An Alpine ice-core record of anthropogenic HF and HCl emissions

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Abstract. Ice-core records of an Alpine glacier from the southern Swiss Alps were used to reconstruct sources of inorganic F and Cl⁻ in precipitation. Our results suggest that sea salt transported together with mineral dust mainly from the Saharan area is the predominant source of Cl⁻ in the southern Alps. However, on the average 16% of the Cl⁻ and most of the F deposition in the period 1937-94 could be related to HCl and HF emissions from anthropogenic sources. The record of non-sea-salt Cl⁻ was found to represent the historical development of HCl emissions mainly from waste incineration in the Swiss Plateau, whereas the F deposition record reflects HF emissions from the aluminum industry in the Swiss Rhone valley. Thus, our data indicate a strong impact of emissions of short lived atmospheric species such as HCl and HF on local and regional precipitation chemistry.

1. Introduction

High elevated cold glaciers in the Alps contain a record of precipitation chemistry over time spans of centuries. Due to their location close to the densely populated and industrialized areas of western Europe they provide important information of human's impact on the environment. Historic effects of anthropogenic activities on the composition of the European background aerosol have been studied mainly at three different glacier sites in the Alps: Colle Gnifetti (Monte Rosa massif, 4450 m a.s.l.), Fiescherhorn (3890 m a.s.l.) and Col du Dome (Mont Blanc massif, 4250 m a.s.l.). Concentrations of aerosol related species NH₄⁺, NO₃⁻, SO₄²⁻, black carbon, lead and other heavy metals showed a marked increase in snow due to the enhanced anthropogenic emissions of their precursors in the twentieth century [Wagenbach *et al.*, 1988; Döscher *et al.*, 1995; Döscher *et al.*, 1996; Schwikowski, 1997; Lavanchy *et al.*, 1999; Schwikowski *et al.*, 1999a; Schwikowski *et al.*, 1999b; van de Velde *et al.*, 1999]. However, historical data representing the influence of anthropogenic emissions of halogen species fluoride (F) and chloride (Cl⁻) on the precipitation chemistry over Europe are lacking.

Historical Cl⁻ records derived from Alpine glaciers have revealed that the most important source of Cl⁻ in this area is sea salt [e.g. Maupetit *et al.*, 1995; Schwikowski *et al.*, 1999a]. There is no evidence of anthropogenic Cl⁻ in these studies, suggesting that anthropogenic HCl emissions (mainly from coal burning and waste incineration, [Lightowers and Cape,

1988]) play only a minor role compared to the fraction of Cl⁻ from sea salt in western Europe. This is in contrast to Greenland ice-core studies, where the excess Cl⁻ (non-sea-salt Cl⁻) shows a notable trend [Mayewski *et al.*, 1993]. Concentrations in the 1950-89 period were found to be twice as high as the preindustrial level [Legrand and Mayewski, 1997].

Natural sources of F in precipitation were investigated in several studies, identifying soil dust particles, sea salt, biomass burning and volcanoes as the main sources [Carpenter, 1969; Brewers and Hayson, 1974; Cicerone, 1981; de Angelis and Legrand, 1994]. Measurements of F in Greenland ice cores [de Angelis and Legrand, 1994] suggest that the primary source of anthropogenic HF in this area is coal combustion. High concentrations of anthropogenic F were also detected in the vicinity of an aluminum refinery or near phosphate fertilizer factories that use apatite as raw material [Cicerone, 1981]. Historical F deposition records in the Alps, however, are not available until now.

In this work concentrations of F and Cl⁻ were analyzed in an Alpine ice core in order to evaluate emission sources of both species and the anthropogenic influence on precipitation chemistry in the Alpine region.

2. Methods

In October 1994 a 125 m long ice core was recovered from the upper Grenzgletscher at an elevation of 4200 m a.s.l. [Eichler *et al.*, 2000a]. The drilling site (45°55' N, 7°52' E) is located at the Monte Rosa massif in the southern Swiss Alps (Wallis Alps) near the Swiss-Italian border. Measurements of the borehole temperatures indicated that the Grenzgletscher consists of cold firn and ice down to an altitude of at least 4000 m a.s.l. [Suter *et al.*, 1995].

In a cold room at -25°C the ice-core sections were cut into 5 cm pieces and the outer 1.5 cm removed with a modified band-saw. Concentrations of F and Cl⁻ were determined in the decontaminated samples by ionchromatography using a gradient pump system (Dionex model DX 500). For details regarding the sample preparation and the chemical analyses see Eichler *et al.* [2000a]. The dating of the ice core was established by annual layer counting using the strong seasonal pattern of NH₄⁺ concentrations and δ¹⁸O values. In addition, reference horizons from Saharan dust falls (1947, 1977, 1990), atmospheric nuclear weapons testing (1958 and 1962) and from the reactor accident in Chernobyl (1986) were used for dating. The resulting time-scale for the 125 m ice core was corroborated by ²¹⁰Pb activity measurements and a simple 1-dimensional ice flow model, revealing that the core covers the time period 1937-94 [Eichler *et al.*, 2000a]. Dating uncertainty is <1 year between 1970 and 1994 and 2 years for the period 1937-69. A mean annual accumulation rate of 2.7 m w.eq. was estimated.

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Figure 1. Record of the Cl^- and F^- concentrations along the ice core. The ice-core depth of 104 m water equivalent represents the total length of 125 m. Because of poor core quality, the section from 58–60 m w.eq. could not be analyzed. Cl^- concentration maxima ($[\text{Cl}^-] > 8 \mu\text{eq/l}$) and F^- concentration maxima ($[\text{F}^-] > 0.8 \mu\text{eq/l}$) accompanied by large Ca^{2+} concentrations ($[\text{Ca}^{2+}] > 10 \mu\text{eq/l}$) are indicated.

Due to the inflow and percolation of meltwater at the drilling site, most probably through a crevasse system in the glacier, a part of the chemical species was leached between 11 and 24 m w.eq. (corresponding to the years 1985–89) [Eichler *et al.*, 2000b]. This especially concerned SO_4^{2-} , Ca^{2+} , and Mg^{2+} , where the concentration records were strongly depleted. In contrast, both species investigated in this study were not significantly affected by this process, indicated by the preserved seasonality (see below).

3. Results and Discussion

Figure 1 shows the F^- and Cl^- concentration records, consisting of a total of 2320 samples. The resolution is about 70 samples per year in the upper part and 25 samples per year in the lower part due to thinning of the ice with depth. Both concentration records exhibit 3 characteristic features, which will be discussed below: (1) several sporadic concentration peaks; (2) strong seasonal fluctuations; and (3) long-term trends.

(1) Maxima in the Cl^- concentration record are accompanied by high Ca^{2+} concentrations and high pH values, indi-

Figure 2. Plot of the Cl^- versus Na^+ concentrations for samples with $[\text{Ca}^{2+}] < 10 \mu\text{eq/l}$. Samples with $[\text{Cl}^-]/[\text{Na}^+] > 2$ are indicated as open circles. Linear regression (thick line) was performed for samples with $[\text{Cl}^-]/[\text{Na}^+] < 2$ (closed diamonds).

cating an input of aerosols from sedimentary dust areas such as the Sahara. The unusual high Cl^- concentration of about 30 $\mu\text{eq/l}$ at 45 m w.eq. depth (Fig. 1), for instance, is related to the Saharan dust fall in 1977 [e.g. Wagenbach and Geis, 1989]. In this case Cl^- originates from sea-salt aerosol, which has its source directly in the Saharan area or was injected into Saharan air masses during transport over the sea [e.g. Coudé-Gaussen, 1991]. This is indicated by the very good correlation between Cl^- and Na^+ (slope = 0.99, $r^2 = 0.85$, significant at the 0.001 level) of the samples with high Ca^{2+} content ($[\text{Ca}^{2+}] > 10 \mu\text{eq/l}$, corresponding to the threefold mean concentration value). The Cl^-/Na^+ ratio (0.99) is in good agreement with the ratio derived from the nearby (1 km distant) Colle Gnifetti site (0.98, [Schwikowski *et al.*, 1999b]). Both ratios are depleted in comparison to the sea-spray ratio of 1.16 [Keene *et al.*, 1986]. The lower ratio was attributed to an additional Na^+ input from mineral dust [Maupetit and Delmas, 1994; Schwikowski *et al.*, 1999b].

Regarding the samples with low Ca^{2+} content ($[\text{Ca}^{2+}] < 10 \mu\text{eq/l}$), we observed an interesting feature. The Cl^- versus Na^+ concentration of these samples is presented in Figure 2. Based on the $[\text{Cl}^-]/[\text{Na}^+]$ ratio we divided the samples into two groups, under the hypothesis that the Cl^- of samples showing a $[\text{Cl}^-]/[\text{Na}^+]$ ratio larger than 2 did not originate from sea-salt aerosol. For samples with a $[\text{Cl}^-]/[\text{Na}^+]$ ratio less than 2 (Fig. 2, diamonds), Cl^- and Na^+ are well correlated, revealing sea spray as the dominant Cl^- source. From the slope of the regression line we derived a ratio of 1.03, similar to that of the samples with high Ca^{2+} content and to that of the Colle Gnifetti (see above). We conclude therefore that the Cl^-/Na^+ ratio of about 1 is characteristic for sea salt transported to this area. The good correlation between Na^+ and Ca^{2+} ($r^2 = 0.71$, all samples, significant at the 0.001 level) indicates that the major part of sea salt arriving at the drilling site is associated with the transport of mineral dust. This evidently supports the explanation of the lower Cl^-/Na^+ ratio compared to the sea-spray value with an additional input of Na^+ from mineral dust. For the second group of samples (Fig. 2, circles), showing partially Cl^-/Na^+ ratios larger than 10, an input of Cl^- from sources other than sea salt must be assumed.

In contrast to Greenland ice cores where F^- spikes reflect emissions of HF by volcanoes [de Angelis and Legrand, 1994], nearly all maxima in the F^- concentration record can be related to an input of Saharan dust aerosols as already ob-

Figure 3. Record of the Cl^- (solid line) and F^- concentrations (dashed line) between 5 and 29 m w.eq. (period 1983–92). 15 point moving averages are shown for both to highlight the seasonality.

served for Cl^- (Fig. 1). *Schwikowski et al.* [1995] found fluorine as an abundant element in dust samples collected at the high-alpine site Jungfraujoch (3450 m a.s.l.) during an outstanding Saharan dust event in March, 1990. However, in contrast to Cl^- only a few of the prominent Saharan dust falls (detected as $[\text{Ca}^{2+}] > 10 \mu\text{eq/l}$, see above) led to increased F concentrations, indicating that the Saharan desert is not a homogeneous source of fluoride-rich minerals. Regarding the entire F record no significant correlation with the other major chemical species was observed, suggesting that a different source was responsible for the major contribution to the F budget over the last 60 years at this site.

(2) In addition to the described maxima both concentration records reveal strong fluctuations. They are due to seasonally varying transport processes from pollutant source regions to the high Alpine sites and were already observed in the snow chemistry of other high Alpine glaciers [e.g. *Maupetit et al.*, 1995; *Schwikowski et al.*, 1999a]. Figure 3 illustrates the seasonal pattern of the F and Cl^- concentrations for the period 1983–92. Higher concentrations of both species in summer snow are due to thermally-driven convection enabling the transport of aerosol-rich air from the atmospheric boundary layer to the high Alpine sites. This vertical motion is suppressed in winter due to the formation of stable low-altitude inversion layers. Therefore, concentrations in winter are low, reflecting conditions in the free troposphere [*Lugauer et al.*, 1998].

(3) For the identification of long term trends in the concentration records 5-year averages were used, thus, averaging year-to-year fluctuations. The historical development of the Cl^- concentration does not show a significant trend with time (Fig. 4). This is consistent with the results from the nearby Colle Gnifetti site, showing no significant differences between the pre-industrial times (1850–80) and the period 1965–81 [*Döscher et al.*, 1995].

The non-sea-salt fraction of Cl^- (nss Cl^-) was calculated using a Cl^-/Na^+ molar concentration ratio of 1, which is assumed to represent the sea-salt ratio at this glacier site (see above). The record of nss Cl^- concentrations is shown in Figure 5A, revealing a strong increase between 1960 and 1985, followed by a steep decrease. The contribution of nss Cl^- to the total Cl^- amounts to 50% at the most with a mean value of 16% for the entire time period. One possible explanation for the trend in the nss Cl^- might be a more efficient degassing of HCl from sea-salt aerosol particles in response to increases in anthropogenically derived HNO_3 and H_2SO_4 according to (1).

However, the maxima in the SO_4^{2-} and NO_3^- concentrations records appear in the ice core between 1970 and 1975, i.e. about 10 years before the nss Cl^- maximum. Furthermore, no significant correlation between the concentrations of nss Cl^- and of $\text{SO}_4^{2-} + \text{NO}_3^-$ was observed ($r^2 = 0.3$, 5-year averages).

Figure 4. 5-year average concentration record of Cl^- .

Figure 5. 5-year average concentration records of non-sea-salt Cl^- (A) and of F (B) (lines) together with historical emission estimates of HCl and HF for Switzerland over the period 1935–90 (dashed lines). Diamonds represent emissions from coal burning, while stars indicate total emissions, derived from BUWAL [1995].

Therefore we assume that mechanism (1) is not responsible for the observed trend in the nss Cl^- concentrations. An additional source of nss Cl^- is direct HCl emission from industrial sources. The largest sources of anthropogenic HCl emissions in western Europe are estimated to be coal combustion (about 75% in 1983) and waste incineration [*Lightowlers and Cape*, 1988]. However, emissions from coal combustion can not explain the observed strong concentration increase after 1960. The use of coal in western Europe was almost constant over the period 1935–85 [*Lavanchy et al.*, 1999], in Switzerland a decrease actually occurred after 1960 [*A. Liechti*, private communication]. In contrast to other western European countries waste incineration is the largest national source of anthropogenic HCl emissions in Switzerland, because most domestic waste is burned. *Lightowlers and Cape* [1988] for instance, estimated HCl emission rates of $12\,000 \text{ t a}^{-1}$ from waste incineration in 1983, but only 700 t a^{-1} from coal burning. Estimates of historical HCl emissions in Switzerland show a strong increase compared to the coal burning level in the period 1960–85 due to rising waste incineration and the large amounts of PVC in waste ([*BUWAL*, 1995], Fig. 5A). Because of the installation of flue gas scrubbers as a consequence of air pollution control measures a decline in emissions has occurred since 1985. The good agreement in the trend between estimated Swiss HCl emissions and our data (Fig. 5A) indicates that the nss Cl^- concentration record at the drilling site is mainly determined by local HCl emissions.

The development of the F concentrations (5-year averages) over the period 1937–94 is shown in Figure 5B. The profile exhibits a steady increase until 1965, followed by a steep decrease. F measurements in a Greenland ice core indicate that coal burning is the most important source of anthropogenic F at this site [*de Angelis and Legrand*, 1994]. However, historical HF emission estimates for Switzerland [*BUWAL*, 1995; A.

Liechti, private communication] reveal that the contribution of HF emissions from coal burning is less than 17% over the last 60 years (Fig. 5B). Increasing HF emissions up to 1970 can be related to increasing aluminum production in nearby plants at Chippis and Martigny in the Rhone valley, which are about 40 km distant from the drilling site. The emission of huge amounts of HF with a maximum of 800 t in 1970 led to severe ecological damage, especially in woods, at that time [Flühler *et al.*, 1981]. As a consequence of the installation of waste-air purification systems a steep decrease in HF emissions occurred after 1970. By comparing our data with the trend in historical emission estimates (see Fig. 5B) we conclude that similar to nssCl^- the major part of F originates from a nearby local source. This is in agreement with the expected short lifetime of HCl and HF in the atmosphere due to their high water solubility, leading to a complete uptake by cloud droplets and subsequent wet deposition close to sources.

Additional evidence of the strong impact of HF and HCl emissions on local precipitation composition was obtained from annual deposition rates. For both species a strong deposition gradient with increasing distance from sources is expected due to the short atmospheric lifetime. Since deposition data close to sources are not available, hypothetical annual deposition rates were estimated using emission data and assuming uniform deposition over Switzerland ($40\,000\text{ km}^2$). They amounted on average to about 120 and $12\text{ mg m}^{-2}\text{ a}^{-1}$ of HCl and HF, respectively, for the time period 1937-94. Measured deposition rates were a factor of about 7 and 2 smaller for HCl and HF (18 and $6.6\text{ mg m}^{-2}\text{ a}^{-1}$), respectively. Assuming that transport and scavenging mechanisms effect both species similarly, the relatively high deposition rate of HF compared to HCl can be attributed to the smaller distance to the source area. This is in agreement with the main source of HF being the aluminum industry in the Rhone valley (about 40 km distant), and the nearest large waste incineration plants emitting HCl being located close to the large cities on the Swiss Plateau (about 100-200 km distant).

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References

- Brewers, J.M. and H.H. Hayson, The terrigenous dust contribution to fluoride and iodide in atmospheric precipitation, *J. Rech. Atmos.*, **13**, 689-697, 1974.
- BUWAL, Vom Menschen verursachte Luftschadstoff-Emissionen in der Schweiz von 1900-2010, *Schriftenreihe Umweltschutz*, **256**, Bundesamt für Umwelt, Wald und Landschaft, Bern, 1995.
- Carpenter, R., Factors controlling the marine geochemistry of fluorine, *Geochim. Cosmochim. Acta*, **33**, 1153-1167, 1969.
- Cicerone, R.J., Halogens in the atmosphere, *Rev. Geophys. Space Phys.*, **19**, 123-139, 1981.
- Coudé-Gaussen, G., *Les Poussières sahariennes, cycle sédimentaire et place dans les environnements et paléoenvironnements désertiques*, J. Libbey Eurotext, 485 pp., 1991.
- de Angelis, M. and M. Legrand, Origins and variations of fluoride in Greenland precipitation, *J. Geophys. Res.*, **99**, 1157-1172, 1994.
- Döscher, A., H.W. Gäggeler, U. Schotterer and M. Schwikowski, A 130 years deposition record of sulfate, nitrate and chloride from a high-alpine glacier, *Water Air Soil Pollut.*, **85**, 603-609, 1995.
- Döscher, A., H.W. Gäggeler, U. Schotterer, M. Schwikowski, A historical record of ammonium concentrations from a glacier in the Alps, *Geophys. Res. Lett.*, **23**, 2741-2744, 1996.
- Eichler, A., M. Schwikowski, H.W. Gäggeler, V. Furrer, H.-A. Synal, J. Beer, M. Saurer and M. Funk, Glaciochemical dating of an ice core from the upper Grenzgletscher (4200 m a.s.l.), *J. Glaciol.*, in press, 2000a.
- Eichler, A., M. Schwikowski and H.W. Gäggeler, Meltwater induced relocation of chemical species in Alpine firn, *Tellus B*, in press, 2000b.
- Flühler, H., T. Keller and H. Schwager in *Waldschäden im Walliser Rhonetal*, W. Bosshard (eds.), Mitteilungen der Eidgenössischen Anstalt für das forstliche Versuchswesen, **57**, 399-414, 1981.
- Keene, W.C., A.A.P. Pszenny, J.N. Galloway and M.E. Hawley, Sea-salt corrections and interpretation of constituent ratios in marine precipitation, *J. Geophys. Res.*, **91**, 6647-6658, 1986.
- Lavanchy, V.M.H., H.W. Gäggeler, U. Schotterer, M. Schwikowski and U. Baltensperger, Historical record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti, Switzerland), *J. Geophys. Res.*, **104**, 21227-21236, 1999.
- Legrand, M.L. and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, **35**, 219-243, 1997.
- Lightowlers, P.J. and J.N. Cape, Sources and fate of atmospheric HCl in the U.K. and western Europe, *Atmos. Environ.*, **22**, 7-15, 1988.
- Lugauer, M., U. Baltensperger, M. Furger, H.W. Gäggeler, D.T. Jost, M. Schwikowski and H. Wanner, Aerosol transport to the high Alpine sites Jungfraujoch (3454 m asl) and Colle Gnifetti (4452 m asl), *Tellus*, **50B**, 76-92, 1998.
- Maupetit, F. and R.J. Delmas, Snow chemistry of high altitude glaciers in the French Alps, *Tellus*, **46B**, 304-324, 1994.
- Maupetit, F., D. Wagenbach, P. Weddeling and R.J. Delmas, Seasonal fluxes of major ions to a high altitude cold alpine glacier, *Atmos. Environ.*, **29**, 1-9, 1995.
- Mayewski, P.A., L.D. Meeker, M.C. Morrison, M.S. Twickler, S.I. Whitlow, K.K. Ferland, D.A. Meese, M.R. Legrand and J.P. Steffensen, Greenland ice core "signal" characteristics: An expanded view of climate change, *J. Geophys. Res.*, **98**, 12839-12847, 1993.
- Schwikowski, M., P. Seibert, U. Baltensperger and H.W. Gäggeler, A study of an outstanding Saharan dust event at the high-Alpine site Jungfraujoch, Switzerland, *Atmos. Environ.*, **29**, 1829-1842, 1995.
- Schwikowski, M., Analytical chemistry in high-alpine environmental research, *Chimia*, **51**, 8-13, 1997.
- Schwikowski, M., S. Brütsch, H.W. Gäggeler and U. Schotterer, A high resolution air chemistry record from an Alpine ice core: Fiescherhorn glacier, Swiss Alps, *J. Geophys. Res.*, **104**, 13709-13720, 1999a.
- Schwikowski, M., A. Döscher, H.W. Gäggeler and U. Schotterer, Anthropogenic versus natural sources of atmospheric sulphate from an Alpine ice core, *Tellus*, **51B**, 938-951, 1999b.
- Suter, S., Die Verbreitung kalter Firn- und Eisregionen im Alpengebiet, *Diploma Thesis*, ETH Zürich, Switzerland, 130 pp., 1995.
- Van de Velde, K., C. Ferrari, C. Barbante, I. Moret, T. Bellom, S. Hong and C. Boutron, A 200 year record of atmospheric cobalt, chromium, molybdenum, and antimony in high altitude Alpine firn and ice, *Environ. Sci. Technol.*, **33**, 3495-3501, 1999.
- Wagenbach, D., K.O. Münnich, U. Schotterer and H. Oeschger, The anthropogenic impact on snow chemistry at Colle Gnifetti, Swiss Alps, *Ann. Glaciol.*, **10**, 183-187, 1988.
- Wagenbach, D. and K. Geis, The mineral dust record in a high altitude Alpine glacier (Colle Gnifetti, Swiss Alps), In *Paleoclimatology and Paleometeorology: Modern and Past Patterns of Global Atmospheric Transport*, M. Leinen and M. Sarnthein (eds.), Kluwer Academic Publishers, Dordrecht, 543-564, 1989.

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