Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland)

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Abstract. Historical records of the concentrations of black carbon (BC) and elemental carbon (EC), as well as of water insoluble organic carbon (OC) and total carbon (TC) covering the time period ~1755–1975 are presented. Concentrations were obtained from an ice core of a European high-alpine glacier, using an optical and a thermal method. Concentrations were found to vary between 7 and 128 $\mu\text{g L}^{-1}$ for BC, between 5 and 130 $\mu\text{g L}^{-1}$ for EC, between 53 and 484 $\mu\text{g L}^{-1}$ for OC, and between 66 and 614 $\mu\text{g L}^{-1}$ for TC. From preindustrial (1755–1890) to modern times (1950–1975) BC, EC, OC, and TC concentrations increased by a factor of 3.7, 3.0, 2.5, and 2.6, respectively. The sum of BC emissions of Germany, France, Switzerland, and Italy, calculated from fossil fuel consumption, and the EC concentration record correlate well ($R^2 = 0.56$) for the time period from 1890 to 1975; this indicates that the ice core record reflects the emissions of western Europe. High pre-1860 concentrations indicate that by that time BC emissions to the atmosphere were already significant.

1. Introduction

Carbonaceous particles from combustion processes alter the radiation balance by absorbing and scattering light (direct effect) and by acting as cloud condensation nuclei (indirect effect) and may thus influence the climate [Intergovernmental Panel on Climate Change, 1995]. These particles have a mean atmospheric residence time of about 1 week [Ogren and Charlson, 1983]. Therefore their spatial distribution is highly inhomogeneous and strongly correlated to their sources. Over 90% of total fossil fuel is combusted at midlatitudes [Cooke and Wilson, 1996]. Biomass burning is the most important source in tropical regions, in savannas, and in boreal latitudes [Lioussse et al., 1996]. Carbonaceous aerosols are composed of three main fractions: organic carbon (OC), black carbon (BC) (or elemental carbon (EC)), as well as inorganic carbon (mainly carbonates). The black carbon fraction is strongly light absorbing and resistant to oxidation at temperatures below about 400°C. It has a polymeric structure resembling the structure of graphitic carbon but with chemical functional groups, so that this fraction has different properties compared to pure graphitic or elemental carbon [Penner and Novakov, 1996]. The separation may be performed thermally, optically, or by solvent extraction [Hansen et al., 1984; Cachier et al., 1989; Petzold and Niessner, 1995]. EC and BC define the same fraction of the carbonaceous aerosol but have a slightly different thermal, optical, and chemical behavior in most cases [Cachier, 1998]. These properties depend on the sources and atmospheric age of carbonaceous aerosols and are responsible for the high degree of complexity of their analysis. Depending on the separation technique,

the resulting fractions may be different. In the following, BC and EC always denote optically and thermally determined values, respectively. Total carbon (TC) is defined as the sum of EC and OC.

Cold glaciers and polar ice sheets are of interest as archives of the chemical composition of the atmosphere, as atmospheric constituents are deposited by wet and dry deposition and are accumulated in the ice [Wagenbach, 1989]. Polar ice core records have yielded long-term information about the changes of chemical and physical constituents of the atmosphere and reflect global emissions. From these ice core records the evolution of Earth's climate and the historic atmospheric composition over several hundred thousand years have been studied (e.g., see Hammer et al., [1997] and papers of the same issue). In contrast, high-alpine glaciers usually cover timescales of several hundred years because of their higher accumulation rates and their relatively small volumes. They are situated close to anthropogenic activity and are therefore assumed to represent the regional history of emissions, especially of species with short lifetimes such as aerosol particles.

Despite the climatic relevance of carbonaceous particles, historical records from ice cores are scarce [Cachier and Pertuisot, 1994; Chýlek et al., 1992], and none are available representing the history of the European source region. This study presents the first historic record of carbonaceous particle deposition over the last 200 years obtained from an alpine ice core, using an optical and a thermal method. Furthermore, we estimated emissions of carbonaceous aerosols from data of historical coal and petroleum consumption over the last 150 years for different European countries and compared them with our records.

2. Experimental

2.1. Ice Core Recovery and Sample Preparation

The investigated ice core was drilled close to the bedrock in 1982 on the glacier saddle Colle Gnifetti, Monte Rosa massif

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Figure 1. Map of central Europe. The circle shows the drilling site of the ice core.

(4450 m above sea level (asl), Switzerland (Figure 1). This ice core was 109 m long and 7.5 cm in diameter and was sealed in polyethylene bags in sections of 0.5- to 0.9-m length at the site. More details about glaciochemical studies at this site can be found elsewhere [Oeschger *et al.*, 1977; Haeberli *et al.*, 1983; Schotterer *et al.*, 1985; Wagenbach, 1989; Döschner *et al.*, 1995, 1996]. Dating of the ice core was performed using stratigraphic markers such as Saharan dust events, the atomic bomb horizon in 1963, and identified volcanic eruptions. The resulting time-scale was corroborated by continuous measurements of ^{210}Pb and by a simplified three-dimensional ice flow model [Döschner *et al.*, 1996]. For the time period 1883–1982 the uncertainty of dating is ~ 2 years, and for 1756–1882 the uncertainty of dating is ~ 5 years [Schwikowski *et al.*, 1999].

Several studies have already been performed on this ice core [Döschner *et al.*, 1995, 1996; Döring, 1999]. Since BC measurements need rather large amounts of ice, a continuous measurement of BC was not possible. Altogether, 54 ice section samples each consisting of up to six subsamples were analyzed. Data shown in this paper are averages of 50-cm sections and represent 37% of the ice core for the time period 1755–1982. The most recent sample (1968) covers a time period of 0.8 years, while the oldest sample (1759) covers a time period of 3.5 years. All samples were prepared in a cold room (-20°C) in a class-100 clean bench. The outermost layer of approximately 0.5-cm thickness was removed by chiseling with a scalpel. A second layer was chiseled from about 100 subsamples and collected for our measurements, while the inner part of the ice core was used for the analysis of heavy metals as described elsewhere [Döring, 1999]. For the other samples the outer layer was removed and the entire inner part of the ice core was used.

Samples (typically 80–200 g) were stored in precleaned polyethylene containers and allowed to melt at room temperature. Occasional shaking of the containers resulted in a better mix-

ing of the samples thus favoring a faster melting of the ice. Melting time was always less than 4 hours. Immediately after melting, the samples were weighed and then filtered through quartz fiber filters (Tissuequartz QAO 2500, Pall). The circular filters were 15 mm in diameter and were preheated for 2 hours in a tubular oven at 800°C . Filtration was performed using a glass unit and resulted in a circular spot of 8 mm in diameter. The containers were rinsed twice with approximately 10 mL pure water (MilliQ, 18 M Ω) to ensure complete transfer of the carbonaceous particles to the filter. Filtration efficiency was tested gravimetrically using suspensions of commercial soot samples (FW2, Degussa) and was found to be 95%. This value is in good agreement with literature data [Cachier and Pertuisot, 1994; Chýlek and Srivastava, 1987].

2.2. Optical and Thermal Methods

Figure 2 shows the optical apparatus for filter sample analysis used in this work. This device is a modified version of the aethalometer [Hansen *et al.*, 1984]. The attenuation of light transmitted through a sample is measured by a photodiode. Direct illumination of the filter by the lamp is avoided (see Figure 2). The inner surface of the lamp housing was white thus enhancing the reflection of light from the wall. A reproducible filter positioning was ensured by placing the sample in a slide. To compensate for the variability of the light beam, transmission through a reference filter was measured simultaneously. The attenuation (ATN) of the light beam intensity is defined as

$$\text{ATN} = \ln(I_0/I)100\%, \quad (1)$$

where I_0 is the measured light transmission through a reference filter and I is the measured light transmission through the sample. The experimental error originates from inhomogeneities of the filter material and of the particle deposition on the filter. In order to minimize the first error, the ATN of every precleaned filter was measured and used as a filter blank in the calculation. To minimize the second error, the ATN was measured 3 times, while rotating the filter between the measurements. The light slot was 6 mm in diameter.

ATN can be converted into an amount of black carbon BC (micrograms) using

$$\text{BC} = \frac{\text{ATN } A_s^2}{\alpha_{\text{API}} A_L}, \quad (2)$$

where α_{API} is the instrumental absorption efficiency [$\text{m}^2 \text{g}^{-1}$] of black carbon aerosol particles deposited on the filter, A_s

Figure 2. Schematic of the optical apparatus.

(0.50 cm²) and A_L (0.28 cm²) are the surface areas of the sample spot and the filter illuminated by the light source, respectively. The calibration factor α_{API} has to be determined independently, using for example, a thermal and an optical measurement of the same sample. Several studies have shown that for different sites and for different seasons α_{API} may vary considerably [Lioussé *et al.*, 1993; Petzold *et al.*, 1997]. This topic will be discussed in detail in section 3.3.

Filter blanks were determined by filtering 20 mL pure water (MilliQ, 18 M Ω) and were equivalent to -0.04 ± 0.05 $\mu\text{g BC}$ using an α_{API} value of 9.3 m² g⁻¹, as discussed below. Even though this blank value is not significantly different from zero, it may reflect changes in the filter material due to the filtering and analysis procedure. The detection limit, defined as 3 times the filter blank error, was hence 0.14 $\mu\text{g BC}$.

The thermal measurement used in this study is based on a thermal separation between OC and EC by a two-step combustion procedure [Cachier *et al.*, 1989]. The apparatus consists of a combustion unit, composed of two ovens in series, followed by a catalyst oven to ensure total oxidation of the combustion products and a total organic carbon analyzer (TOC700, O.I. Analytical), which accumulates the CO₂ produced during the combustion and measures it with a nondispersive infrared detector at the end of a combustion step [Lavanchy *et al.*, 1999]. This setup allows the measurement of the OC and EC contents of the same sample. In the first combustion step, OC was analyzed by oxidation in pure oxygen at a temperature of 340°C during 42 min, based on a procedure of Cachier *et al.* [1989]. To minimize charring, a flash heating (within less than 1 min) ensured a rapid heating to this temperature. The remaining carbon, defined as EC, was oxidized at 650°C. The method was optimized using aliquots of ambient aerosol samples for different precombustion temperatures and duration [Lavanchy *et al.*, 1999]. Possible pyrolytic conversion of OC to EC (charring) and possible loss of EC during the precombustion step are error sources of the thermal separation, caused by the variable chemical and physical properties of both compounds. As a consequence, the EC to OC ratio depends on the efficiency of the thermal separation. In contrast, the TC data have a higher accuracy, since TC is not influenced by this problem [Countess, 1990].

Combustion of carbonates may result in a positive EC artifact during the thermal measurements. The presence of carbonates in ice core samples is mainly due to CaCO₃ which in the Alps is often associated with Saharan dust events [Maupetit and Delmas, 1994; Wagenbach *et al.*, 1996]. Maupetit *et al.* [1995] found a mean HCO₃⁻ concentration of 22.1 $\mu\text{eq L}^{-1}$ (corresponding to 1.35 mg L⁻¹ HCO₃⁻) in a different ice core drilled at the Colle Gnifetti. At the EC combustion temperature of 650°C, dissociation of carbonates, for example, CaCO₃, may be neglected [Petzold and Niessner, 1995]. Nevertheless, to avoid possible positive EC artifacts, carbonates were removed prior to thermal analysis by pipetting 50 μL 0.1-M HCl 3 times onto the sample spot.

The detection limits of EC and OC are dominated by the variability of the blank loads of the precleaned filters, which were 1.74 ± 0.60 $\mu\text{g C}$ for OC and 0.38 ± 0.47 $\mu\text{g C}$ for EC. The detection limits were thus 1.81 $\mu\text{g C}$ for OC and 1.42 $\mu\text{g C}$ for EC, the latter being 3 times higher than the detection limit of the optical apparatus. All analyses were performed using both methods, since both methods have their specific advantages and disadvantages. Note that with the described

procedure only the water insoluble fraction of organic carbon is determined in contrast to the analysis of aerosol samples.

2.3. Analysis Procedure

The light attenuation of the filter samples was measured 3 times. ATN₀ was defined as the attenuation of the precleaned filter prior to sample filtration. The attenuation measured after the filtration was denoted ATN_S and resulted from the attenuation by black carbon and mineral particles. After thermal analysis, that is the determination of OC and EC, when the carbon content of the filter had been removed, ATN_E was measured to correct ATN_S for the contribution of mineral dust and the filter blank. This correction turned out to be important since the mineral particle content of ice core samples is several orders of magnitude higher than the black carbon content. Even though α_{API} of desert dust is about a factor of 100 smaller than α_{API} of BC [Hansen *et al.*, 1993], the contribution to the attenuation by mineral particles may still be significant. The attenuation due to black carbon (ATN_{BC}) is then

$$\text{ATN}_{\text{BC}} = \text{ATN}_S - \text{ATN}_E, \quad (3)$$

and the attenuation due to mineral particles (ATN_{MP}) is

$$\text{ATN}_{\text{MP}} = \text{ATN}_E - \text{ATN}_0. \quad (4)$$

As discussed in section 2.2, the experimental error of the ATN measurement mainly results from filter inhomogeneity. This error averages to 2.6%, and thus ATN_{MP} and ATN_{BC} have an uncertainty of 3.7%.

3. Results and Discussion

3.1. Attenuation of the Ice Core Samples

ATN_{BC} and ATN_{MP} were determined for each sample according to (3) and (4) and normalized to the sample volume. The values for the time period 1755 to 1975 are shown in Figure 3. It can be seen that the total attenuation increased after about 1890 and that this increase is caused by higher values of ATN_{BC}. ATN_{MP} does not show a significant trend, indicating that BC and mineral particles have different sources. This is consistent with the finding for Ca concentrations which do not exhibit a trend either [Schwikowski *et al.*, 1999].

ATN_{MP} accounts for 13% of the total attenuation, on average, with maximum and minimum values of 30% and 3%, respectively. Concentrations of Fe, Mn, and Ti determined in the same samples by inductively coupled plasma optical emission spectrometry after thermal analysis showed a good correlation with ATN_{MP} ($R^2 = 0.71$, $R^2 = 0.72$, $R^2 = 0.78$, respectively, and $N = 53$). Fe was the most abundant of these elements (93%), and the red-brown color of many samples was attributed to hematite (Fe₂O₃) [Schütz, 1989]. Fe₂O₃ is, besides black carbon, one of the few aerosol components that absorbs visible light. Assuming that all Fe consisted of Fe₂O₃ and that Fe₂O₃ accounted for 100% of ATN_{MP} and using the measured Fe concentrations, we derived an instrumental absorption efficiency for Fe₂O₃ of 0.13 ± 0.02 m² g⁻¹. When using quartz fiber filters in the optical apparatus, the efficiency of the particles is believed to be enhanced by a factor of about 1.9 because of multiple scattering [Bodhaine, 1995]. Using this factor, an absorption efficiency for suspended Fe₂O₃ particles of 0.07 m² g⁻¹ is obtained. Given that Fe₂O₃ amounts to about 6% of desert dust [Tomadin *et al.*, 1989], this value compares with the reported absorption efficiency for desert dust ranging

Figure 3. Stacked bar graph of the contribution of black carbon (BC) (ATN_{BC}) and of mineral particles (ATN_{MP}) to the total attenuation. The sums of ATN_{BC} and ATN_{MP} (dashed line) and ATN_{MP} (solid line) are shown as a running mean over three samples. Both a timescale and a depth scale in meter water equivalents are given.

between 0.005 and 0.07 $m^2 g^{-1}$ [Pinnick *et al.*, 1993]. Thus it is reasonable to assume that ATN_{MP} stems completely from Fe_2O_3 .

3.2. BC, EC, OC, and TC Concentrations in the Ice Core

As shown in (2), the BC values depend on the instrumental calibration factor α_{API} . The range of literature values for aerosol samples obtained with aethalometers is between 4 and 20 $m^2 g^{-1}$ [Lioussé *et al.*, 1993; Petzold *et al.*, 1997]. The high variability is attributed to changes in origin and in physical and chemical properties of the carbonaceous aerosols [Lioussé *et al.*, 1993]. To avoid large errors, a specific calibration is required, for example, analyzing the same aerosol sample with an optical and a thermal method.

In the following experiments we used a calibration performed with aerosol sampled by an aethalometer at the high-alpine site Jungfraujoch (Switzerland, 3454 m asl). The mean value over a 2-year sampling period yielded $9.3 \pm 0.4 m^2 g^{-1}$ [Lavanchy *et al.*, 1999]. This calibration was considered to be representative of high-alpine aerosol samples and was assumed to be appropriate for snow samples.

Figure 4 shows the measured concentrations of BC, EC, OC, and TC in the ice core samples along with 10-year averages for the time period 1755 to 1975. It can be seen that for the time period 1800–1850 the 10-year averages partly consist of only one sample. However, these samples also represent at least 2 years. Large fluctuations in concentrations of 1 order of magnitude are observed in all four records. The concentrations varied between 7 and 128 $\mu g L^{-1}$ for BC, between 5 and 130 $\mu g L^{-1}$ for EC, between 53 and 484 $\mu g L^{-1}$ for OC, and between 66 and 614 $\mu g L^{-1}$ for TC. The higher variability in the more recent samples is at least partly due to the shorter time averages and is the result of different efficiencies of vertical transport in summer and winter, which is the main process bringing polluted air from the planetary boundary layer (PBL)

to high altitudes [Baltensperger *et al.*, 1997; Lugauer *et al.*, 1998]. Correlation R^2 between the various parameters is generally high: 0.77 (OC-EC), 0.47 (OC-BC), 0.98 (OC-TC), 0.84 (TC-EC), 0.53 (TC-BC), and 0.81 (BC-EC).

The BC, EC, OC, and TC concentrations start to increase after 1890. Box plots in Figure 5 show the average concentrations, the minimum and maximum as well as the 95th, 75th, 50th, 25th, and 5th percentiles during the preindustrialized period (1755–1890), the beginning of industrialization in Switzerland until the end of the Second World War (1890–1950), and modern times (1950–1975). It can be seen that on average the BC, EC, OC, and TC concentrations increase from the first to the last time period by factors of 3.7, 3.0, 2.5, and 2.6, respectively. This increase is attributed to enhanced anthropogenic emissions and can be compared to the increase of sulfate concentrations reported for the same ice core, beginning in 1890. The sulfate concentration increased by a factor of 5.8 [Doscher *et al.*, 1995] between the periods 1850–1880 and 1965–1981. For the period 1890–1975, sulfate and TC concentrations exhibit a correlation coefficient $R^2 = 0.43$, reflecting the fact that both species have a common dominating source, that is, combustion. Before 1890 the correlation coefficient between the two species is $R^2 = 0.02$.

Compared to the EC and TC concentration records of the Greenland EUROCORE ice core [Cachier and Pertuisot, 1994], the measured EC and TC concentrations are higher by a factor of 10 to 20. This difference in concentration is attributed to the proximity of the Colle Gnifetti ice core to anthropogenic combustion sources.

3.3. Instrumental Absorption Efficiency α_{API}

For the whole record the EC concentration is comparable to the BC concentration. This indicates that as a first approximation the calibration of the optical apparatus with high-alpine

Figure 4. Ice core concentrations (dashed line) and 10-year averages (solid line) of organic carbon (OC), elemental carbon (EC), BC, and total carbon (TC) for the time period 1755 to 1975. BC concentrations were calculated using $\alpha_{\text{API}} = 9.3 \text{ m}^2 \text{ g}^{-1}$.

aerosol is also adequate for snow samples. However, there are small differences in the records.

The difference might be due to an underestimation of the EC concentration resulting from catalytic oxidation of EC during the precombustion procedure. Metal oxides (e.g., Mn and Fe) have been shown to act as soot oxidation catalysts under tight contact conditions [Lahaye *et al.*, 1994; Neeft *et al.*, 1996]. The mineral particles in our ice core samples contain significant amounts of metal oxides, such that a catalytic effect is conceivable. Lin and Friedlander [1988] showed that a similar catalytic effect reduced the oxidation temperature of EC during thermal analysis. However, we assume that the impact of this effect on our measurements is low since the trend of the EC record is in good agreement with that of the BC record ($R^2 = 0.81$, see section 3.2.) and since both records show comparable concentrations.

Alternatively, individual values of α_{API} were calculated using the ATN_{BC} and the EC measurements. Figure 6 shows that the resulting values of the 10-year averages vary between 2.1 and

$25.2 \text{ m}^2 \text{ g}^{-1}$. Slightly lower values were found prior to the twentieth century. The mean value of α_{API} over the entire time period was $10.5 \pm 4.8 \text{ m}^2 \text{ g}^{-1}$. This value is similar, to within the standard deviation, to measurements of high-alpine atmospheric aerosol.

Snow samples from the present, collected on the campus site of the University of Bern and at the high-alpine site Jungfraujoch (Switzerland, 3454 m asl), gave α_{API} values ranging between 5.1 and $9.7 \text{ m}^2 \text{ g}^{-1}$ (open circles and open and solid diamonds in Figure 6). These values are comparable to the last 10-year average of the ice core ($10.2 \text{ m}^2 \text{ g}^{-1}$).

The relatively good agreement between atmospheric aerosol and snow samples is interesting, since in the former the carbonaceous aerosol particles are assumed to be coated with scattering material, while in the latter the water soluble fraction of scattering material is removed. For in situ measurements of aerosol particles this effect is thought to reduce α_{AP} [Lioussé *et al.*, 1993; Cachier and Pertuisot, 1994]. From the present results one might conclude that this effect is of minor

Figure 5. Box plots for three different time periods. The minimum and maximum as well as 95th, 75th, 50th, 25th, and 5th percentiles of BC, EC, OC, and TC concentrations are shown.

importance when using a quartz fiber filter with its inherent multiple scattering. Note that this is not necessarily true for other filter materials.

However, the calculated α_{API} shows a pronounced variability over the whole record (Figure 6). This finding was compared with data from the Greenland ice core EUROCORE, where α_{API} was reported to vary between 9 and 31 $\text{m}^2 \text{g}^{-1}$ [Cachier and Pertuisot, 1994]. A significant difference was found between ice samples from the first half of the twentieth century, with α_{API} values ranging between 18 and 25 $\text{m}^2 \text{g}^{-1}$, and older ice samples, with α_{API} values ranging between 8 and 12 $\text{m}^2 \text{g}^{-1}$. Cachier and Pertuisot [1994] presumed that this variability results from the fact that different combustion sources dominated; that is, coal combustion dominated in the first half of the twentieth century, and biomass burning dominated in the nineteenth century. Following this assumption, coal combustion might explain our high α_{API} values during the

Figure 6. The calculated instrumental absorption efficiency α_{API} of the ice core samples (dashed line and shaded circles) and of 10-year averages (solid line). In addition, α_{API} measured for snow samples of surface snow from Bern on November 14, 1995 (open circles), of surface snow from Jungfraujoch on February 20, 1998 (open diamond), and of snow in 10-cm depth from Jungfraujoch on February 20, 1998 (solid diamond) are shown.

first half of the twentieth century. Note that all these values are given for α_{AP1} , and no corrections are made so far for possible enhancements due to multiple scattering in fibrous filters as described by Bodhaine [1995].

3.4. Comparison of Carbon Concentration and Estimated Emissions

We compared our ice core measurements with estimated BC and TC emissions from different European countries. The aim was to test to what extent our particulate carbon records represent the emissions from European countries.

Combustion of coal, wood, and petroleum products were the main sources of BC and TC in western Europe during the investigated period. Their relative contribution to the total emission changed with time. For Switzerland, wood combustion (87%) was the main type of energy production in 1850 [Bergier, 1978; Marek, 1992] and was therefore the main source of carbonaceous particles. Coal became the most important combustion fuel (80%) at the end of the nineteenth century and continued to be until petroleum products gained in importance after the Second World War [Marek, 1992; Bundesamt für Energiewirtschaft (BEW), 1987]. Presently, fossil fuel combustion accounts for over 99% of the emitted BC in western Europe [Cooke and Wilson, 1996]. In contrast, biomass burning, an important source in boreal latitudes and the tropics, is of lower importance in Europe during modern times [Lioussé et al., 1996].

Because of the short residence time of carbonaceous particles in the atmosphere, we restricted our study to the countries surrounding the ice core site, that is, Switzerland, Italy, France, and Germany, and to the main sources. As sources, hard coal, brown coal, and petroleum products, that is, diesel oil, motor gasoline, jet fuel, kerosene, and heavy fuel oil were considered. Wood combustion was not included, despite the importance of this source before 1900, because of lack of data.

The annual databases used [Mitchell, 1992; Marek, 1992; BEW, 1987] cover continuous production and trade data for the time period from 1820 to 1985 for coal and from 1860 to 1985 for petroleum. Detailed consumption statistics were not available, and therefore fuel consumption was calculated as production plus import minus export.

The calculated fuel consumption data were converted into BC and TC emissions using emission factors (EF) and carbon densities presented in Table 1. EFs of TC were calculated from the sum of the BC and OC emission factors. The applied EFs are means for industrial and domestic use and for developed and developing countries [Cachier, 1998]. They take into account that domestic fuel combustion is less efficient than industrial fuel combustion [Cooke and Wilson, 1996]. No information was available about the reduction of EFs through air pollution control systems and the evolution in combustion techniques. Hence EFs were assumed to be constant over the last 200 years.

The EFs of different petroleum products vary significantly [Cachier, 1998], and hence knowledge of the relative usage of different petroleum products is needed. Since this information was not available, we based their relative consumption on the European production rates for 1970 [Department of International Economic and Social Affairs, 1983] and assumed them to be constant over the investigated period. The other products were assumed to have a small EF and were therefore considered to behave similarly to heavy fuel oil (Table 1). Because of

Table 1. Relative Use of the Petroleum Products in 1970 in Europe and Emission Factors for TC and BC and Carbon Density of Each Fuel

	Relative Use of Petroleum Products, ^a %	EF, g (kg C, Fuel) ⁻¹		Carbon Density (Fuel), kg C kg ⁻¹
		TC ^b	BC ^c	
Petroleum products				
Diesel	27	10	5	0.9 ^d
Motor gasoline	14	0.5	0.1	0.9 ^d
Kerosene	2	1.5	0.3	0.9 ^d
Jet fuels and aviation gasoline	2	2	1	0.9 ^d
Heavy fuel oil	54	0.1	0.02	0.9 ^d
Hard coal		6	3	0.915 ^d
Brown coal (lignite)		19	4	0.315 ^e

^aValues are for European production 1970 [Department of International Economic and Social Affairs, 1983].

^bSource is Cachier [1998]: This is the sum of EF for OC and BC; values are adapted from Cachier [1995], Lioussé et al. [1996], and Cooke and Wilson [1996].

^cCachier [1998]: Values are adapted from Cachier [1995], Lioussé et al. [1996], and Cooke and Wilson [1996].

^dRoempp et al. [1997].

^eRoempp et al. [1997]: A water content of 45% and 70% carbon content of the dry brown coal is assumed.

Abbreviations are as follows: EF, emission factors; TC, total carbon; and BC, black carbon.

the high EF and its widespread use, diesel oil dominates the production of BC and TC from petroleum products.

Hard coal and petroleum products were assumed to consist of 91.5% and 90% carbon, respectively [Roempp et al., 1997]. For the brown coal we assumed a water content of about 55% [Roempp et al., 1997] and a carbon content of 70% of the dried brown coal [Roempp et al., 1997], resulting in a carbon density of 31.5%.

Table 2 lists the 10-year averages of the estimated BC (Table 2a) and TC (Table 2b) emissions from Switzerland, France, Italy, Germany and of the sum of these countries (labeled "All Countries"). Table 2 includes the emissions of the different fuel sources for each country. Today the use of petroleum products dominates BC and TC emissions in Switzerland and Italy, whereas in Germany coal combustion is the most important source of BC and TC. The total emissions of all countries are dominated by the emissions from Germany and hence are dominated by coal combustion. In 1985, coal consumption accounted for 70% of the total BC emissions. In the inventory of Penner et al. [1993], which includes wood and biomass burning, coal use accounted for 60% of the BC emissions in western Europe.

For 1985 we estimated a total BC emission of 1.34 Tg. This value is of the same order of magnitude as the studies of Cooke and Wilson [1996] and Penner et al. [1993] for western Europe, where estimated BC emissions were 1.09 Tg yr⁻¹ (for 1984) and 0.59 Tg yr⁻¹ (for 1980), respectively. Our value does not include emissions of the other western European countries and does not consider biomass burning and wood combustion. Including emissions from the remaining western European countries and adding the omitted sources, our value would be higher, indicating that emission estimates are of the right order of magnitude but need further refinement.

Figure 7 shows the record of the 10-year means of the estimated BC emissions for the sum of all countries surrounding the drilling site and the EC ice core records. A similar

Table 2a. Ten-Year Averages of the Estimated BC Emissions for Switzerland, France, Italy, and Germany and the Sum of These Countries for the Time Period 1816–1985

Period	Switzerland			France			Italy			Germany			All Countries		
	Hard Coal	Petroleum	Total	Hard Coal	Petroleum	Total	Hard Coal	Brown Coal	Total	Hard Coal	Brown Coal	Total	Coal	Petroleum	Total
1816–1825							3.87		3.87			3.87	3.87		3.87
1826–1835				7.19		7.19	5.05		5.05			5.05	11.5		11.5
1836–1845				13.2		13.2	9.09		9.09		1.01	10.1	23.3		23.3
1846–1855				22.5		22.5	17.1		17.1		2.53	19.6	42.1		42.1
1856–1865	0.425		0.425	41.3		41.3									
1866–1875	0.988	0.021	1.01	59.5		59.5	1.15		1.16		5.95	0.008	88.5	0.003	88.5
1876–1885	1.64	0.031	1.67	77.3		77.3	2.44		2.48		10.6	0.144	152	0.200	153
1886–1895	2.89	0.055	2.94	96.1		96.1	5.75		5.82		16	0.463	222	0.571	223
1896–1905	5.21	0.089	5.3	125		125	11.7		11.8		24.6	0.848	329	1.01	330
1906–1915	8.32	0.098	8.41	149		149	14.5	0.441	15.1		50	1.24	484	1.43	486
1916–1925	6.57	0.072	6.64	155		155	25.2	0.794	26.1		92.9	1.19	687	1.45	689
1926–1935	8.6	0.374	8.97	213		213	21.6	1.58	23.5		143	0.38	501	0.82	502
1936–1945	6.68	0.288	6.96	147		147	34.5	0.79	36.1		182	3.28	510	9.37	519
1946–1955	7	1.41	8.41	188		188	24.6	2.52	28.2		248	1.91	685	7.73	692
1956–1965	7.15	5.87	13	205		205	25.1	2.53	34.7		279	6.2	585	30.3	591
1966–1975	2.01	15.2	17.3	147		147	29.2	2.21	67.5		421	49.1	1080	134	1220
1976–1985	1.53	15.5	17.1	123		123	32.4	2.75	138		304	156	942	396	1340
				44.2		250	112	2.39	159		249	171	920	426	1350

Values are given in Gg yr⁻¹.**Table 2b.** Ten-Year Averages of the estimated TC Emissions for Switzerland, France, Italy, and Germany and the Sum of These Countries for the Time Period 1816–1985

Period	Switzerland			France			Italy			Germany			All Countries		
	Hard Coal	Petroleum	Total	Hard Coal	Petroleum	Total	Hard Coal	Brown Coal	Total	Hard Coal	Brown Coal	Total	Coal	Petroleum	Total
1816–1825													7.8		7.8
1826–1835				14.4		14.4							10.1		23
1836–1845				26.3		26.3							23		49.3
1846–1855				45		45							46.2		91.2
1856–1865	0.85		0.85	83		83							109		193
1866–1875	1.98	0.043	2.02	119		119	2.29		2.3		28.2	0.016	334	0.006	334
1876–1885	3.28	0.63	3.94	155		155	4.88		5.0		50.5	0.297	489	0.412	490
1886–1895	5.78	0.113	5.89	192		192	11.5		11.7		76.1	0.957	725	1.18	727
1896–1905	10.4	0.184	10.6	249		249	23.3		23.5		117	1.75	1110	2.08	1110
1906–1915	16.6	0.201	16.8	298		298	29.1	2.09	31.4		238	2.55	1770	2.95	1770
1916–1925	13.1	0.149	13.3	311		311	50.3	3.77	54.4		441	2.45	2030	2.99	2030
1926–1935	17.2	0.773	18.0	426		426	43.2	7.48	51.4		681	0.782	2700	1.7	2700
1936–1945	13.4	0.595	13.9	295		295	69.0	3.77	74.5		864	6.78	2420	19.3	2430
1946–1955	14.0	2.91	16.9	376		376	49.2	12	63.4		1180	3.94	2380	15.9	2390
1956–1965	14.3	12.1	26.4	410		410	58.4	10.5	76.7		1990	12.8	3330	62.6	3390
1966–1975	4.02	31.5	35.5	294		294	64.8	13	143		2150	101	3140	277	3410
1976–1985	3.06	32.1	35.1	246		246	88.3	11.4	232		2380	353	3220	879	4100

Values are given in Gg yr⁻¹.

increase starting in 1880 is attributed to enhanced fossil fuel combustion. The good correlation between 1880 and 1975 ($R^2 = 0.56$) indicates that the ice core, indeed, reflects the carbonaceous aerosol emissions of western Europe, which is consistent with the corresponding sulfate record [Schwikowski *et al.*, 1999]. Therefore the ice core record might be used to derive the level of emissions for the time period where no emission data are available. Before 1890 the measured EC concentrations are at a constant level, indicating that between 1755 and 1890 particulate carbon was emitted at a more or less constant rate. Wood combustion is believed to be the main source for that time period [Marek, 1992].

Table 3 gives correlation coefficients between BC emissions and the BC record and between TC emissions and the TC record. The correlation coefficients increase in the sequence BC, EC, and TC. We believe that the differences in the correlation coefficients result from the accuracy of the analyses. As discussed in section 2.2, the measurements of both EC and BC include possible systematic errors, whereas systematic errors can be neglected for TC measurements.

The high correlation between OC and EC is at first astonishing, considering that OC includes both primary and secondary OC and that the correlation between EC and secondary OC should be lower because of other sources of secondary OC. From the good correlation one may hypothesize that a large fraction of secondary OC is water soluble, which is removed during the filtration step. This hypothesis is corroborated by the good correlation (Table 3) between primarily emitted TC and TC measured in the ice core.

4. Conclusions

We presented historical records of BC, EC, OC, and TC concentrations covering the time period 1755–1975. They were obtained by analysis of ice core samples from a European high-alpine glacier using an optical and a thermal method. Concentrations varied between 7 and 128 $\mu\text{g L}^{-1}$ for BC, between 5 and 130 $\mu\text{g L}^{-1}$ for EC, between 53 and 484 $\mu\text{g L}^{-1}$ for OC, and between 66 and 614 $\mu\text{g L}^{-1}$ for TC.

Throughout the record, short-time concentration fluctuations by 1 order of magnitude occurred for all species and were attributed to the seasonal variations as a result of enhanced

Table 3. Correlation Coefficient R^2 of the Correlations Between BC and EC Concentrations in the Ice and the Estimated BC Emissions and Between the TC and the Estimated TC Emissions for the Time Period 1880 to 1975

Ice Records	Estimated BC Emissions	Estimated TC Emissions
BC	0.46	
EC	0.56	
TC		0.93

vertical transport of air from the PBL in summer. An increase in concentrations was observed superimposed on the fluctuations. From preindustrialization (1755–1890) to modern times (1950–1975), BC, EC, OC, and TC concentrations increased by factors of 3.7, 3.0, 2.5, and 2.6, respectively.

The sum of the estimated BC emissions of Germany, France, Switzerland, and Italy calculated from fossil fuel consumption was shown to correlate ($R^2 = 0.56$) with the record of EC concentrations for the time of enhanced fossil fuel use, that is, 1890–1975. This observation provides evidence that the presented EC record reflects the particulate carbon emissions of western Europe. Hence, for time periods without emission data, the level of emissions might be deduced from this record.

Compared to the Greenland EUROCORE ice core records [Cachier and Pertuisot, 1994], the presented EC and TC concentrations are higher by a factor of about 10–20. This difference in concentration is attributed to the proximity of the Colle Gnifetti ice core to the combustion sources.

The trends of EC and BC concentration records show the expected good agreement ($R^2 = 0.81$). Furthermore, the concentrations are fairly comparable, indicating that the instrumental calibration factor α_{API} of the optical apparatus was representative of these ice samples when calibrated with atmospheric aerosol. Using the attenuation and EC data, a calibration yielded a mean value $\alpha_{\text{API}} = 10.5 \text{ m}^2 \text{ g}^{-1}$, which agrees with α_{API} of present-day snow samples and the calibration value ($\alpha_{\text{API}} = 9.3 \text{ m}^2 \text{ g}^{-1}$).

Furthermore, attenuation measurements showed that absorption due to mineral particles varied between 2 and 30%. No significant increase was observed, suggesting that particulate carbon and mineral particles have different sources.

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Figure 7. EC concentrations (10-year averages) for 1820 to 1975 and the sum of estimated BC emissions of Switzerland, France, Italy, and Germany. Hard coal, brown coal, and petroleum products are included as sources.

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