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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources and distribution of trace species in Alpine precipitation inferred from two 60-year ice core paleorecords" *by* A. Eichler et al.

A. Eichler et al.

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Response to comments of Referee #1, #2, and the second comment of Referee #3

General statement of the Authors

During the time our paper was under revision we started the analysis of a new ice core from FG, which was drilled about 100 m distant from the site described in this work. The new data reproduce well the records of stable isotopes and anthropogenic species. Unfortunately, we observe differences in the records of sea salt and mineral dust species, which we are not able to explain at the moment. This might have implications on some of the interpretations presented in the manuscript. It is not possible to carefully analyse the new core and to investigate the observed discrepancies in a few weeks. Therefore, in agreement with the editor of the journal we do not submit a re-

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vised version of our manuscript this time and leave it at the discussion stage in ACPD. After the analysis of the new core from FG is completed we plan to resubmit the paper considering these new results.

Response to the comments of Referee #1

1) General comments

Unfortunately, the German references are very important for the paper and the corresponding studies have not been published in English journals. Particularly, the reference to the work of Fliri about the relation between weather situations and precipitation in the Alpine area over longer time periods and with a high geographical resolution can not be replaced.

2) Specific comments

-2.1.) The stable isotope signal at FG and GG is fairly well correlated with the instrumental record of atmospheric temperature (period 1983-84: Schotterer et al., 1997, period 1980-94: Eichler et al., 2001, period 1974-83 - this manuscript). At GG net annual accumulation rates are in reasonable agreement with precipitation amounts at the closest high-mountain weather station (Eichler et al., 2000). Thus, we assume that winter precipitation is preserved in the records (see also response to comment 2.3 of Referee #2).

-2.2.) A study at the Alpine site Weissfluhjoch comparing new snow and snow pit samples showed that dry deposition is negligible for Cl-, NO3-, SO42-, NH4+, and H+ (Baltensperger et al., Atmos. Environ. 27A, 1881-1890 (1993)). However, for coarser mineral dust particles, deposited e.g. during Saharan dust events, a contribution from dry deposition cannot totally be ruled out. Under the relative humid conditions in the Alps, sublimation is generally not affecting the glaciochemical record. Relocation of certain ions by meltwater percolation has been observed in the section from 11 to 24 m w.eq. of the GG core (Eichler et al., 2001) and this part of the core was therefore not

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considered in the interpretation, as we state in the manuscript. For wind erosion see response to comment 2.3 of Referee #2.

-2.3.) The observed independence of the concentrations in the ice on accumulation rates indicates the existence of a large atmospheric reservoir of the considered trace species. There is no change in accumulation pattern associated with the change of weather pattern in the 1960s.

-2.4.) Concentrations of all trace species are log-normally distributed. Therefore correlation analyses have to be performed using the logarithms of the concentrations.

-2.5.) It is already mentioned that aerosol of sea salt composition can have its source in the Sahara (page 9, first paragraph). However, we agree with the referee that some references about halite deposition can be included. Unfortunately, it is not possible from our study to discriminate between different source regions in the Sahara. For this, not only Ca2+ and Mg2+ as soil tracers but other trace elements have to be considered (e.g. Lanthanide patterns, isotopic patterns).

-2.6.) is clarified in the new paper

-2.7.) SO2 emissions are actually even higher in winter because of increased energy consumption and domestic heating (e.g. SO2 in rural area in Switzerland in the year 2002 in μg/m3: Jan.: 7 Febr.: 3 Mar.: 5 April: 4 May: 2 Jun.: 1 Jul.: 1 Aug.: 1 Sept.: 2 Oct.: 4 Nov.: 4 Dec.: 4, source: BUWAL, http://www.umwelt-schweiz.ch/buwal/de/fachgebiete/fg_luft/luftbelastung/index.html)

-2.8.) concentrations of anthropogenic species on the one hand and mineral dust and sea salt species on the other hand

-2.9.) Smaller correlation coefficients in summer indicate that in this season the source area is the vicinity of the Monte Rosa, representing only parts of France and Italy.

3) Technical Corrections: will be included in the new paper.

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Response to the comments by Referee #2

1) General comments A comparison with published data from CDD and partly from CG (considering the special accumulation characteristics) will be performed in the new manuscript in order to justify our argumentation (see also Specific comments 2.5., 2.6.). We think that correlation analysis is a suitable tool for attributing major source of trace species (anthropogenic, sea salt, Saharan dust), but we agree with the referee that for comparison of trends a more detailed trend analysis is necessary. Unfortunately, the German references are very important for the paper and the corresponding studies have not been published in English journals (see responses to Referee #1).

2) Specific comments

-2.1.) Introduction To our knowledge all studies dealing with long-term north-south gradients of pollution in the Alps are cited (first and second paragraph, page 3). We agree with the referee that in the Alps only a few sites are suitable, and these were selected for the studies. The SNOSP program was described in detail, since this is the only study of geographical differences in the deposition of trace species with a broad coverage of the entire Alpine area. We will add that this study was performed on winter snow only, allowing including also lower elevated glaciers. Studies of Preunkert et al. (2001a and b) are also cited (third paragraph, page 2). We referred to peat bog studies, aiming at investigation of north-south differences (Weiss et. al., 1999) (second paragraph, page 3) as well as to studies of Van de Velde (third paragraph, page 2.

-2.2.) Site description The borehole temperatures ranged from -1 to -9 °C, the corresponding diagram and its discussion is given in Eichler et al., 2000a. Therefore we do not include it in this manuscript, but we will add a sentence and the reference. The precision of the borehole temperatures and detailed description of the measurement can be found in Suter, et al., 2001.

-2.3.) Chemical analysis and dating The ice core sections were cut into 5-20 cm long segments with a band saw, and the outermost, probably contaminated 0.5-1.5 cm were

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removed. We have not included a precise description of the identification of the horizons used for the dating of both cores to keep this part of the manuscript short. More details can be found in the corresponding papers (Schwikowski et al., 1999a, Schotterer et al., 1997, Eichler et al., 2000a). The dating uncertainties are ś1 year for FG and $<$1 year for GG (period 1970-1994) and ś2 years (period 1937-1969), which will be included with the corresponding references in the new paper. Since we are dealing with glacier archives, advantages and disadvantages of this kind of archive are inherent. Thus, effects of wind erosion on accumulation rates can not totally been excluded. However, since both ice core sites are located in relatively flat and vast parts of the FG and GG, we assume that wind erosion is of minor importance. This is supported by the fact that e.g. the stable isotope signal at FG is fairly well correlated with the instrumental record of atmospheric temperature (Schotterer et al., 1997). Also precipitation anomalies such as the well-known heavy snowfall in January and February 1951, causing a large number of avalanches (Pfister, 1999) are well preserved in the FG and GG records.

-2.4.) Precipitation characteristics Indeed, the FG belongs to the northern and the GG to the southern Alps, and both are separated by the Rhone valley. This valley receives very low precipitation amounts, in contrast to both Alpine chains with high precipitation rates of mainly different origin. Whereas the northern site is mainly influenced by W-precipitation, at the southern site precipitation during SW (foehn) situations is dominant. The different weather regimes are responsible for a different transport of pollution to both sites. The weather-type classification of Fliri was used, since this is the only study including Alpine weather type statistics and precipitation characteristics with a high geographical resolution in the Alpine area covering longer time periods (about 30 years). Fig. 2 is very important to illustrate the differences in the precipitation characteristics at both Alpine chains and will therefore not be removed, but the consequences for the drilling sites discussed. The last paragraph gives an assumption based on the different precipitation regimes and will be moved to the results section. From the correlation analyses only the main sources of the trace species were determined and not

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the minor ones. But we agree with the referee that other sources have to be discussed as well.

-2.5.) Annual cycles The T values at Gd. St. Bernard are mean seasonal values over the period 1974-83. The difference between mean summer and winter temperatures is 12.5 °C. The corresponding d18O difference in the same time period at FG and GG is about 6.4 per mille, resulting in a d18O/temperature coefficient of 0.5 per mille per °C, in agreement with published values (e.g. Schotterer et al., 1997). Typical summer/winter ratios of the anthropogenic species NH4+, NO3-, and SO42- (3, 2, and 2) do not agree with results from the CDD site, revealing ratios of 14, 4, and 4 (Preunkert et al., 2000), respectively. This is due to differences in the seasonal dissection criteria. Our dissection is based on the d18O record. This is justified, since a correlation between the isotopic and the temperature signal is observed in the time period investigated. Preunkert et al. used for dissection the NH4+ record (10 ppb boundary between summer and winter half year), which then automatically results in winter concentrations of NH4+ of around 10 pbb. Thus, winter concentrations of the anthropogenic species observed at the CDD site are lower compared to the FG and GG site, whereas concentrations in summer show reasonable agreement. We will add a discussion considering the results from CDD in the new version accordingly.

-2.6.) Long term trends There is a good agreement in the general trends of NH4+, NO3-, and SO42- concentration records between FG, GG, and CG. This is not the case for the CDD site. The concentration maxima of SO42-, for instance, are in 1970-75 for the first three sites, but in the 1980s for the CDD site (considering 5-year means). Interestingly, Spanish SO2 emissions peak in the 1980s as well, whereas Italian and French SO2 emissions reveal there maximum already in 1970-75, comparable to the SO42- concentration record of the more eastward sites FG, GG, and CG. Furthermore, the NO3- concentration records at the FG, GG, and CG site do not show the continuous increase between 1940 and 1990, as observed at the CDD site, but slightly decreasing concentrations between 1970 and 1990. We will add a discussion considering the

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results from CDD and CG in the new version accordingly. In our case the increase of the Na+ concentrations at FG in the 1960s due to an increase of soil derived Na+ can be excluded since: a) concentrations of the other sea salt species K+ and Cl- increased to the same extend, whereas soil tracers Ca2+ and Mg2+ remained on a constant level, b) Na+ and Ca2+ concentrations are only specifically correlated for the period 1945-61 but not for the period 1962-87 (see Figure 9). For the CDD a Na+ record is published (Legrand et al., 2002), but not interpreted in terms of trends, except an increase of the winter values between 1925-70 (5 ng/g) and 1975-85 (9 ng/g), which was related to the growing use of salt for deicing roads. From the raw Na+ data shown in Figure 1 of that paper, it is impossible to see if there is a trend or not.

The question mark in Table 2 is removed.

Response to the second comments by Referee #3

1. Comment A comparison with published data from CDD and partly from CG (considering the special accumulation characteristics) will be performed in a new manuscript (see Specific comments 2.5. and 2.6. of Referee #2). The ammonium trends between CG and GG are in good agreement, when using the same averaging periods. A corresponding figure will be included in the new paper.

2. Comment Considering mean values in the period 1974-83 for Gd. St. Bernard, the annual temperature amplitude is 15°C (not 20°C) between January and August. The difference between the coldest 3 month (winter) and warmest 3 month (summer) is 12.5°C (not 18°C). The corresponding d18O difference in the same time period at FG and GG is about 6.4 per mille, resulting in a d18O/temperature coefficient of 0.5 per mille per °C, in agreement with published values (e.g. Schotterer et al., 1997). In fact, our seasonal dissection criteria differ from that used by Preunkert et al. (2000). The dissection is based on the d18O record. This is justified since a correlation between the isotopic and the temperature signal is observed in the time period investigated. Preunkert et al. used for dissection the NH4+ record (10 ppb boundary between sum-

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mer and winter half year), which then automatically results in winter concentrations of NH4+ of around 10 pbb. A smoothing of the seasonal amplitude of the d18O record does not affect the seasonal dissection.

Response to paragraph 4 Trend curves for NO3- and the comparison with NOx emission data of Ardenne et al. (2001) will be shown in the new paper. We did not state that no gaseous NH3 reaches the high altitudes. However, the high cross correlations between the anthropogenic species suggest that the transport of the main part of NH4+ occurs as aerosol. The concentration maxima of the anthropogenic species in the 1970s can be found at the FG, GG, and CG (considering 5-year means). We do not believe that the maximum found at all 3 sites is due to high vertical transport efficiency in a few adjacent years, since all years between 1970 and 74 show such high concentrations. For the more westward CDD site the SO42- concentration maximum is observed in 1980. Interestingly, Spanish SO2 emissions peak in the 1980s as well, whereas Italian and French SO2 emissions reveal their maximum already in 1970-75, comparable to the SO42- concentration record of the more eastward sites FG, GG, and CG.

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