A 130 YEARS DEPOSITION RECORD OF SULFATE, NITRATE AND CHLORIDE FROM A HIGH-ALPINE GLACIER

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Abstract. An ice core from a high-alpine glacier (Grenzgletscher, Colle Gnifetti, Monte Rosa massif, 4450 m a.s.l., Switzerland) was used to reconstruct the pollution history of Central-Europe. Concentrations of the most important acidifying species sulfate and nitrate as well as of chloride were measured in 1151 samples with 5 cm resolution from the top 60 m of a 109 m long firn/ice core. This corresponds to a mean time resolution of 8 (bottom) to 14 (top) data points per year. A ²¹⁰Pb nuclear dating showed that the ice core covers a time period between 1850-1981 and that the mean accumulation rate was 0.33 m water equivalent per year. Between the two time periods 1850 - 1880 and 1965 - 1981 the mean sulfate concentrations increased by a factor of 5.8 ± 0.9 and for nitrate by a factor of 2.3 ± 0.3 . The mean concentrations at the beginning of the industrial time (period 1850 - 1880) was 0.078 ± 0.008 mg/l for sulfate and 0.067 ± 0.005 mg/l for nitrate. The mean chloride concentration was 0.047 ± 0.004 mg/l and did not show a trend in concentration over the time period investigated. A distribution analysis of the measured concentrations for the two time periods 1850 - 1865 and 1965 - 1981 was performed which showed that the data have a nearly log-normal distribution.

Key words: Alps, Chloride, Deposition record, Ice core, Nitrate, Sulfate

Introduction

Sulfate and nitrate concentrations in Greenland ice cores have increased since the beginning of the industrial age, due to emissions of the precursor gases SO₂ and NO_x (Neftel *et al.* 1985; Finkel *et al.* 1986; Mayewski *et al.* 1990), that were presumably dominated by US-emission sources for this receptor site. On the other hand, high-altitude glaciers in the Alps are assumed to reflect more directly the anthropogenic emissions of pollutants in Europe (Oeschger *et al.* 1977; Schotterer *et al.* 1985; Wagenbach *et al.* 1989; Maupetit *et al.* 1995).

Atmospheric species accumulated in high-alpine glaciers are assumed to represent four different origins: 1. the free troposphere via long-range transport, 2. the planetary boundary layer via convective transport, 3. local emissions in the immediate vicinity of the glaciers, and 4. emissions at large distances from the Alps with high ejection heights (atomic bomb debris, volcanic eruptions, Saharan soil dust).

The vertical exchange of air masses in the alpine region exhibits a pronounced seasonality due to the specific topography. During summer high concentrations of atmospheric aerosols are found even at the highest sites in the Alps, resulting from convective mixing with planetary boundary layer air. During winter these high-alpine sites are decoupled from regional aerosol sources due to an increased atmospheric stability (Baltensperger *et al.* 1991). This seasonality of the atmospheric aerosol causes a high annual variability of the respective species in the deposited snow (Wagenbach *et al.*

1994). Summer snow, therefore, is assumed to reflect the concentration of species of regional origin, whereas during winter the observed concentrations in fresh snow are supposed to reflect true continental background conditions (Wagenbach *et al.* 1988; Nickus *et al.* 1995).

The core drilling site at Colle Gnifetti fulfills two main requirements to serve as an archive for atmospheric constituents: First, the mean firm temperature is -14°C , and, therefore, percolating meltwater refreezes immediately below the surface preventing a disturbance of underlying layers (Oeschger *et al.* 1977; Alean *et al.* 1984). Second, complications by ice-flow are marginal, since the Colle Gnifetti is a rather plain glacier saddle. The total ice depth at the core drilling site used for this study is 124 m (Schotterer *et al.* 1985).

^{210}Pb measurements were used to determine the mean annual accumulation rate and to date the ice core back to 1850 (Füeg 1994). The observed mean annual accumulation rate of 0.33 m w.eq. (meter water equivalent) is only about 15 % of the estimated total annual precipitation amount at this altitude (2.5 - 3 m w.eq. $\cdot\text{y}^{-1}$; Schirmer and Manig 1965). The observed deficit is most likely caused by surface erosion of fresh snow at this wind-exposed location, removing most of the winter precipitation. This prevents dating by annual layer counting of chemical or isotopic signals (Oeschger *et al.* 1977; Schotterer *et al.* 1985; Wagenbach *et al.* 1988).

Electrical conductivity measurements (ECM) on a core drilled parallel to the one analyzed in this work demonstrated an increase of acidity during the 20th century which could be correlated with increased concentrations of nitrate and sulfate (Schotterer *et al.* 1985). A more complete, though not highly time-resolved measurement of nitrate and sulfate for the uppermost 40 m of the same core was published later (Wagenbach *et al.* 1988). Average concentrations of sulfate and nitrate for surface samples (1970 - 1986) were found to be significantly higher than those from the deeper samples (1890 - 1910) (see also Tab. I).

In this work the highly resolved time series of the anionic species nitrate, sulfate and chloride were measured in order to evaluate the anthropogenic influence on the snow concentrations at Colle Gnifetti during the 19th and 20th centuries. Statistical methods were used to determine the factor of increase as well as the mean values for the two time periods 1850 - 1880 (236 samples) and 1965 - 1981 (236 samples). The first time period represents the beginning of the industrial age and the second the maximum emission rates of SO_2 and NO_x , prior to reduction of air pollution. In order to prove whether the low and high concentrations of the species reflect different origins, the shapes and the variances of the distributions were investigated for two corresponding time periods (1850 - 1865, 1965 - 1981).

Experimental

The 109 m long ice core was recovered during an ice core drilling campaign in 1982 at Colle Gnifetti (4450 m a.s.l.), Monte Rosa massif (Schotterer *et al.* 1985). The diameter of the electromechanically drilled core was 7.5 cm. The 0.5 to 0.9 m long core sections were sealed at the drilling site in polyethylene bags and kept frozen at -30°C until the processing presented in this paper started in 1993.

In a cold room, maintained at -15°C , the core sections were cut into 5 cm long samples using a band saw. To reduce surface contamination 0.5 cm of the outer part of the core was removed mechanically. Samples were melted prior to analysis using a microwave oven. Special cleaning of all vials were performed in order to avoid any contamination. The concentrations of chloride, nitrate and sulfate were measured in a single analysis by ion chromatography (SYKAM system equipped with DIONEX columns).

Results and Discussion

Fig. 1 shows the concentrations of sulfate, nitrate and chloride determined in the 1151 samples representing the core length of 60 m analyzed in this work. Taking into account the measured densities, this corresponds to 44 m w.eq. Due to bad core quality, a few core sections could not be used for chemical analysis. The resolution in the upper part of the core is about 14 data points per year. Caused by the increasing density with depth, the resolution in the lower part is only about 8 data points per year. In addition to the depth scale, a time scale is given in Fig. 1 which was obtained by ^{210}Pb nuclear dating (Füeg 1994). Furthermore, some stratigraphic markers are shown that were used to corroborate the ^{210}Pb dating such as historically well-known Saharan dust events in 1901/02 and in 1936/37 (Haeberli *et al.* 1977 and references therein) and in 1977 (Schotterer *et al.* 1985) - identified by yellowish firm layers - and the atomic bomb horizons in 1958 and 1962/63 found via tritium measurements (Schotterer 1995).

Fig. 1: Measured concentrations of sulfate, nitrate and chloride in an ice core from Colle Gnifetti as a function of depth in m water equivalent. A time scale deduced from a ^{210}Pb nuclear dating is also shown, along with some well known time horizons (see text).

Fig. 1 shows higher average concentrations and higher variabilities of sulfate and nitrate in the top of the core compared to those from the bottom of the core. In contrast, the chloride concentration record does not show a trend with time. Even in the uppermost part of the core with the highest resolution no clear seasonal signature was found for the three species, confirming the results from previous studies that a varying part of the annual snow deposition can be removed by wind erosion at this site (Oeschger *et al.* 1977; Schotterer *et al.* 1985; Wagenbach *et al.* 1988).

In Fig. 2 the logarithmic concentration values of the three species chloride, nitrate and sulfate are plotted versus the depth of the core. In order to smooth the data the locally weighted regression smoother loess (S-PLUS 1993) with the smoothing parameter span = 0.2 was used. This regression model can be applied only if the residuals of the predicted values (smoothed curve) are symmetrically distributed, as it is indeed the case for our logarithmic data set (Fig. 2). This means, high and low concentrations are equally

Fig. 2: Logarithmic values of the data depicted in Fig. 1. The solid lines show the smoothed values. The dashed lines are to guide the eye, the horizontal solid parts represent the mean values for the corresponding time periods.

weighted. For the logarithmic concentration values of nitrate a linear increase is observed from about 1930 to about 1965 which is equivalent to an exponential increase of the non-logarithmic data. Prior to 1930 and after 1965 the average nitrate concentrations remain approximately constant. For sulfate the exponential increase starts at about 1885 and ends also at about 1965.

The observed local maxima of the smoothed curve at the beginning of the 1970's in the nitrate and sulfate concentrations are not significant; they might be induced by different annual snow accumulation rates of the actually preserved snow. Additional measurements between 1965 and present time are required to study whether nitrate and sulfate concentrations remained constant or even show a decrease, as a result of legislation politics to reduce SO_2 and NO_x emissions. For the two time periods 1850 - 1880 and 1965 - 1981, with approximately constant concentration levels, a variance analysis between the two groups which are assumed to be representative for the respective time periods was performed. As a result of the variance analysis we obtained that sulfate concentrations increased by a factor of 5.8 ± 0.9 and nitrate concentrations by a factor of 2.3 ± 0.3 . Chloride did not show a significant difference between the two periods. The first time period should represent the pre-industrial situation and the second the period of maximum release of SO_2 and NO_x by anthropogenic emissions.

For the time periods 1850 - 1880 and 1965 - 1981 the logarithmic data have a nearly normal distribution shape (similar to the reduced groups in Fig. 3), from where the mean levels were estimated. The resulting mean values for the two time periods are summarized in Table 1. In addition, the average concentration values (average of non-logarithmic data) are given for the same periods in order to compare them with already published data.

Table 1

Nitrate, sulfate and chloride mean values and their standard errors (2σ confidence level) of the log-normal distributions and the average concentration values of the core sections representing the time periods 1850 - 1880 and 1965 - 1981. All numbers in mg/l.

Time period	Chloride		Nitrate		Sulfate	
	Mean $\pm 2\sigma$	Average	Mean $\pm 2\sigma$	Average	Mean $\pm 2\sigma$	Average
1850-1880	0.047 ± 0.004	0.062	0.067 ± 0.005	0.080	0.078 ± 0.008	0.10
1890-1910*				$0.06 \pm 0.02^*$		$0.11 \pm 0.05^*$
1965-1981	0.049 ± 0.006	0.073	0.159 ± 0.016	0.22	0.45 ± 0.06	0.69
1970-1986*				$0.28 \pm 0.11^*$		$0.48 \pm 0.27^*$

* data from Wagenbach *et al.* (1988)

In general, our average values are in good agreement with the literature data (Schotterer *et al.* 1985; Wagenbach *et al.* 1988) though slightly different time periods were analyzed. One exception is possibly the modern sulfate concentration, where our value of 0.69 mg/l seems to be slightly higher than 0.48 mg/l given by Wagenbach *et al.* (1988). This could be caused by the fact that by Wagenbach *et al.* (1988) snow layers with obvious Saharan dust layers were excluded from the data analysis. We consider therefore the analysis via

a determination of the mean values from the log-normal distributions more appropriate, since single values with exceptional high concentrations do not significantly influence the mean value.

In order to investigate possible differences in the increase of high and low concentrations for the "pre-industrial" (1850 - 1865) to "modern" (1965 - 1981) time periods, the variances and the distribution shapes of the logarithmic data were compared. In Fig. 3 the probability densities (width=1, $n=118$) and quantile-quantile plots (qq-plot) of the logarithmic values for each species and the two investigated time periods are shown. One prerequisite for such a qq-plot is that time resolutions are identical for each time period, otherwise an increase of the variance could be induced. Consequently, the time resolution of the data from the time period 1965-1981 was reduced by averaging to 118 data points. As corresponding time period the group with 118 data points from 1850 - 1865 was chosen.

Fig. 3 : Top: probability density plots of the logarithmic data for chloride, nitrate and sulfate for the two time periods 1850 - 1865 (dashed line) and for 1965 - 1981 (solid line). Bottom: corresponding quantile-quantile plots of the logarithmic data.

The density plots show that for all time periods and all species the logarithmic data have a nearly normal distribution shape. For chloride and sulfate we observe a linear correlation in the qq-plot (Fig. 3). This means that these distributions are very similar for both time periods. The slopes of the correlation lines are slightly higher than one (1.4 for sulfate and 1.3 for chloride). This means that the variances increased by 40% and 30%, respectively. An additional analysis performed between the data from the time periods 1965 - 1981 and 1865 - 1880 showed that this slope parameter can vary by about 20 %. We therefore have to conclude that the variances of the logarithmic data of chloride and sulfate concentrations have slightly increased between 1850 - 1865 and 1965 - 1981. From this slight increase it is, however, not possible to deduce significantly different increases of low and high concentrations. This could be explained by the fact that conti-

mental background concentrations and concentrations originating from convective mixing increased by the same factor. In this case our low concentrations would indeed reflect continental background conditions. On the other hand, it can't be excluded that even the low concentrations are influenced by transport of air masses from the planetary boundary layer to the Colle Gnifetti. In that case, our data would not allow to deduce the contribution by continental background, presumably due to a predominant lack of winter precipitation.

For nitrate, for yet unknown reasons, the distribution shapes for both time periods are slightly more different. This might indicate a (partly) different origin of nitrate - or its precursors - for pre-industrial times compared to modern times.

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