

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.

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Response to comments by referee # 3

The referee made one general and five more detailed comments. In the following we respond to them individually.

General comment The main goal of the current study is the comparison of 60-year records of chemical species from two Alpine ice cores (Fiescherhornletscher, FG, northern Alps and Grenzletscher, GG, southern Alps). Along with a statistical weather type analyses geographical and seasonal trends in the deposition of trace species are investigated. To our knowledge no such study has been published. Comparisons of different ice core records are limited in the time resolution as well as time period investigated and have not considered any meteorological data. These comparative studies

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took into account records from FG and Colle Gnifetti (CG) (only the concentrations of Cl⁻, NO₃⁻, SO₄²⁻, and NH₄⁺ averaged over the period 1965-81, Schwikowski et al., 1999a) and from Col du Dome (CDD) and CG in the period 1982-91 (concentration records of Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, and Ca²⁺, Preunkert et al., 2000). However, it is well known that due to the special topography at the CG saddle, mainly summer snow is preserved, resulting in an extremely low annual net accumulation of 0.3 m water equivalent (w.eq.). Thus, seasonal data are not accessible from CG. We therefore used in this study data from the nearby GG site, with complete accumulation of precipitation (2.7 m w.eq. per year). Chemical records from this site in the southern Alps have not been published, except of the Cl⁻ and F⁻ record in order to estimate anthropogenic HCl and HF emissions (Eichler et al., 2000b), and the NH₄⁺ record for annual layer counting (Eichler et al., 2000a). In summary, we presented new data and performed an innovative type of analyses. We therefore consider this comment as unjustified.

1) We agree with the referee that the investigation of the accumulation characteristics is one of the most important subjects to confirm the reliability of ice core records in term of their atmospheric relevance. For GG Eichler et al. (2000a) showed that precipitation at this site is regularly distributed throughout the year and corresponds roughly to the actually fallen precipitation. The same was demonstrated for FG (Schwikowski et al., 1999a, Schotterer et al., 1997). Nevertheless, we agree with the referee that this part is missing in the manuscript and we will add it accordingly. As discussed above, parts of the annual net accumulation at CG are removed by wind erosion. Consequently, no seasonal information has been obtained from this site. Therefore, we do not discuss the chemical records from CG in the current work. The apparent discrepancy between the trends in the ammonium records from CG and GG mentioned by the referee is caused by different averaging periods (GG: 5-years, CG: 10-years averages). A similar ammonium trend is obtained for both sites are, when averages over the same time intervals are calculated.

2) The referee misinterpreted the data presented in Figure 3. The variation in the d18O

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record for the GG site is 6L' (Figure 3, left axis) and the corresponding temperature variation at Gd. St. Bernard is about 11°C (right axis), in agreement with published d18O/temperature relationships for high-altitude sites (e.g. Schotterer et al, 1997). The temperatures and d18O values shown in Figure 3 are seasonal averages (e.g. winter: December-February) over a 10 years period and not minimum or maximum values. At GG the difference between d18O values in January (-22 L') and August (-11 L') is about 11L' (see e.g. Eichler et al., 2001, period 1980-94), corresponding to a temperature difference of about 20°C as mentioned by the referee and in agreement with other studies. The same argument can be used to explain the apparent 4 times higher winter concentration of chemical species compared to the studies mentioned by the referee. Concentrations of chemical species shown in Figure 3 are as well seasonal averages over a 10-years period. Concentrations of NH₄⁺, for instance, are definitely below 1 ueq/l (compared to 4 ueq/l, Figure 3), when looking at minimum values in winter (see Eichler et al., 2000a).

3) In Legrand et al. (2002) a Na⁺ record from CDD is presented, but not interpreted in terms of trends, except an increase of the winter values between 1925-1970 (5 ng/g) and 1975-1985 (9 ng/g), which was related to the growing use of salt for deicing roads. 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) concentration 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). However, since we agree with the referee that the interpretation of the observed increase in the concentrations of sea salt species at FG as induced by "climatic change" has to be established at other Alpine sites (including CDD and GG), we will remove Figure 9 and the interpretation of the observed increase in the revised version.

4) In fact, we have not compared our NO₃⁻ and NH₄⁺ records with the NO_x und NH₃ emission estimate data of van Ardenne et al. (2001) mentioned by the referee. We

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therefore will add an additional paragraph in Chapter 3.3.: The evolution of NO_3^- concentrations at both sites was compared with NO_x emission estimates for different European countries (van Ardenne et al., 2001). Significant correlations were found with emission data of France, Italy, Switzerland, and Austria (0.01 level). Since the trends in the NO_x emission estimates for these 4 countries in the period 1940–1990 are very similar, a more distinct determination of the source region is not possible. The disagreement in the trend between the NO_3^- records and the NO_x data of Germany and Spain is consistent with the difference between the trends of the SO_4^{2-} records and the SO_2 estimates of those countries. On the other hand, no significant correlations between the trend of the NH_4^+ concentrations at GG and FG and the NH_3 emission estimates of France, Italy, Germany, Spain, Switzerland, and Austria (van Ardenne et al., 2001) were found. Interestingly, emission data of all countries do not show the decrease after the 1970s, as observed in the NH_4^+ concentration records. The NH_3 emissions increase between 1940 and 1980 and are constant during the period from 1980 to 1990. This indicates that contrary to SO_4^{2-} and NO_3^- , the NH_4^+ concentration record does not absolutely reflect the emission history of the precursor species. The short chemical lifetime of the highly reactive NH_3 hinders its transport as gaseous species over longer distances in the atmosphere. Its transport to the high-elevated sites of the Alps is connected closely to the formation of aerosol particles by gas-to-particle conversion involving H_2SO_4 and/or HNO_3 , indicated by the high correlation between NH_4^+ concentrations and SO_4^{2-} and NO_3^- . This explains why the NH_4^+ concentration maxima at FG and GG occurred in the 1970s, corresponding to those of SO_4^{2-} and NO_3^- . A similar phenomenon was observed for the ^{210}Pb input at GG (Eichler et al., 2000a). ^{210}Pb activities showed a maximum in the 1970s, although the annual input of ^{210}Pb at this site should be constant over the last 60 years. This was related to an increased number of aerosol particles during this time, acting as transport vehicles.

5) We agree with the referee that data sets from FG and CG are already published and we mentioned this in the introduction. However, chemical records from GG have not yet been published and this is the first comparative study including a statistical

weather type analyses to infer geographical and seasonal trends in the deposition of trace species in the Alps.

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