, the emissions from power plants and industry in each model layer are moved one model layer closer to the ground, corresponding to a peak in the effective emission height distribution of about 200 m.

3.2. Elemental Carbon (EC) Emissions

[12] Elemental carbon (EC, or black carbon (BC); the terms are often used interchangeably, and are difficult to define [e.g., *Gelencsér*, 2004]) is an important component of the carbonaceous aerosol. The EC data used in the 2002 simulation is based on a new inventory for annual national emissions developed by *Kupiainen and Klimont* [2007]. Estimates of EC, organic carbon (OC) and PM_1 emissions were based upon an extensive review of the literature, and further checked for consistency with estimates of fine PM included previously in the model. This inventory is identical to that used in the CARBOSOL carbonaceous modeling studies [*Simpson et al.*, 2007; *Tsyro et al.*, 2007].

[13] The data assembled for the historical SO_2 and NO_x inventories discussed above, together with additional activity statistics, were combined with appropriate emission factors for EC. The range of emissions factors for EC found in the literature varies considerably, however (factor 10 or more [e.g., *Cooke et al.*, 1999; *Bond et al.*, 2004; *Kupiainen and Klimont*, 2007]), and so the inventories for EC must be acknowledged to have considerably greater uncertainty than those for SO_2 and NH_3. Our base estimate for 1985 is based upon the *Bond et al.* [2004] emission factors, being the most up to date compilation at the time this study was undertaken, but we additionally consider the variation in emissions factors for the road transport sector. The emission estimates up to 1985 in this study are considered to come from combustion without emission control. The highest emission factors for EC occur for diesel vehicles, followed by hard coal combustion in rail traffic and burning of wood in fireplaces.

[14] Two emission estimates for elemental carbon have been used, one with constant emission factors over time (denoted EC-C), and one where emission factors for road transport are allowed to increase backward in time, from 1985 to 1965, by up to a factor of five, following *Novakov et al.* [2003] (denoted EC-V). Thus the EC-C and EC-V estimates are identical (based upon *Bond et al.* [2004]) for 1985, but they differ substantially around 1970, when the combination of high traffic density and high emission factors leads to maximum emissions.

[15] Open biomass burning (OBB, including forest and agricultural fires) are not implemented in the standard EMEP model used here. *Gelencsér et al.* [2007] performed a source apportionment of $PM_{2.5}$ organic aerosols over Europe and found median contributions of EC from biomass burning to be about a factor 20–35 lower than the contributions of fossil fuel origin at three different CARBOSOL mountain sites (Puy de Dome, Schauinsland and Sonnblick) in summer. In winter, the contribution was somewhat higher (factor 6–15), but EC from fossil fuel combustion was still predominant.

[16] Using the emission factors suggested by *Andreae and Merlet* [2001] would suggest changes in sulphate, ammonium and EC from OBB of similar orders of magnitude. Thus we conclude that although forest fires may make significant contributions on an episodic basis to concen-

Table 1. European Emissions of EC, 1920–1985, Used in the Calculations[a]

Year	Residential/Domestic Combustion (S2)	Road Traffic (S7)	Other Mobile Sources (S8)	Total
1920	471	0.4	83	632
1930	466	40	107	707
1940	443	72	104	723
1950	442	142	113	794
1960	427	450	123	1148
1970	328	792	158	1429
1980	257	616	271	1265
1985	253	325	259	949

[a]Estimate EC-V, with variable emission factors, see section 3.2. Total includes S2, S7, S8 plus other emission sectors. Units Gg. Labels in parentheses refer to emission SNAP sector codes.

trations over Europe, and likely to the Alpine region, the available evidence suggests that European OBB emissions make only small contributions at CDD on the basis of a full summer or winter average.

[17] The annual emissions calculated using method EC-V are shown in Table 1. The European total EC emissions increase from 630 Gg in 1920 to 950 Gg in 1985, and a maximum of 1430 Gg was reached around 1970. On a global scale, the emission inventories from *Ito and Penner* [2005] and *Novakov et al.* [2003] show a gradual increase with emission peaks late in the 1980s and 1990s, in contrast to our estimated emissions which peak around 1970. However, the steepest increase was found outside Europe, namely in China, thus the European and the global trends are hardly comparable. *Novakov et al.* [2003] estimated a factor 4 decrease for Great Britain between 1950 and 1980, which is not far from our estimate (factor 3 decrease).

[18] The moderate trend in our emission estimate masks large changes in especially the transport sectors. Emissions from road transport (denoted S7) increase from less than 0.4 Gg in 1920 to almost 800 Gg in 1970 and 325 Gg in 1985. Emissions from other mobile (denoted S8) sources (including railways), increase from ~80 Gg in 1920 to 260 Gg in 1985.

[19] The residential sector (S2) is the far most important of all EC emissions up to approximately 1960, and indeed dominates completely the year 1920 estimate. EC emissions level off from around 1950, followed by a decrease by a factor of 2 from about 1960 as a result of phasing out of coal burning in the residential sector in EU-15 countries and in Scandinavia. In the same period the road (S7) and off-road (S8) emissions increase as a result of increased availability of oil, and a huge increase in the transport of goods and passengers. The emissions of wood burning were found to be relatively constant, at about 60 Gg, throughout the period of the study (because of a fairly stable rural population), hence the relative importance of wood burning emissions are larger for earlier years.

[20] In total, emissions from stationary sources (basically all emissions except emissions in the transport sectors S7 and S8) decrease somewhat from ~550 Gg in 1920 to 370 Gg in 1985. The different trends in the transport sectors and emissions from stationary sources are important because of the different seasonality of the emissions: road traffic and other mobile sources emit at rather constant rates over the year, whereas stationary sources have much larger emissions in wintertime. For instance, emissions from the residential sector (S2) are a factor 5–8 larger in winter than in summer. Thus the change in emissions will impact summer and winter concentrations of EC differently.

[21] Unfortunately, the emission estimate for 2000 and the historical inventory for 1920–1985 were developed by different groups and with somewhat different input data. The year 2000 inventory [*Kupiainen and Klimont*, 2007] has the advantage of using highly detailed statistics on fuel usage and activity data that were simply not available for the historical emissions work. Total European emissions in the historical inventory for 1985 were ~950 Gg, whereas emissions for the year 2000 inventory were ~680 Gg, i.e., a reduction of ~30%.

3.3. Natural Emissions

[22] Biogenic emissions of dimethyl sulfide (DMS) are implemented in the model as monthly averaged emission data derived from *Tarrasón et al.* [1995]. These DMS emissions are treated as SO_2 as inputs to the calculations. Sulfur emissions from volcanoes are included for Italy and treated as point sources at a height determined by the altitude of the volcanoes. Emissions of NO_x from lightning are included as monthly averages on a T21 ($5.65 \times 5.65^\circ$) resolution [*Köhler et al.*, 1995]. Biogenic emissions of isoprene and monoterpenes are calculated as a function of land use, temperature and solar radiation, using procedures detailed in *Simpson et al.* [1999, 2003a].

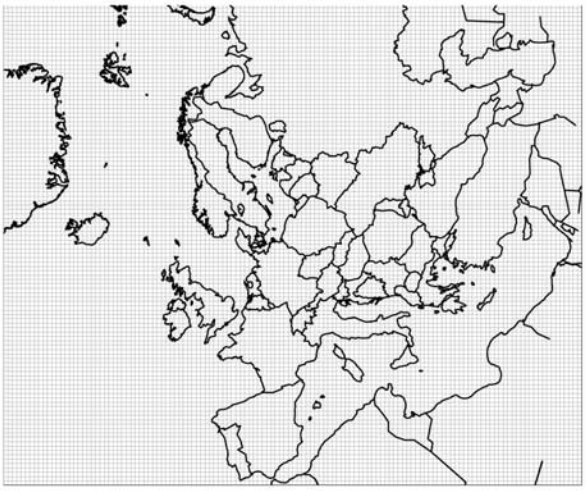
3.4. Ship Emissions

[23] Total releases of SO_2, NO_x, NMVOCs and CO from ship traffic in the Atlantic Ocean, North Sea, Baltic Sea, Black Sea and Mediterranean Sea are used following *Lloyd's Register of Shipping* [1995, 1998, 1999]. These estimates are of the same magnitude as those derived by ENTEC (Environmental and Engineering Consultancy) for 2000 [*Whall et al.*, 2002], thus we assume that they are valid for 2000. In the model calculations we have assumed a 2.5% increase per year, consistent with the increase of international shipping emissions from 1995 to 2000 in the work by *Endresen et al.* [2003]. The ship emissions of SO_2, NO_x, NMVOCs and CO in the period from 1920 to 1975 have been assumed to be directly proportional to the register tons related to the steam and motor ships as detailed by *Mitchell* [1981].

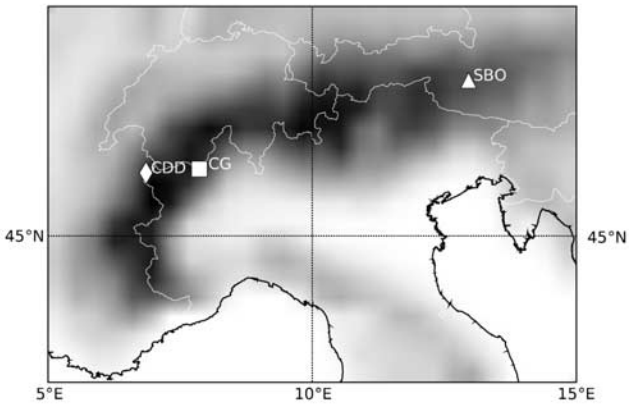
4. EMEP Unified Model Calculations

4.1. Model Description

[24] The Eulerian EMEP model is a multilayer atmospheric dispersion model designed to simulate the long-range transport of air pollution over several years. The model is fully documented by *Simpson et al.* [2003a] and *Fagerli et al.* [2004] and some applications of the model are given by *Fagerli et al.* [2003], *Simpson et al.* [2006a, 2006b] and *Fagerli and Aas* [2007] for sulfur and nitrogen species and by *Jonson et al.* [2006] for ozone and NO_2. The model domain is centered over Europe but also includes most of the North Atlantic and the north polar regions (Figure 1). The model has 20 vertical layers in σ coordinates below 100 hPa. It is primarily intended for use with a horizontal resolution of ~50 km × 50 km (at 60°N) in the



(a) EMEP model domain



(b) Location of CDD, CG and SBO

Figure 1. EMEP model domain used for this study and the location of CDD, CG and Sonnblick (SBO).

EMEP polar stereographic grid. The model uses meteorological data from PARLAM (PARalell version of HIRLAM) [*Benedictow*, 2002], a dedicated version of the operational HIRLAM model (High Resolution Limited Area Model) maintained and verified at MET.NO. The chemical scheme includes about 140 reactions between 70 species. SO_2 is oxidized to sulfate both in gas phase with OH and in aqueous phase through H_2O_2, O_3 and O_2 catalyzed by metal ions, assuming a fixed pH value of 4.5. The sulfur chemistry is coupled to the photochemistry, thus changes in the oxidation capacity may change the SO_2 oxidation rate and vice versa. The partitioning between NH_3 and ammonium aerosols is calculated by using the EQSAM module detailed by *Metzger et al.* [2002a, 2002b]. The dry deposition module makes use of a stomatal conductance algorithm originally developed for calculation of ozone fluxes, here applied in the model to all pollutants for which stomatal control is important [*Emberson et al.*, 2000a, 2000b, 2000c; *Simpson et al.*, 2001, 2003b; *Tuovinen et al.*, 2001, 2004]. Parametrization of the wet deposition processes in the EMEP model includes both in-cloud and subcloud scavenging of gases and particles, using scavenging coefficients.

[25] As a part of the CARBOSOL project, the EMEP chemical transport model has been extended to cover carbonaceous aerosol, including EC [*Simpson et al.*, 2007; *Tsyro et al.*, 2007]. Emissions, and wet and dry deposition are simulated in a similar way as sulfate, although with somewhat lower removal rates to reflect the more hydrophobic nature of EC. Using current emission levels, *Simpson et al.* [2007] and *Tsyro et al.* [2007] found fairly good agreement with current-day levels of EC at sites from the EMEP and CARBOSOL networks.

4.2. Boundary Conditions

[26] Boundary conditions (BIC) for a number of species are described with simple functions. These have been designed to enable concentration values that correspond to observations. The concentrations are adjusted in the vertical and for latitude and time of the year (monthly) to match the observed distributions. The annual cycle of each species is represented with a cosine curve, using the annual mean near-surface concentration, the amplitude of the cycle, and the day of the year at which the maximum value occurs. The parameters used to set the prescribed boundary conditions are described by *Simpson et al.* [2003a] and *Fagerli et al.* [2004].

[27] Our default BIC set is based on measurements from the period around 1980. To account for changes in the concentrations at the boundaries, we have applied two sets of scaling factors. The first set is used to scale the BIC for the years 1980–2003. The scaling factors have been defined on the basis of the EPA (U.S. Environmental Protection Agency) emissions (*U.S. Environmental Protection Agency* [2000] and updates on their web page, http://www.epa.gov) for SO_2 and NO_x emissions for the 1980–2003 period. Although U.S. NH_3 emissions have been relatively stable during this period, SO_2 emissions have decreased by more than 40% and NO_x emissions by approximately 20% (1980–2002, http://www.epa.gov), hence the trend in ammonium aerosol will be determined by sulfate and nitrate availability rather than by changes in NH_3 emissions [*Fagerli and Aas*, 2007]. Therefore the changes in BIC for ammonium aerosols were set by weighting the trend of SO_2 emissions with 2/3 and NO_x emissions with 1/3.

[28] The second set of scaling factors was developed for the period prior to 1980. In winter, CDD is located above the boundary layer most of the time and the source apportionment at present day, which will be presented in section 7, shows that in winter the dominant part of the sulfate (and nitrate) at CDD originates from sources located outside the western boundary of the EMEP domain. Therefore the changes in concentrations in the winter ice core data are a reasonable indicator of the trend in the boundaries and used as a scaling factor backward in time, relative to the prescribed 1980 levels. This is of course not fully true, as emissions from European emissions sources contribute to the deposition at CDD. Moreover, it limits the validation of our model results to summer values, when BICs are far less important. However, it is difficult to find alternatives. There are no other alpine ice core records with separate summer and winter values, and total year records would be inappropriate as contributions from European sources would be

Table 2. Summary of the Model Calculations

Set	Simulated Years	Meteorology	Emissions
	Sulfate and Ammonium		
1	–	1990, 1995–2003	1990
2	1920–1980 (every 10th year), 1985, 1990, 1995, 2000	1997	as appropriate
3	1920–1980 (every 10th year), 1985, 1990, 1995, 2000	2003	as appropriate
4	1980, 1985, 1990, 1995–2003	as appropriate	as appropriate
	Elemental Carbon		
5	2002	2002	2000
6	1920–1980 (every 10th year), 1985	1997	EC-V and EC-C, appropriate years
7	1920–1980 (every 10th year), 1985	2000	EC-V and EC-C, appropriate years[a]

[a]Three additional sets of calculations were performed using EC-V emissions and omitting emissions from sectors S2, S7 and S8 in separate runs.

large. The anthropogenic sulfate trend recorded in Greenland ice cores corresponds to SO_2 emissions from various regions, including North America and Eurasia, thus they do not either represent a unique North American sulfate signal. Another alternative would be to use historical global model calculations, but this was not available to us at the time when this study was carried out. In addition, the global model results also suffer from uncertainties in emissions, oxidation rates and model formulations themselves. Therefore we consider that using the winter CDD ice core data to set BICs represent the most robust approach.

[29] For ammonium, we used the trends of NH_3 emissions from United States derived from *van Aardenne et al.* [2001].

[30] For elemental carbon, background levels are assumed to be zero for this work. At the site Mace Head in Ireland, which is well suited to sampling air masses crossing the Atlantic from North America [*Cavalli et al.*, 2004; *Kleefeld et al.*, 2002], very low concentrations of EC are observed (typically 50 ng m^{-3}). *Gelencsér et al.* [2007] performed measurements of ^{14}C at Sonnblick in winter, at a sampling time where the station was most likely to be in the free troposphere, and found EC concentrations of 20 ng/m^3 STP. Compared to the typical summer values sampled at VO (40–50 ng m^{-3} STP) [*Legrand et al.*, 2007], the background would constitute around 40–50%. Although the conditions at Sonnblick were supposed to reflect the tropospheric background, the site might still be influenced somewhat from ground level sources, and the value can be regarded as an upper limit for the background contribution.

[31] In order to investigate the influence of the background values on the EC trends at CDD, the trend in the EC boundary condition values are also needed. However, the data needed to set a reliable trend in the EC boundary conditions are not available. EC ice core data from Colle Gnifetti exist [*Lavanchy et al.*, 1999], but these do not separate between winter and summer. Historical inventories for U.S. EC are available [e.g., *Ito and Penner*, 2005], but are very uncertain.

[32] We are aware that the assumption of zero EC background contribution does introduce some uncertainty in to the comparison of especially the wintertime trends in EC levels. However, rather than adding additional complexity to the comparison by introducing very uncertain parameters, we focus on the more certain summer values and discuss possible implications for the EC winter trends.

4.3. Choice of Model Layer

[33] There are several challenges when setting up a regional model to simulate atmospheric concentrations at high elevated Alpine sites. In winter, these sites are decoupled from the polluted planetary boundary layer and are representative of free tropospheric conditions. In summer, a more efficient convective upward motion of air masses from the polluted boundary layer enhances the atmospheric levels of pollutants. Consequently, concentrations are much higher in summer than in winter at these elevated sites, in contrast to surface concentrations that are more similar over the seasons.

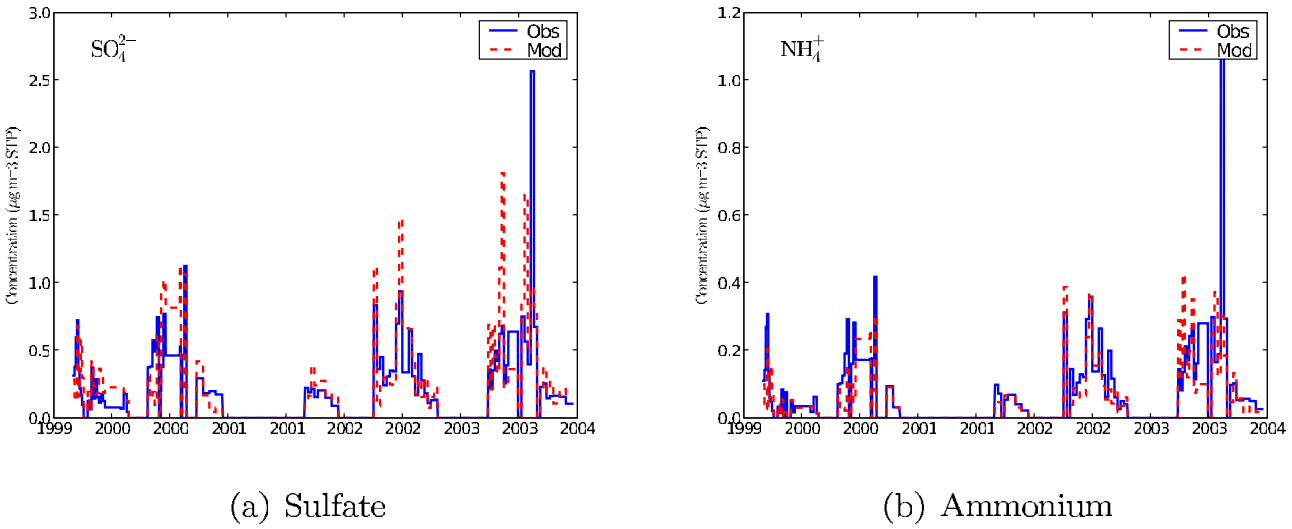
[34] The EMEP Unified model has a horizontal resolution of 50 km $\times$ 50 km and thus a rather rough topography. For instance, the grid cell representing the CDD site has a height of 1700 m above sea level. In the vertical, the model has approximately 10 layers within the boundary layer and 10 above (up to 100 hPa). The relative height of CDD is 2661 m, corresponding to model layer 10. Since the model does not resolve the fine-scale structure of the Mount Blanc massif, it does not take into account for instance local meteorological conditions leading to more vertical mixing than the model predicts at this height. Thus the model layer representing the air mass arrival pattern characteristic for CDD is most likely somewhat closer to the ground than suggested by using a direct calculation of the relative height.

[35] We used the air measurements available at the VO site (section 2.2) located close to the CDD ice core drilling site to decide which model layer is appropriate to be used. This was done by selecting the model layer that gave the best representation of the summer to winter ratio of concentrations, since this should reflect the relative height of the model layer compared to the topography. On this basis, model layer 13 ($\sim$3500 m) was adopted for model outputs.

4.4. Model Runs

[36] For sulfate and ammonium four different sets of simulations were performed (Table 2). Set 1 consists of ten runs using the same (1990) emissions but different meteorology (1990, and from 1995 to 2003). This set was designed to examine the impact of the meteorological variability on the ice core records at CDD.

[37] Set 2 uses the 1997 meteorology with emissions and boundary conditions for every tenth year from 1900 to 1980, plus 1985, 1990, 1995, and 2000. Set 3 is identical



(a) Sulfate (b) Ammonium

Figure 2. Comparison of simulated and observed concentrations (μg m^{-3} STP) of sulfate and ammonium at Vallot Observatory, 1999–2003.

to set 2 but with 2003 meteorology. These two sets simulate the trend from 1920 to 2000. Because no meteorological data are available back to 1920, we have used two different meteorological years to calculate historical concentrations. The meteorological years 1997 and 2003 were chosen for two reasons. Firstly, after considering the results from set 1, 1997 and 2003 stood out as two extreme years, giving the lowest and highest concentrations at CDD, respectively. Secondly source-receptor matrices were available only for the 2003 meteorology, thus the resulting simulated trend could be related to the sources for this year.

[38] Finally, set 4 uses appropriate meteorology, emissions, and boundary conditions for 1980, 1985, 1990 as well as 1995–2003, and therefore provides the most accurate results. These calculations have also been used in the comparison with available atmospheric data at the VO located close to the CDD drill site.

[39] Three additional sets of simulations were done for EC (Table 2). Elemental carbon at CDD is simulated for 2002 in order to compare with present-day observations of EC at CDD (set 5).

[40] Set 6 simulates EC concentrations for every tenth year from 1920 to 1980 plus 1985 using the 1997 meteorology. Set 7 is identical to set 6 but with 2000 meteorology. The effect of a likely change in emission factors over the past for road transport on the trends of EC is investigated by applying two different emission inventories (EC-C and EC-V, see section 3.2) in both sets. In addition, we estimated the contributions from the different sectors using the 2000 meteorology and the EC-V emissions in sectors S2, S7 and S8 in separate runs.

5. Present-Day Ammonium and Sulfate Levels at CDD

[41] Figure 2 shows the comparison between simulated (model layer 13, ~3500 m) and observed concentrations in air for sulfate and ammonium. The model captures very well the observations, both with respect to the seasonality and absolute levels. The lower summer (from April to September) to winter (from October to March) contrast for sulfate (a factor of less than 3) than ammonium (a factor of 4) seen in observations is also well reproduced by the simulations. This higher summer to winter ratio for ammonium than for sulfate can be explained by the different seasonality of the corresponding surface concentrations. Ammonia emissions result predominantly from agriculture activities, which peak in spring/summer time. Furthermore, the production of ammonium from ammonia is limited by the availability of sulfate and nitric acid (and air temperature), resulting in a rather constant summer to winter ratio of ammonium at the surface. In contrast, the majority of the SO_2 emissions stems from combustion in energy and transformation industries (stationary sources), which are higher in winter than in summer (typically a factor 2–3 in northern Europe, less in southern Europe), resulting in a winter maximum for sulfate surface levels. Therefore the enhanced transport in summer is counteracted by lower surface sulfate levels in that season.

6. Meteorological Variability

[42] Ideally, the calculation of long-term trends should be performed by using the meteorology of the actual years, and for each year up to recent time. In this way, change in weather patterns and interannual meteorological variability would also have been considered in the calculated trends. Unfortunately, there is no such historical archive available in the PARLAM-PS meteorology which we used as input to the EMEP Unified model. Therefore, in the historic calculations of trends we have used the same meteorological conditions for all the years. However, in order to investigate how large the meteorological variability is in the high-elevated Alpine regions, and especially the magnitude of the variability compared to the trends, we have performed a set (set 1, section 4.4) of calculations where we have kept emissions constant (1990 emissions) and varied the meteorology. The resulting sulfate concentrations at CDD, resolved on monthly basis, is shown in Figure 3. On a monthly basis the modeled concentrations vary by as much

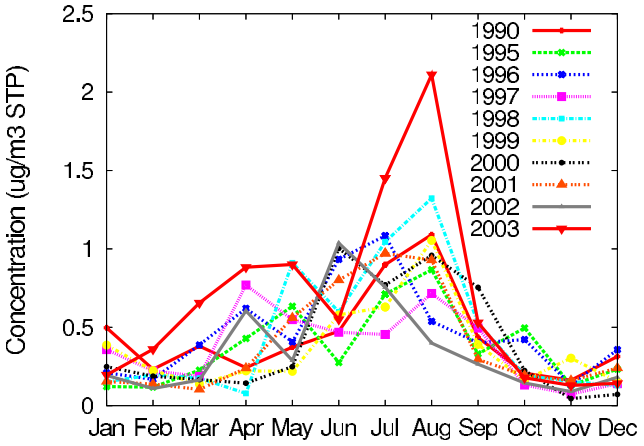


Figure 3. Variability in concentrations (μg m^{-3} STP) of sulfate due to meteorological variability at Col du Dôme. The different lines show the results using different meteorological years. All calculations are done with 1990 emissions.

as a factor of 5 from year to year. For instance the modeled concentrations of sulfate in August, based on 1990 emissions, vary between 0.4 and 2.15 μg m^{-3} STP. In January, the concentrations range from 0.15 to 0.50 μg m^{-3}. The large variability in concentrations caused by the different meteorology is seen for ammonium as well. Of course the impact of the meteorological variability is weaker (a factor of 2–3) when half year summer and winter concentrations, which correspond to the time integrated information extracted from the ice cores, is considered. Nevertheless the magnitude of the meteorological variability still remains significant with respect to long-term changes shown by ice records for the different components (an increase by a factor of 3 for ammonium and 6 for sulfate, see section 8).

[43] *Casty et al.* [2005] analyzed changes in temperature and precipitation in the Alps from 1500 to 2003. Temperature was shown to increase overall from 1900 to the present day, but the most remarkable feature was the much higher temperatures seen for the last 10 years of the reconstruction. The years 1994, 2000, 2002 and 2003 were the warmest years since 1500 in the greater Alpine region.

[44] Trends in precipitation were much less marked. Although some dry and wet periods do occur, the most obvious feature of the precipitation changes were the year to year variability over the last 100 years. Although it seems likely that trends in climate have some influence on the deposition of species at CDD, it is very difficult to assess this contribution. However, the fact that *Casty et al.* [2005] found no significant trends in precipitation amounts, and only moderate changes in temperature, over this period would suggest no dramatic change in air mass origins.

7. Present-Day Source Apportionment at CDD

[45] In this section we investigate the origin of pollutants arriving at CDD by analyzing source-receptor relationships (country to grid) for 2003. We refer to *van Loon et al.* [2005] for a technical description of these kinds of calculations. Numerous discussions on how to deal with source relationships in Eulerian models, for instance problems related to the nonlinear chemistry, can be found elsewhere [e.g., *Wind et al.*, 2004]. For example, reducing SO_2 emissions in one country may induce higher ammonia deposition there, but lower ammonium deposition in a nearby country since reduced sulfur may limit the formation of ammonium aerosols and thereby the long-range transport of ammonium. The source-receptor matrix for NHx is thus approximate, but the relationships should give a good indication of the relative contribution of different source areas.

[46] The year 2003 was a rather extreme meteorological year with respect to the summer conditions (very warm and dry summer in Central and South Europe, see *Beniston* [2004] or *Marmer and Langmann* [2007]). It has been shown [*van Loon et al.*, 2005] that the individual contributions from one country to another (or to a grid) can vary substantially for secondary inorganic aerosols from year to year. That is mainly true for the small contributions that in general correspond to inputs related to long-range transport. In contrast, the main contributions are more similar from year to year. For the European Alps, the average meteorological variability of the six largest transboundary contributions to the secondary inorganic aerosols was found to be around 20%.

[47] For sulfate in summer, Spain, Italy, France and Germany are found to be the largest contributors (in total ~50%) whereas other significant emission sources (e.g., from Great Britain, GB) are less important (see Figure 4). This supports the attempt made by *Preunkert et al.* [2001] in comparing the long-term trend of sulfate extracted from CDD ice cores with past SO_2 emissions from different countries.

[48] In winter, Spanish, Italian, French and German sources are still the main contributors. However, the individual contribution are smaller, and there are more countries that contribute to the concentrations. For example, for sulfate, the 4 largest contributors (Spain, Italy, France, Germany) accounts for around 50% of the total in summer against 18% in winter. This is again in agreement with the results from *Preunkert et al.* [2001] who found that the recorded increases of sulfate in winter at CDD from 1925 to 1994 matched better with the trend of emissions from total Europe and partly USA. The percentage contribution from the boundaries (mainly hemispheric transport from USA) is much larger in winter compared to summer. This is expected since CDD is a high-elevated site which receives much less pollution from European ground level sources in winter being above the boundary layer most of the time. The absolute contribution of the inorganic aerosols from the boundaries to CDD is approximately equal in summer and winter. This is a result of the boundary conditions for the inorganic aerosols which are essentially independent of altitude and season in the free troposphere, in accordance with observational data [*Warneck*, 2000]. Volcanic emissions also contribute to a substantial part of the observed concentrations in winter. The volcanic emissions are released directly into the free troposphere, thus they are less dependent on the boundary layer mixing, in contrast to anthropogenic pollutants.

[49] For NHx the source apportionment reveals a similar pattern as for sulfate but the contributions from Spain, Italy,

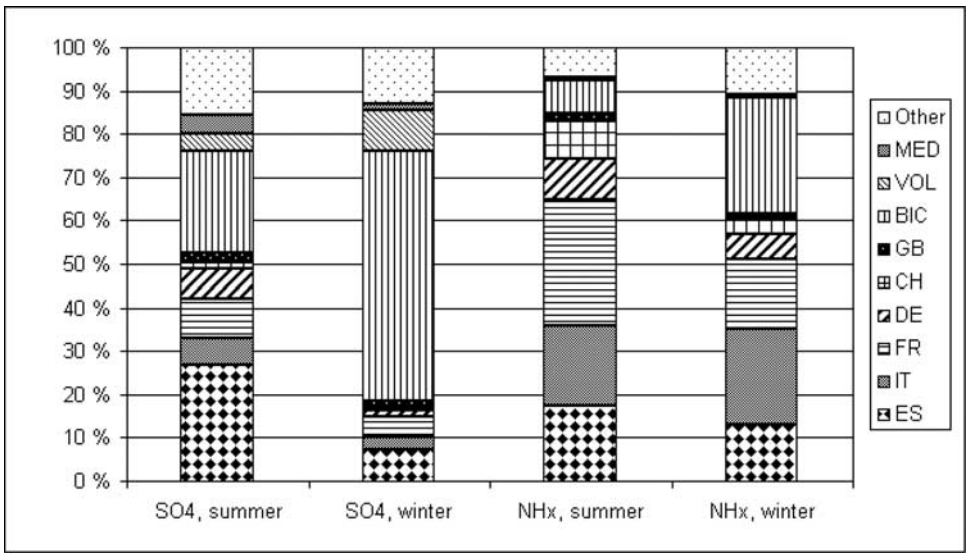


Figure 4. Source allocation for concentrations of sulfate and ammonium plus ammonia (NHx) for Col du Dôme for 2003: contributions from Spain (ES), Italy (IT), France (FR), Germany (DE), Switzerland (CH), Great Britain (GB), boundary conditions (BIC), international ship traffic in the Mediterranean Sea (MED) and volcanoes (VOL).

France and Germany are higher for NHx than for sulfate in summer as well as in winter. The reason is that whereas the concentrations of NHx and sulfate at the boundaries are similar (in volume mixing ratio), the strength of the emission sources of ammonia in these countries are stronger than for SO_2. For instance, France released 750 Gg NH_3 and 505 Gg SO_2 in 2003. Furthermore, there are no ammonia emissions from volcanoes or international ship traffic, which contributes significantly ($\sim$10%) to sulfate concentrations at CDD. In total, the sources close to CDD gain a larger weight in the source apportionment for NHx for 2003.

8. Historical Long-Term Trends of Inorganic Aerosols

[50] In this section we compare simulated past atmospheric concentrations of sulfate and NHx at CDD with corresponding long-term trends extracted from CDD ice cores.

[51] The seasonal FAR relationships investigated at CDD [*Preunkert et al.*, 2002] were used to invert the ice core concentrations to corresponding ambient air concentrations. These FAR values are, however, relatively uncertain. Furthermore, the dissection of annual snow layers into winter and summer snow layers relies heavily on the ammonium concentration criteria. As described in section 2.1, a criteria of 10 ppb has been used, and the absolute values of the winter ice core concentrations are relatively sensitive to this value, especially for ammonium. Moreover, these winter values represent "low" winter values as high episodes are excluded. The summer values are less sensitive to the ammonium selection criteria, as adding a small part of winter snow (with low concentrations) to the summer snow (with high concentrations) would have a minor influence of the total value. As a consequence, the absolute values of concentrations derived from the ice cores and the model simulated concentrations can be very different, especially for the winter values. Therefore we do not focus on the agreement of absolute levels but rather on the trends.

[52] Although the winter ice core data are more uncertain than the summer data, we have chosen to included both seasons. The comparison of model simulations and ice core data serves as a consistency check rather than a pure model validation.

8.1. Sulfate Trends

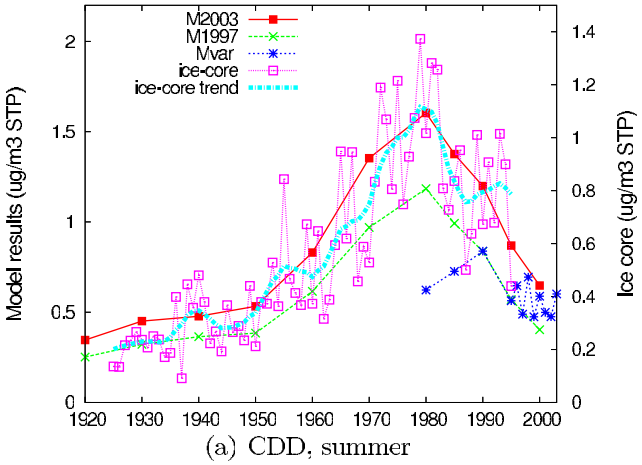
[53] As shown in Figure 5, the simulated trend using level 13 of the model (section 4.3) and the inverted summer ice core record are in excellent agreement with a weak increase between 1920 and 1950, a steep increase toward the maximum around 1980, and then a significant decrease over the last two decades. There is large interannual variability in the ice core values, partly because of meteorological variation (as can be seen from the 1980–2003 model results that has been performed with actual meteorological conditions), and partly because of uncertainty in the extraction of individual ice core values.

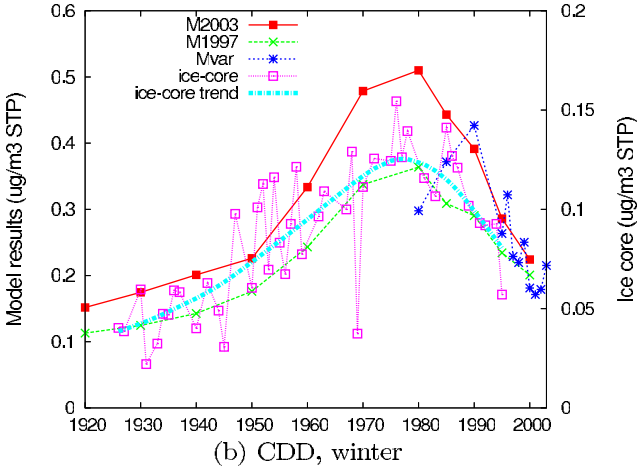
[54] As seen in Figures 4 and 6, the peak around 1980 can be explained by the large contributions from Spain, France, Germany and Italy (and the BIC) for which emissions peaked in the 1970s to 1980s, with the later peak being especially prominent for the largest contributor, Spain.

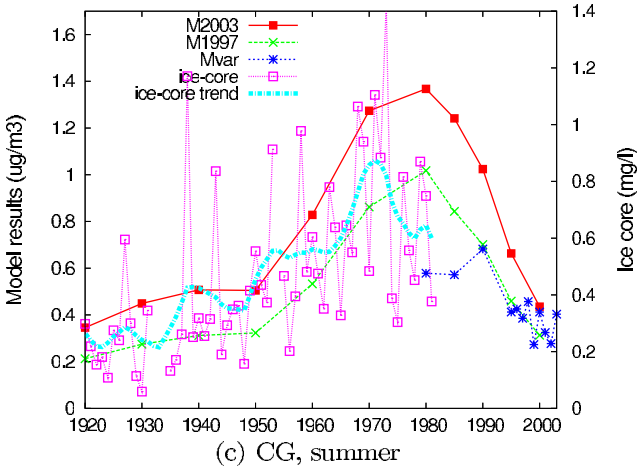
[55] The simulated winter trend in the ice core record at CDD for the period 1980–1994 agree very well with the trend extracted from the ice cores. The winter trend in the ice core record at CDD indicates a regular increase from 1925 to 1980, whilst in the summer record the increase from 1960 to 1980 is four times higher than in the previous period (Figure 5).

[56] In the previous section, we found that BIC (transport from USA), volcanoes and numerous small contributions from countries European wide make up the dominant input of sulfate at CDD in winter in 2003. Because the trend in BIC was set to match the trend in the winter CDD ice core

up to 1980, the similarity of the model simulations and ice core data for the period prior to 1980 is merely a confirmation that the influence of European sources in the earlier period have not been large enough to dominate over the BIC contribution.







8.2. NHx Trends

[57] As shown in Figure 7, the CDD ice core record show increasing ammonium concentrations in summer until around 1980 (a factor 3) and then a stabilization or a weak increase. This record is in good agreement with the model results which predict a maximum around 1980–1985 and an increase of a factor of 2.6 between 1920 and 1980, both for calculations using 1997 and 2003 meteorology (Figure 7). The general pattern of past ammonium changes, characterized by a maximum in 1980 followed by a plateau up to 1994, which contrasts with the sulfate trend, can be recognized in the historical NH_3 emission trends (Figure 6). However, emissions from all the countries that make significant contributions to the depositions at CDD increase only by a factor of two. Since the meteorological conditions in the two long-term modeled time series are constant, the higher enhancement of ammonium levels in the model results than in the NH_3 emission input suggests a higher rate of ammonium aerosol formation over the recent decades. Since the production of ammonium aerosols are limited by the availability of sulfate and nitric acid, for which concentrations have increased more than the ammonia emissions up to 1980, a larger proportion of NH_3 is converted to ammonium aerosols in 1980 than in 1925.

[58] For winter, the model calculations suggest an increase of a factor of 2.3 from 1920 to around 1980, somewhat smaller than the corresponding summer trend. The more moderate increase of levels in winter is probably caused by the higher influence of BIC. As described in section 4.2, the BICs prior to 1980 are scaled by the development of NH_3 emissions from USA, which amount to a factor of 2.2 between 1890 and 1980. Since the development of the chemical climate in USA has been similar to that of Europe (with increasingly higher SO_2 and NO_x levels throughout the century and thus a more efficient conversion of NH_3), the trends in the BIC should probably have been higher and the simulated trend of winter level is possibly somewhat underestimated. No obvious winter long-term trends of ammonium is seen in the CDD snow layers (Figure 7). However, the scatter of the individual values are as large as the expected trend, thus a trend cannot not be easily detected. This can also be noted from the model results for the later years when the meteorology for the actual years have been used. For instance, the difference between the modeled values for 2002 and 2003 are almost as large as the trend, despite the fact that the emissions used in the two runs are very similar. Secondly,

Figure 5. Comparison of modeled trends (model layer 13) and ice core records for sulfate at Col du Dôme (CDD) and Colle Gnifetti (CG). Dashed line with crosses is model simulations using 1997 meteorology (set 2), solid line with solid squares is model simulations using 2003 meteorology (set 3), dashed line with stars is model simulations using emissions and meteorology as appropriate for every year (set 4) dashed line with open squares is ice core record and thick dashed line is smoothed profile (first component of single spectra analysis with a 5-year time window). See section 4.4 for a description of the different sets. The ice core data have been inverted to air concentrations for CDD but not for CG.

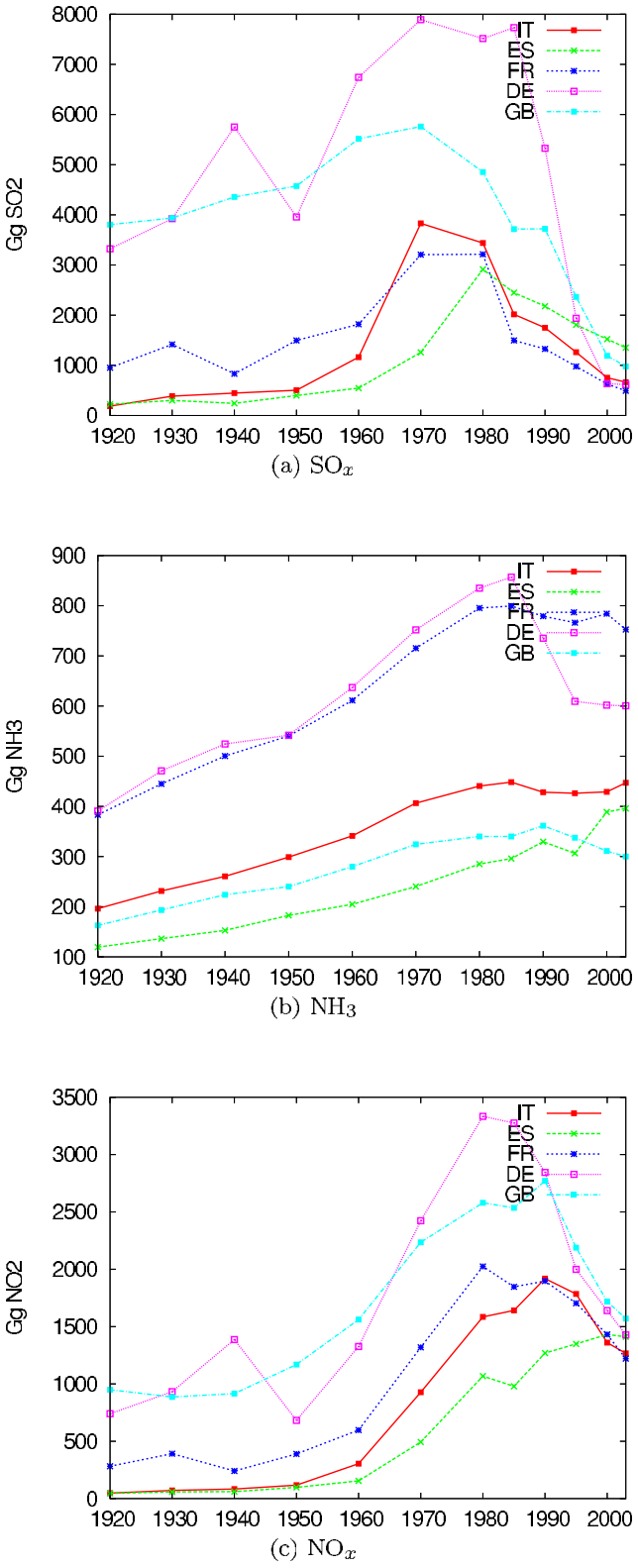


Figure 6. Emissions of SO_2, NH_3 and NO_x for Italy (IT), Spain (ES), France (FR), Germany (DE) and United Kingdom (GB) for 1920–2003.

the dating of the ice core (e.g., the definition of winter snow layers) is based on the ammonium stratigraphy, e.g., a part of the ice core is defined as "winter" when the ammonium levels are low [*Preunkert et al.*, 2001]. It is possible that this ammonium concentration criteria does not work very well for the more ancient part of the ice core when the ammonium concentrations are lower, and that small parts of summer snow are mixed into the winter layers. For sulfate, however, this would have a weaker effect because of the less pronounced seasonality of sulfate compared to ammonium. An alternative explanation for the increase in ammonium concentrations in the ice core from around 1960 and backward in time is that only a part of the winter snow is accumulated in the deeper part of the CDD ice core. *Preunkert et al.* [2000] found a systematic decrease in the winter to summer snow accumulation with increasing depth in the CDD ice core. The snow in the deeper part of the ice core originates from the slope upstream to the drill site, which is more exposed to wind erosion. It is therefore possible that the dry and cold winter snow is missing in the deeper part of the CDD ice core and that only winter snow from the mild periods, when the snow is more sticky, is collected. The fact that model simulations and the ice core data agree much better for the 1960–1994 period than for the 1925–1960 period indeed suggests partly incomplete winter snow deposition in the lower part of the CDD ice core.

[59] In conclusion, these comparisons between simulated past atmospheric concentrations and inverted CDD ice core records of major inorganic aerosol lead to rather consistent findings for both sulfate and ammonium. This is particularly useful for ammonium since estimates of past NH_3 emissions are a priory far more uncertain than those of SO_2.

9. Historical Long-Term Trends of Elemental Carbon Aerosol at CDD

[60] Compared to inorganic aerosols like ammonium and sulfate, less data on EC are available for CDD present-day atmospheric concentrations and in the ice core record. Furthermore no investigation of FAR relationship has yet been carried out for EC at the ice core drill site. Present day simulations (2002, albeit with year 2000 emissions) of elemental carbon at CDD give a summer average of 44 ± 46 ng m^{-3} STP. This result is in good agreement with the data collected at VO in 2004, which show typical summer values of 40–50 ng m^{-3} STP [*Legrand et al.*, 2007]. The model predicts lower levels in winter than in summer (8 ± 18 ng m^{-3} STP) at CDD but no present-day wintertime EC measurement data are available for comparison. As described in section 4.2, free troposphere EC values sampled at Sonnblick were around 20 ng m^{-3} STP. Since our EC boundary conditions are set to zero in these calculations, we probably largely underestimate the winter concentrations at CDD.

[61] Figure 8 shows the calculated trend for CDD and CG for the period 1920–1985 using 2000 meteorology. The absolute concentrations are somewhat higher (~20%) in the simulations where we have used 1997 meteorology, but the trends are similar.

[62] *Legrand et al.* [2007] found that the level of EC in summer CDD layers was enhanced from 4.2 ± 4.7 ngC g^{-1}

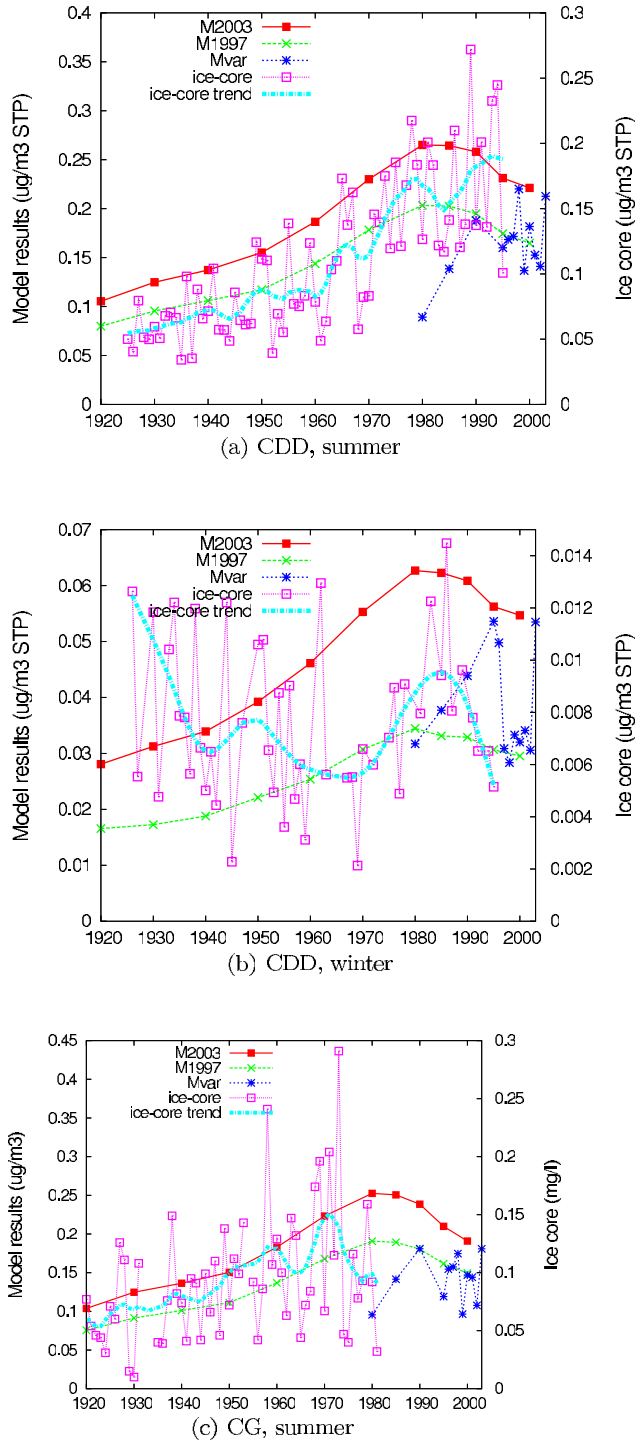


Figure 7. Comparison of modeled trends (model layer 13) and ice core records for NHx at Col du Dôme (CDD) and Colle Gnifetti (CG). Dashed line with crosses is model simulations using 1997 meteorology (set 2), solid line with solid squares is model simulations using 2003 meteorology (set 3), dashed line with stars is model simulations using emissions and meteorology as appropriate for every year (set 4), dashed line with open squares is ice core record and thick dashed line is smoothed profile (robust spline). See section 4.4 for a description of the different sets. The ice core data have been inverted to air concentrations for CDD but not for CG.

in 1925–1936 to 16 ± 7 ngC g^{-1} in 1962–1967, and tends to decrease again to ~10 ngC g^{-1} in 1989–1991. The EC-C simulations suggest rather unchanged atmospheric concentrations at CCD from 1920 to 1940 followed by a regular increase by a factor of two from 1940 to 1985 (Figure 8). These EC-C simulations therefore differ from the ice record with an absence of maximum around 1970 and a weaker long-term change. However, the assumptions made concerning variable emission factors for road traffic emissions (section 3.2) have a very strong effect on the simulated trends, especially for summer. The model simulations with the EC-V emission estimates predict an increase in EC levels of about a factor of 4–5 between 1920 and 1970, giving a better match between the ice core and modeled data (Figure 8). The latter results suggest that the EC-V emission estimates are more realistic, but they also illustrate the large uncertainties involved in these calculations.

[63] As seen in Figure 8, the simulated summer and winter trend at CDD using EC-V emissions are very different with a much lower increase in winter (a factor of 2 to 3) than in summer (a factor of 4 to 5) between 1920 and 1970. This difference is caused by the larger increase of mobile source emissions (S7 and S8) compared to the emissions from stationary sources since stationary combustion sources dominates in wintertime whilst the emissions in summer originates predominantly from mobile sources. Investigations of EC in winter CDD layers were limited to a few samples, but a similar level was found in 1982–1984 and 1937–1939 (2.4 ngC g^{-1} and 3.8 ngC g^{-1}, respectively) whereas the level in 1973–1976 was slightly higher (6.5 ngC g^{-1}) [*Legrand et al.*, 2007]. Although further studies are needed here to confirm such a more moderate long-term change in winter with respect to summer in Alpine ice core record, this is consistent with the model simulations. As discussed above, the assumption of zero EC boundary conditions is a major uncertainty in the calculation of winter EC concentrations at CDD. However, the consistency between the simulated and the ice core trend indicates that either the background levels have changed with the same trend as the influence from European sources, or, less likely, that the background level (boundary conditions) is a negligible source for the EC sampled at CDD.

[64] Another uncertainty in our model simulation for EC trends at CDD is the lack of inclusion of biomass burning in our emission inventories. A number of studies have shown that forest fire emissions from North America can have significant impacts over 1000s of km, including over Europe [*Forster et al.*, 2001; *Simmonds et al.*, 2005; *Stohl et al.*, 2006]. Indeed, during the extreme forest fire episode of August 1998, *Forster et al.* [2001] showed that Canadian forest fire emissions accounted for almost 60% of the enhancements in CO seen at the background sites of Mace Head, Ireland. Enhancements in black carbon at Mace Head were lower than those of CO (because of the greater washout of BC), but still significant compared to normal background concentrations. However, these papers have largely dealt with specific episodes, so do not allow a direct estimate of the OBB contribution to measurements at CDD. As discussed in section 3.2, *Gelencsér et al.* [2007] found EC from biomass burning to be minor compared to EC from fossil fuel for high-elevated sites at present day, especially in summer.

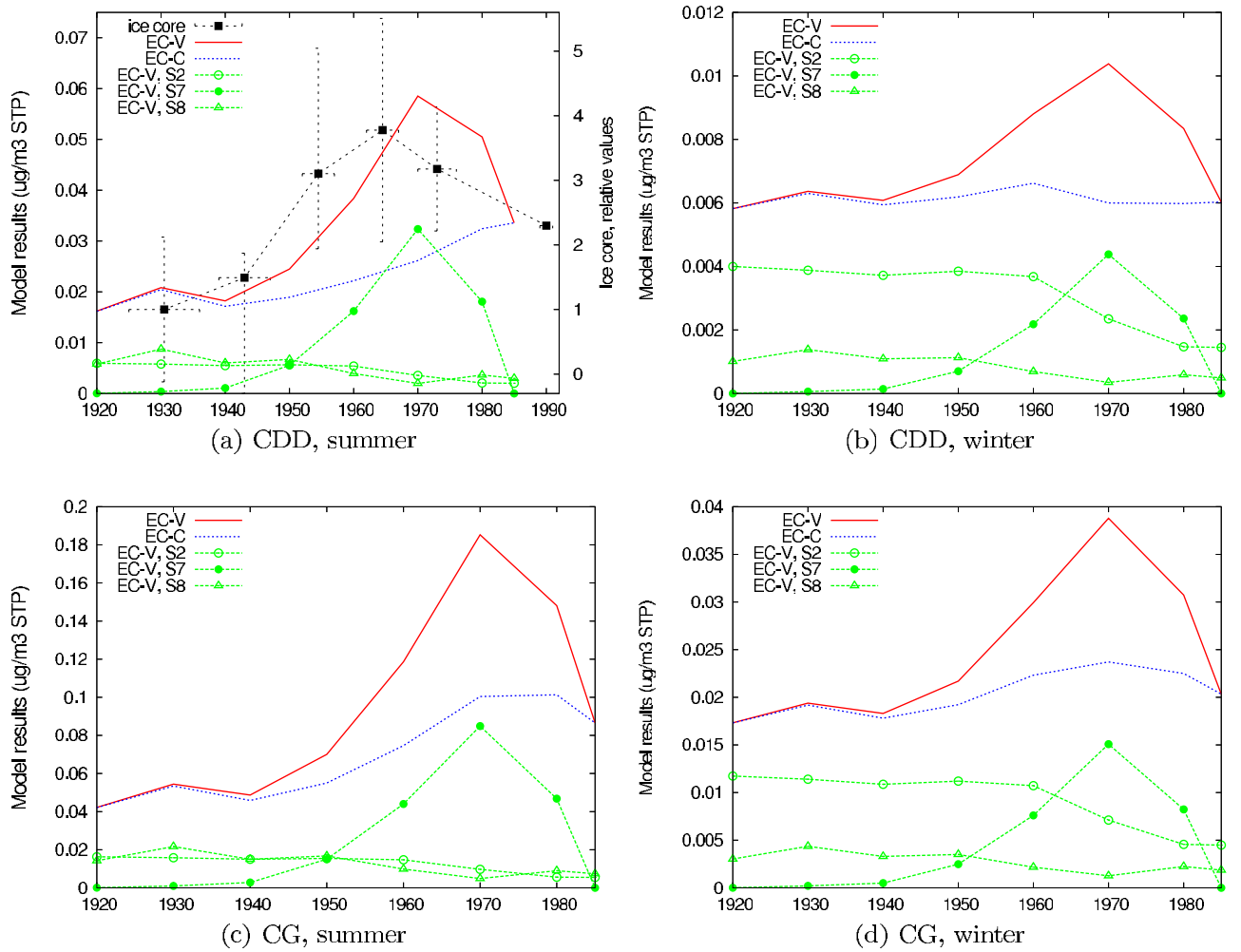


Figure 8. Modeled trends at Col du Dome (CDD) and Colle Gnifetti (CG), model layers 13, year 2000 meteorology. Solid line is total EC with varying emission factors (EC-V). Dotted line is EC with constant emission factors (EC-C). Dotted lines with marks show contributions from domestic emissions (open sector S2, open circles), road traffic (sector S7, with variable emission factors, solid circles), and from other mobile sources (sector S8, triangles). For CDD summer, ice core data are given relative to ~1930 (black, dotted line with solid squares). See *Legrand et al.* [2007] for absolute numbers and a detailed discussion of these ice core samples.

[65] Although estimates exist of the historical trends in anthropogenic emissions, including domestic biomass burning [*Ito and Penner*, 2005], it is harder to assess the changes in the contribution from wildfires to the trends over this period. A number of results suggest, however, that forest fire emissions have not contributed significantly to the observed trends of aerosol at CDD during the 20th century. Results presented by *Holdsworth et al.* [1996], based upon examination of NH^+_4, black carbon and concentrations of insoluble microparticles at ice cores in Greenland and Canada, suggest that the major period of biomass burning in North America occurred in the last half of the 19th century. Concentrations of all of these "marker" species (albeit imperfect) show little change from around 1920 to the end of the century.

[66] Thus, although forest fires may make significant contributions on an episodic basis to concentrations over Europe and likely the Alpine region, most likely neither European nor American OBB sources are responsible for the observed trends at CDD.

10. Comparisons With Another Alpine Ice Core at CG

[67] The source-receptor relationships presented in section 7 indicate that in summer Spain, France, Italy and Germany account together for 50% of total sulfate at both CDD (Figure 4) and CG (not shown). There are however some differences when moving eastward from CDD to CG; the Spanish and French contribution decrease but are compensated by increasing contributions from Germany and Italy. From Figure 6 we see that emissions from Germany and France were relatively constant between 1970 and 1980, whilst Spanish emissions maximized in 1980 and those from Italy in 1970. As a result the model predicts a maximum in summer sulfate levels in 1980 at both CDD and CG but the

increase between 1970 and 1980 is less pronounced at CG than at CDD.

[68] In Figure 5 we compare model simulations with the sulfate CG ice record. As seen from Figure 5, simulations and ice record are in reasonable agreement from 1920 to 1970. In the CG ice cores a rather sudden decrease of concentrations is observed after 1970. One reason for this difference with respect to CDD may of course be the lower influence of Spanish emissions at this site. However, there may be some differences in behavior of the snow packs also. At CG summer snow is mainly preserved whereas the dry snow in winter is strongly eroded by wind. It is possible that after 1970 the CG snow layers start to contain a small amount of winter snow, causing lower concentrations in the snow packs. Note that, when a careful seasonal dissection is applied to recent CG snow deposits, a good agreement is found for sulfate level for both summer and winter [*Preunkert et al.*, 2000].

[69] In contrast to the observations for sulfate, there is a large difference in elemental carbon concentrations simulated at CDD compared to CG (see section 9), the latter having concentrations some 5 times higher in summer (Figure 8). This difference in simulations arises from the rather large EC emissions from the Po valley in the vicinity of the CG site. As noted in section 3.2, summertime EC emissions are usually dominated by road traffic sources, and in the EMEP grids (including Milan) just northeast of CG emissions reach up to $\sim$500 kg km^{-2} yr^{-1}. Emissions on the French side of the Alps and around CDD are typically factors of 2–10 lower than this. As discussed by *Legrand et al.* [2007], ice core concentrations of EC are also almost 6 times higher at CG than at CDD in summer ice. The methods deployed to gain these ice core data were different at the two sites and can possibly lead to a difference by a factor of two at the best. Our simulations point out that this large difference between the two sites is more likely to be caused by the different impact from the emissions in the Po Valley.

11. Conclusions

[70] Previous studies of Alpine ice cores have relied on emission estimates available for annual timescales, and have had to make assumptions concerning the countries likely to contribute to the ice core trends. In this study the use of the EMEP chemical transport model allows for a more systematic evaluation of the sources contributing to a given site, and takes into account differences in both emissions and meteorological factors over the years. Furthermore, the model can account for nonlinear changes in the emission-deposition relationships, for instance due to changes in the oxidative capacity of the atmosphere or in the equilibrium between ammonium, sulfate and nitrate aerosols and nitric acid, sulfuric acid and gaseous ammonia.

[71] In summertime, the high Alpine CDD site lies within the boundary layer, and is subject mainly to European influences. In wintertime the site is usually above the boundary layer, and the influence of sources from outside our model domain is much larger, in particular for sulfate and most likely also for EC. The winter simulations for sulfate are to a large extent tied to the winter ice core values, as these are used to scale the inflow from the western boundary. In summer, the larger contributions from European sources give rise to a different trend with a greater increase of sulfate, especially in the 1960–1980 period, in good agreement with the ice core record.

[72] Both the NHx trend derived from the summer CDD record and the simulated summer trend show a higher enhancement of levels between 1920 and 1980 ($\sim$ factor of 3) than the ammonia emissions in surrounding areas ($\sim$ factor of 2). The model simulations indicate that these nonlinearities in the emission-deposition relationship can be explained by a faster conversion of gaseous ammonia to ammonium aerosols caused by higher availability of sulfuric acid and nitric acid resulting from the large increase of SO_2 and NO_x emissions during the last century.

[73] For EC, emissions in summertime are dominated by mobile sources. Therefore summer trends in the historical development of EC are driven much more by the emission trends for this sector than by trends in the stationary combustion sources. The combination of decreasing historical emission factors for vehicles and increasing road traffic leads to a maximum in EC emissions for road transport around 1970, which is reflected in the simulated EC trend and also in agreement with the ice core record.

[74] For the inorganic aerosols sulfate and ammonium the absolute levels, as well as the trends, are rather similar at CDD and CG. For elemental carbon, the model simulations demonstrate that the considerably higher concentrations ($\sim$ factor 6) in the CG summer ice compared to CDD at least partly can be explained by the vicinity of the CG site to the large sources in the Po Valley.

[75] Despite the large uncertainties in the emission data, especially for EC but also for NH_3, the agreement between model simulations and the ice core records is rather encouraging and indicates that the historical emission inventories are reasonable. This study also shows that the combination of historical inventories and modeling is a valuable tool when interpreting ice core trends and comparing data from different sites.

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