JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 107, NO. D12, 4139, 10.1029/2001JD001165, 2002

Seasonally resolved Alpine and Greenland ice core records of anthropogenic HCl emissions over the 20th century

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Received 30 July 2001; revised 6 November 2001; accepted 14 November 2001; published 21 June 2002.

[1] The continuous highly resolved records of Cl^-, Na^+, and Ca^{2+} in ice cores from Col du Dôme (4250 m elevation, French Alps) and Summit (3240 m elevation, central Greenland) are used to reconstruct the history of atmospheric HCl pollution over Europe and Greenland since the early 20th century. The evaluation of the HCl amount in summer snow deposits at high-elevation Alpine sites is complex since continental emissions (soils, halide evaporites, and possibly manure-fertilized fields) account for 80% of the chloride budget and only one fifth of Cl^- is related to HCl. During the preindustrial era the HCl content of summer Alpine snow layers fluctuated between 0 and 6 ng g^{-1}, likely in relation with a highly variable interannual biomass burning activity in western Europe. From 1925 to 1960 the HCl levels were slightly higher (3–9 ng g^{-1}), mainly due to growing coal burning emissions in western Europe. In the late 1960s a sharp increase of HCl levels (up to 17 ng g^{-1}) took place as a result of the setup of waste incineration in western Europe, this process contributing 3–4 times more than coal combustion to the HCl budget of summer Alpine snow layers deposited between 1970 and 1990. In winter, sea spray emissions dominate (∼78%) the total Cl^- level of Alpine snow layers. The HCl trend in these snow layers remained limited to ∼2 ng g^{-1} over the 20th century, likely in relation to waste incineration after 1965. In Greenland snow layers most of particulate Cl^- originates from sea spray, 1/3 to 2/3 of Cl^- being present as HCl in spring and summer, respectively. The Greenland HCl ice core records indicate a preindustrial HCl level close to 4 ng g^{-1}, which is found to be mainly due to the sea-salt dechlorination, while the contribution of passive volcanic HCl emissions at high northern latitudes can be neglected. The input from sea-salt dechlorination has been enhanced by a factor of 2–3 during the second half of the 20th century similarly to the increase of the atmospheric acidity in response to growing NO_x and SO_2 anthropogenic emissions.

INDEX TERMS: 0325 Atmospheric Composition and Structure: Evolution of the atmosphere; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; *KEYWORDS:* Alpine ice core, Greenland ice core, hydrochloric acid, anthropogenic emissions, waste incineration, coal burning

1. Introduction

[2] In addition to HNO_3 and H_2SO_4, HCl represents the third mineral acid contributing to the acidity of precipitation and is one of the major constituents of reactive atmospheric chlorine. Some large uncertainties still exist on the strength of HCl sources, which include continental (passive volcanic emissions, biomass burning, coal combustion, and waste incineration) and oceanic (dechlorination of sea-salt aerosol) emissions [*Keene et al.*, 1999, and references therein]. In addition to these primary emissions the chlorocarbons oxidation was recently proposed as a significant source of HCl for the global background atmosphere [*Sanhueza*, 2001]. Due to these uncertainties it remains difficult to evaluate to what extent anthropogenic processes may dominate natural HCl emissions. Such gaps stimulate the studies of HCl in ice cores extracted from glaciers located in continental midlatitude regions as well as from drill sites more exposed to marine influence, such as at the Greenland ice cap.

[3] Greenland ice core studies have inferred a trend of HCl over the last few decades [*Mayewski et al.*, 1993; *Fischer*, 1997], but the cause of this change remains unclear (growing primary HCl emissions from industrialized regions of the Northern Hemisphere or enhanced sea-salt dechlorination by

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0148-0227/02/2001JD001165$09.00

increasing acidification of the atmosphere). In these studies the HCl content of ice was evaluated by using either total Na^+ [*Fischer*, 1997] or total Na^+ corrected from its soil contribution (using calcium) [*Mayewski et al.*, 1993] as a tracer of sea salt and has assumed that sea-salt aerosol contains Cl^- and Na^+ in similar proportion than in seawater. However, it remains unclear if this last assumption is valid and if other Cl^- containing particles emitted from continents can be neglected in these calculations.

[4] A recent study of the HCl (using total Na^+ as a tracer of sea salt and the seawater Cl^-/Na^+ ratio) in an Alpine ice core extracted in the Monte Rosa massif revealed an increase of annual levels from 1965 to 1985 [*Eichler et al.*, 2000]. This annual change was attributed to the development of HCl emissions from waste incineration from the Swiss Plateau, suggesting a poor spatial representativeness of Alpine ice records for this species. However, the detailed examination of the spatial representativeness of Alpine ice records requires the separation of winter and summer trends that are representative of different air masses (tropospheric background in winter versus boundary layer in summer) [*Preunkert et al.*, 2001b].

[5] In this paper, on the basis of examination of Cl^- and Na^+ as well as Ca^{2+}, we first examine in more detail the origins of particulate Cl^- and Na^+ present in snow layers deposited at high-elevation Alpine and Greenland sites. On the basis of a more accurate estimate of the HCl level in these snow layers, we then examine the long-term seasonally resolved changes of HCl since the beginning of the 20th century over Europe and central Greenland. That permits us to discuss the relative contribution of natural versus anthropogenic sources to the HCl budget and to evaluate the major anthropogenic processes influencing these marine and continental remote atmospheres.

2. Drill Site Characteristics, Ice Core Dating, and Analyses

[6] A 126 m long ice core extracted in 1994 at Col du Dôme (CDD) (4250 m above sea level (asl), located near the Mont Blanc summit), was analyzed for major ions (Na^+, NH_4^+, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-}) with a seasonal resolution. This was performed at the Laboratoire de Glaciologie et Géophysique de l'Environnement (LGGE) along the upper 117 m of the core (1050 samples) which correspond to the well-dated part of the core (75 ± 5 years) [*Preunkert et al.*, 2000] and from 117 to 126 m depth at the Institut für Umweltphysik (IUP) (Figure 1). For major ion determinations the ion chromatography accuracy is typically 5%. CDD ice samples were cleaned at LGGE by using an electric plane device previously developed at IUP [*Fischer et al.*, 1998]. The validity of the decontamination procedure was tested by checking blank values obtained on pieces of frozen ultrapure water. Mean blank values (11 samples) obtained at LGGE were 0.4 ± 0.3 ng g^{-1} for Cl^-, 0.6 ± 0.3 ng g^{-1} for Na^+, and 4.3 ± 2.1 ng g^{-1} for Ca^{2+}. Mean blank values (∼40 samples) obtained at IUP using an autosampler were slightly higher, 1.7 ± 1.4 ng g^{-1} for Cl^-, 1.3 ± 1.0 ng g^{-1} for Na^+, and 3.2 ± 3.4 ng g^{-1} for Ca^{2+}. Hence data obtained on the bottom part of the CDD core were corrected for these blank values. The Summit core was cleaned using a lathe developed at LGGE [*Legrand et al.*, 1993]. Owing to the larger ice fraction removed by this procedure from the entire core (instead of lamellae from the CDD ice core), all ions blank values corresponding to the decontamination step were found insignificant for the Summit core.

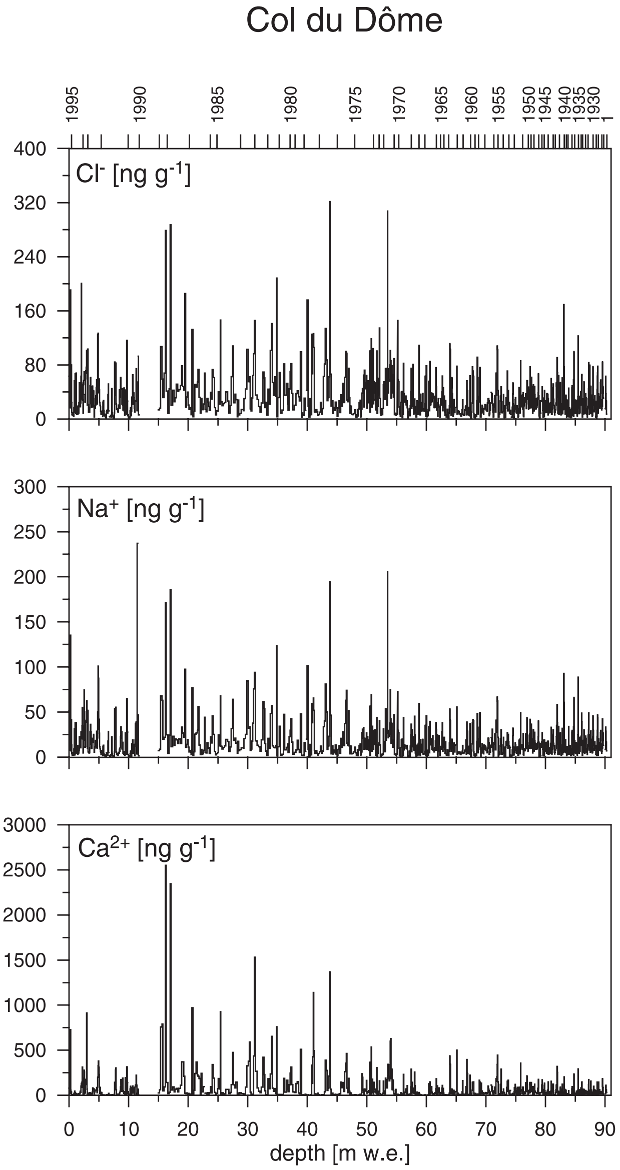

Figure 1. High-resolution depth profiles (in meters water equivalent (mwe)) of chloride, sodium, and calcium along the upper 90 mwe of the 1994 Col du Dôme (CDD) core. The dating reported on the top refers to *Preunkert et al.* [2000].

[7] Along the CDD ice core, annual layer thickness ranges from 3 to 0.2 m water equivalent (mwe) from the surface to a depth of 90 mwe (i.e., 117 m depth) [*Preunkert et al.*, 2000]. The studies of seasonal variations of NH_4^+ [*Preunkert et al.*, 2000], F^- [*Preunkert et al.*, 2001a] and SO_4^{2-} [*Preunkert et al.*, 2001b] indicate that seasonally resolved records are here available for these species until 1925. Such well-marked seasonal changes characterized by summer maxima reflect distinct seasonal atmospheric conditions prevailing there due to the presence or absence of upward advection of air masses from the boundary layer in

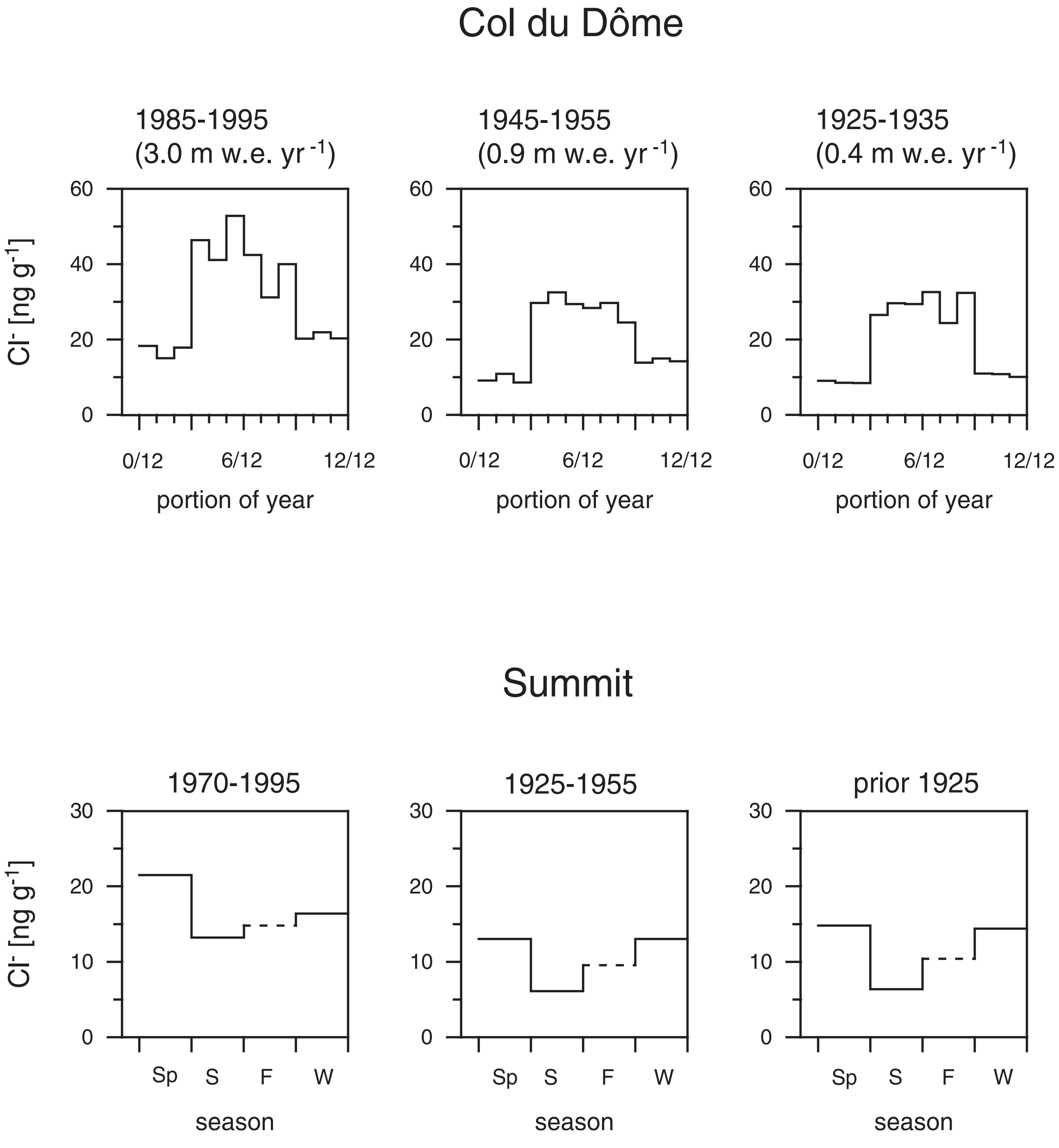

Figure 2. Mean seasonal cycle of chloride in snow layers deposited over various time periods at (top) CDD and (bottom) Summit.

summer and winter [*Baltensperger et al.*, 1997; *Preunkert and Wagenbach*, 1998]. This summer/winter contrast leads to different source region apportionment at the site as shown for sulfate (a part of western Europe in summer instead of total Europe in winter) [*Preunkert et al.*, 2001b]. For Cl$^-$ we found (Figure 2) summer maxima with summer to winter ratios of 2–3 over the 1925–1935, 1945–1955, and 1985–1995 time periods.

[8] We also examined a high-resolution chemical record (470 samples) extracted from a Summit (central Greenland) ice core (Figure 3). The dating of this ice core indicates an annual snow accumulation close to 0.23 mwe and a possible error of 2 years over the time period from 1870 to 1992 [*Legrand and De Angelis*, 1996]. A specific difficulty dealing with the HCl record in ice cores extracted in polar regions characterized by low snow accumulation with respect to the situation at midlatitude glaciers comes from the fact that this species is present in the atmosphere in the gas phase, which may be remobilized after deposition and during firnification [*De Angelis and Legrand*, 1995; *Legrand and Mayewski*, 1997]. It was shown that this process is particularly important at sites where the annual

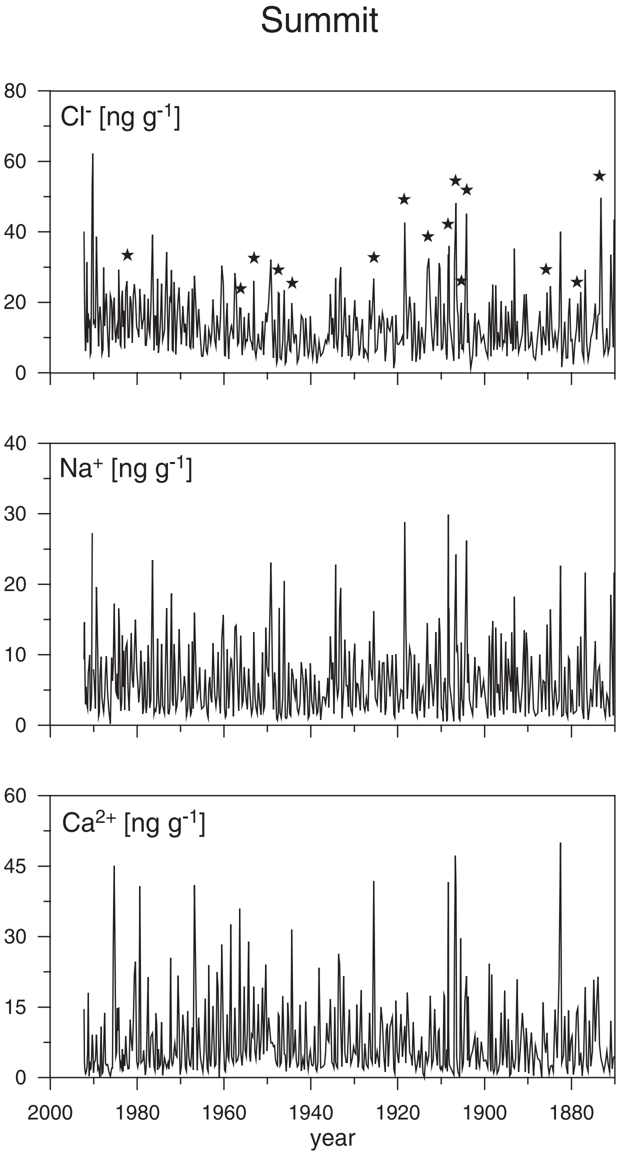

Figure 3. High-resolution profiles of chloride, sodium, and calcium along a Summit (central Greenland) ice core spanning the 1870–1993 time period. The dating of this core reported on the bottom refers to *Legrand and De Angelis* [1996]. Stars reported on the chloride profile refer to snow layers regarded as contaminated by volcanic inputs (see section 3.3).

snow accumulation rate is as low as 0.03 mwe. However, *Stanzick* [2001] investigated the spatial variability of pre-bomb ^{36}Cl levels and bomb ^{36}Cl inventories in central Greenland over a large snow accumulation range (down to 0.10 mwe per year) and found no significant losses. Since ^{36}Cl is expected to be deposited in the form of HCl, we may neglect re-emissions of this species at Summit. On the basis of examination of the seasonal variations of Na^+, NH_4^+, and Ca^{2+} contents and following previous works [*Whitlow et al.*, 1992; *Legrand and Mayewski*, 1997; *Fischer et al.*, 1998], we assigned three seasons: spring characterized by Ca^{2+} maximum, summer characterized by Na^+ and Ca^{2+} minima, and winter characterized by Na^+ maximum and NH_4^+ minimum. At that site the Cl^- level exhibits a winter/spring maximum (Figure 2) with a mean winter/spring to summer ratio close to two. A 44-year record of 10-day back trajectories at 500 hPa suggests that air masses arriving at Summit in winter and spring correspond to transport from North America as well as from Asia/Europe [*Kahl et al.*, 1997]. Most of the time, in summer, air masses arriving above Summit come from North America, these shorter trajectories being related to a less vigorous circulation in summer than in winter/spring.

3. Evaluation of HCl and Aerosol-Derived Chloride Levels in Ice Cores

3.1. Evaluation of HCl Levels

[9] Cl^- is incorporated in precipitation as HCl as well as various Cl^- containing aerosols. The simplest example is the case of a marine precipitation for which, as far as the aerosol input from continents can be neglected, it is legitimate to assume that Cl^- is mainly provided as HCl and sea-salt aerosol. In this case the amount of HCl can be derived by subtracting the sea-salt chloride contribution to total chloride as follows:

$$[\mathrm{HCl}] = [\mathrm{Cl}^-] - 1.8q\,[\mathrm{Na}_m^+]. \qquad (1)$$

Here Na_m^+ is the marine sodium (identical to the total sodium in the absence of significant continental input) and q ($q < 1$) refers to the fractionation factor considering a possible deviation of the chloride to sodium ratio in sea-salt aerosol from the respective seawater mass ratio (1.8).

[10] In continental precipitation the sea spray chloride contribution is weaker, and the problem becomes much more complex since this use of sea-salt correction is biased by the presence of leachable sodium in continental input [*Legrand et al.*, 1988; *Legrand and Delmas*, 1988], and chloride containing aerosols may also originate from soil weathering and halide evaporites. Furthermore, *Simeonov et al.* [1999] suggested that a significant fraction of Cl^- and Na^+ present in precipitation from central Austria comes from manure-fertilized field emissions, which are rich in Na^+ and Cl^- (sodium to chloride mass ratio of 1.6) and poor in Ca^{2+}.

[11] The aerosol-derived Cl^- fraction in continental precipitation would depend on Na^+ and Ca^{2+} levels since Na^+ is mainly present in halide components (sea spray, evaporites, and manure-fertilized fields emissions) and Ca^{2+} in soils. We therefore examine the dependence of Cl^- to Na^+ and Ca^{2+} contents ($[Cl^-] = a + k_{Na}[Na^+] + k_{Ca}[Ca^{2+}]$) in snow layers deposited before 1955, a period over which the anthropogenic Cl^- input, mostly related to coal combustion, remained moderate (see section 4). This

Table 1. Values of Coefficients of the Multiple Regressions of Cl^- to Na^+ and Ca^{2+} ($[Cl^-] = a + k_{Na}[Na^+] + k_{Ca}[Ca^{2+}]$) in Snow Layers Deposited Prior to 1955 at CDD and Summit

Site, Season	a	k_{Na}	k_{Ca}	Number of Samples	R^2
CDD, Summer	3.4	1.465 ± 0.054	0.0251 ± 0.0132	240	0.8
CDD, Winter	−0.5	1.74 ± 0.056	0.1399 ± 0.0873	69	0.9
Summit, Spring	4.6	1.27 ± 0.08	0.0027 ± 0.067	63	0.8
Summit, Summer	2.7	1.13 ± 0.19	0.40 ± 0.15	63	0.36

Table 2. Mean Levels of Na^+, Nonsoil Na^+, Cl^-, HCl, and Ca^{2+} in Spring and Summer Snow Layers Deposited at Summit Between 1870 and 1993[a]

Species	Spring, ng g^{-1}	Summer, ng g^{-1}
Na^+	8 ± 5	2 ± 1
	(7 ± 4)	(2 ± 1)
Nonsoil Na^+	7 ± 5	2 ± 1
	(6 ± 4)	(2 ± 1)
Cl^-	17 ± 8	8 ± 5
	(14 ± 6)	(6 ± 2)
HCl	6 ± 4	5 ± 5
	(4.5 ± 2.5)	(3.5 ± 2.0)
Ca^{2+}	15 ± 7	3 ± 2
	(14 ± 5)	(3 ± 2)

[a] For calculations of nonsoil contributions of sodium, as well as HCl, see section 3. Values in parentheses correspond to the snow layers deposited prior to 1955.

was performed (Table 1) for snow layers deposited between 1925 and 1955 at CDD, excluding samples containing Saharan dust, and between 1870 and 1955 at Summit, excluding samples suspected to be contaminated by volcanic inputs (section 3.3). Assuming that k_{Na} and k_{Ca} values have not changed over time, the HCl level can be evaluated as follows:

$$[HCl] = [Cl^-] - (k_{Na}[Na^+] + k_{Ca}[Ca^{2+}]). \qquad (2)$$

[12] Because of the poor accuracy of the multiple regression for summer Summit snow layers ($R^2 = 0.36$, Table 1), we used k_{Na} and k_{Ca} spring values for calculating HCl levels in both spring and summer layers. The low Na^+ and Ca^{2+} levels in summer layers (Table 2) would, however, lead only to small differences on the HCl evaluation. Depending on sites and seasons, the k_{Na} values significantly differ from the Cl^-/Na^+ seawater ratio of 1.8, which was employed in the previous studies of HCl in ice cores. The use of the conventional sea-salt correction (equation (1) with $q = 1$) produces a significant bias on the results. For instance, the mean HCl level of summer CDD layers calculated using this conventional correction is 3 ng g^{-1} lower than the one calculated by using equation (2).

[13] Of particular importance is the estimate of uncertainties when dealing with the low-impurity content which characterizes deposition at remote regions. These uncertainties are usually dominated by the analytical accuracy (i.e., here Cl^-, Na^+, and Ca^{2+}), which accounts for 5% accuracy and blank standard deviations. An additional uncertainty in evaluating HCl content is related to the uncertainties in the coefficients (k_{Na} and k_{Ca}) reported in Table 1. The resulting errors have been estimated by state of the art error propagation calculations.

[14] The estimated mean half-year HCl levels of summer and winter CDD snow layers are plotted in Figure 4 along with their uncertainties. The uncertainties are typically close to ±3.5 ng g^{-1} (±2.7 ng g^{-1} when samples suspected to contain Saharan dust are not considered) in summer and ±1.5 ng g^{-1} in winter. In summer they mainly result from analytical errors in Na^+ and Cl^- determinations. Larger uncertainties are encountered for years during which samples suspected to contain Saharan dust input are present (as in 1989, Figure 4). In winter, due to lower Cl^- and Na^+ levels than in summer (Table 3), the uncertainties are resulting from both the accuracy of Na^+ and Cl^- determinations and the blank variability for these two species. Note that in spite of fewer samples containing Saharan dust in the bottom of the CDD core, the standard error of HCl evaluation is there relatively high (±3.5 ng g^{-1}) due to a larger standard deviation of Cl^- and Na^+ blank values corresponding to this set of analysis, as emphasized in section 2. In Greenland the uncertainties (not shown) are close to ±1.5 ng g^{-1} in spring and ±0.5 ng g^{-1} in summer.

3.2. Aerosol-Derived Sodium and Chloride in Alpine and Greenland Snow Layers

[15] In this section we examine the meaning of the k_{Na} and k_{Ca} coefficients derived from the multiple regressions (Table 1) in terms of origins of aerosol-derived chloride and sodium present in snow layers deposited at the two drill sites. Using Ca^{2+} and Na^+ as tracers of the input related to soil weathering and halide components (sea spray, evaporites, and possibly manure-fertilized fields emissions), respectively, the Cl^- level of snow layers can be expressed as

$$\begin{aligned}[Cl^-] &= [HCl] + \gamma([Na^+] - \alpha[Ca^{2+}]) + \beta[Ca^{2+}] \\ &= [HCl] + \gamma[Na^+] + (\beta - \gamma\alpha)[Ca^{2+}], \end{aligned} \qquad (3)$$

where γ is the mean chloride to sodium mass ratio in the halide components, and α and β are the sodium to calcium and chloride to calcium mass ratios in soils (leachable fractions), respectively.

[16] At CDD in summer, comparison of the coefficients of the multiple regression and equation (3) indicates a Cl^-/Na^+ mass ratio γ (identical to k_{Na}) of 1.465. The examination of the linear relation between Na^+ and Ca^{2+} in snow layers deposited at CDD in summer (Figure 5) shows that, in addition to the input related to soil weathering, other sodium sources (sea spray, evaporites from continents, and possibly manure-fertilized fields) contribute there to the Na^+ budget as suggested by the relatively low correlation coefficient ($R^2 = 0.59$) and the nonzero y intercept (~7 ng g^{-1}). The slope of the regression reported in Figure 5 suggests a typical Na^+/Ca^{2+} mass ratio in soils (α) of 0.156. This value and the k_{Ca} value lead to a Cl^-/Ca^{2+} ratio in soils (β) of 0.254. This value is consistent with the slope of the Cl^- to Ca^{2+} correlation reported in Figure 5 (0.264). Introducing α, β, and γ values in equation (3), we found that particulate Cl^- accounts for 81% of the total Cl^- level (30 ng g^{-1}, Table 3) of summer CDD snow layers deposited between 1925 and 1995, of which soils and halides contribute in similar proportion (47 and 34%, respectively), the remaining fraction (19%) being related to the presence of HCl.

[17] In winter at CDD, due to a lower input from soils as depicted by the Ca^{2+} content of 5 ng g^{-1} (instead of 55 ng g^{-1} in summer; Table 3), the Cl^- related to halide components dominates (70%) the total Cl^- level of 10 ng g^{-1}. The fraction of Na^+ coming with halide components is almost two times larger in summer than in winter (Table 3). Since sea spray emissions are higher in winter than in summer, the observed reverse seasonal change for the sea spray/evaporite Na^+ fraction suggests that in summer, as a result of an efficient upward transport from the continental boundary layer, halide (evaporite and possibly manure-fertilized field)

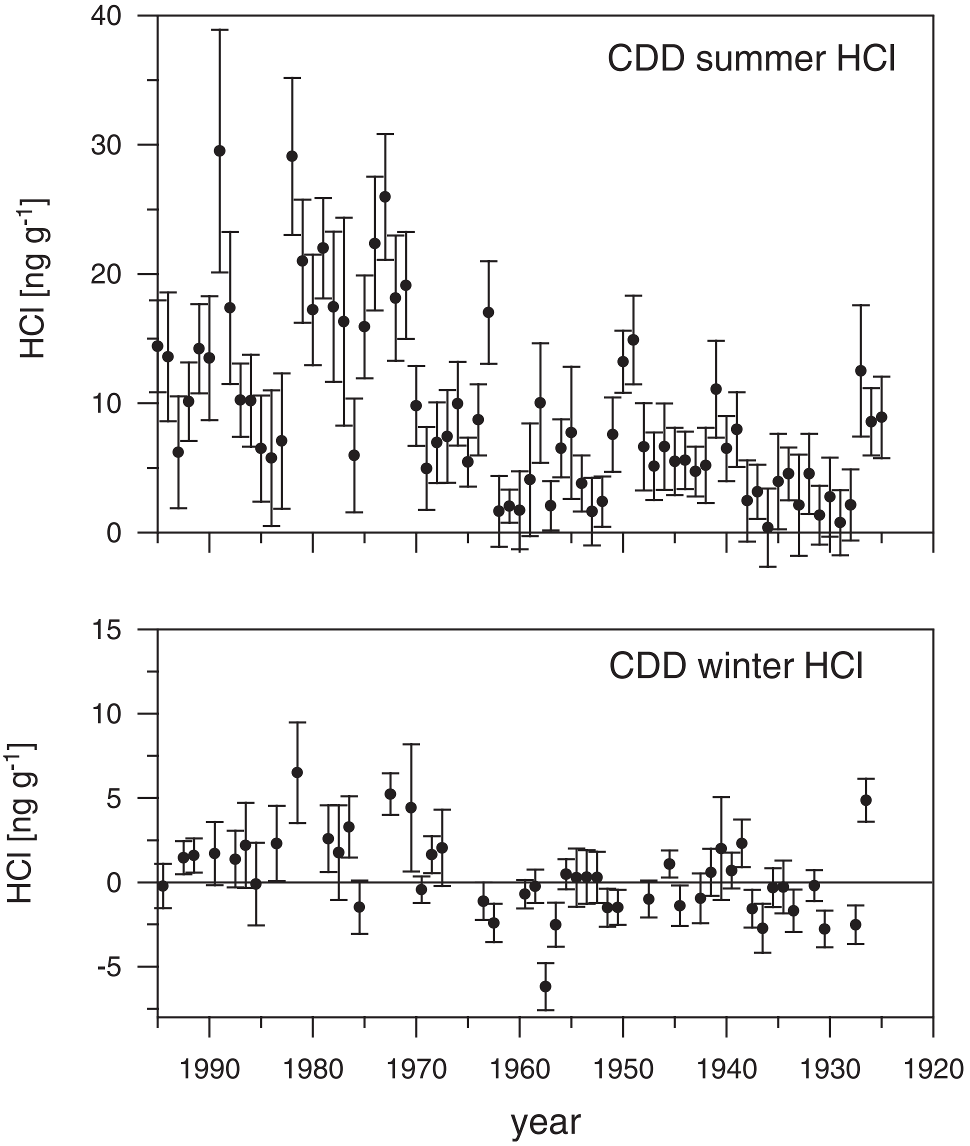

Figure 4. Annual (top) summer and (bottom) winter means of HCl in the CDD ice core. Vertical bars refer to the standard errors of the seasonal HCl means.

emissions dominate this sodium fraction, while in winter, due to a more active cyclogenis over the Atlantic ocean, sea spray likely dominates. Note that the γ value of 1.74 suggests a limited sea-salt aerosol fractionation at that season. As depicted in Figure 2, the winter Cl^- level was 2 times larger over the 1985–1995 decade than between 1925 and 1955. The examination of the long-term trend of Cl^- and Na^+ (not shown) indicates indeed that the Cl^- level, which fluctuated between 5 and 10 ng g^{-1} from 1925 to 1970, was enhanced to 18 ng g^{-1} over the 1975–1985 decade. Similarly, the Na^+ level close to 5 ng g^{-1} from 1925 to 1970 reached 9 ng g^{-1} over the 1975–1985 decade, suggesting an additional input of Cl^-, mainly in the form of NaCl at that time. Such a recent increase of the NaCl content of winter CDD snow layers is possibly related to the growing use of salt for deicing the roads (from 200 kt of NaCl in the early 1970s to 1200 kt in the 1980s in France, for example) and the subsequent spray of liquid by the car traffic.

[18] In Greenland snow layers the soil input is maximum in spring, as depicted by the mean Ca^{2+} level of 15 ng g^{-1} (Table 2). Using a Na^+/Ca^{2+} ratio (α) of 0.1 reported for dust input reaching Greenland [*De Angelis et al.*, 1997], we

Table 3. Same as Table 2 for Summer and Winter Snow Layers Deposited at CDD Between 1925 and 1995[a]

Species	Summer, ng g^{-1}	Winter, ng g^{-1}
Na^+	15 ± 13	5 ± 7
	(14 ± 9)	(4 ± 5)
Nonsoil Na^+	7 ± 8	4 ± 7
	(7 ± 7)	(3 ± 5)
Cl^-	30 ± 23	10 ± 14
	(25 ± 14)	(8 ± 9)
HCl	7 ± 12	1 ± 3
	(3.5 ± 6)	(0 ± 2)
Ca^{2+}	55 ± 63	5 ± 4
	(43 ± 35)	(5 ± 3)

[a] Values reported in parentheses correspond to the snow layers deposited prior 1955.

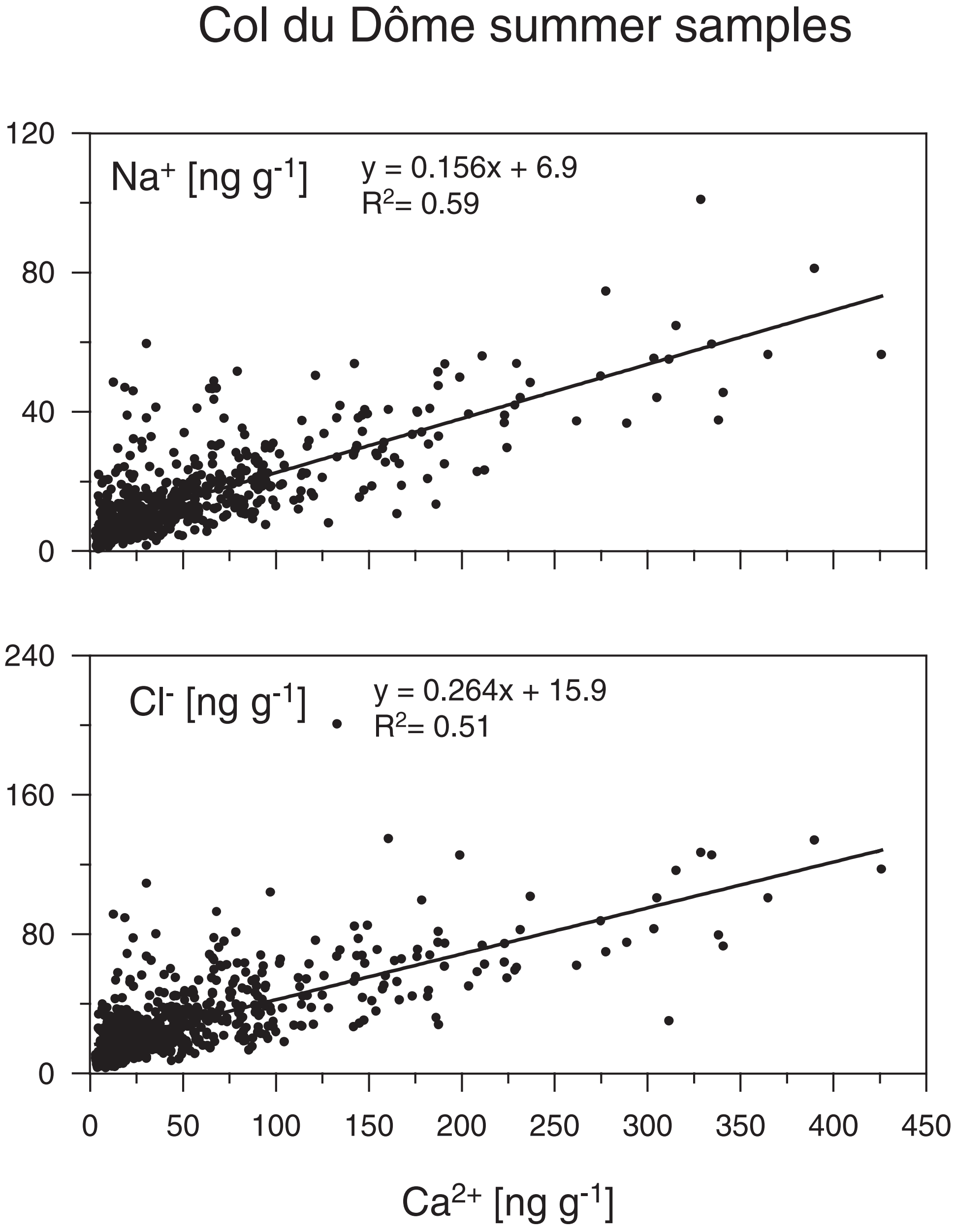

Figure 5. (top) Sodium and (bottom) chloride versus calcium in summer CDD layers excluding Saharan dust samples (see section 3.3).

calculate a β value of 0.13. Cl^- present in Summit spring snow layers originates in soils (12%) and halides (thought to be dominated there by sea spray) (50%), the remaining part being related to HCl (38%). In summer the sea spray and soil contributions are lower than in spring, as depicted by the Na^+ and Ca^{2+} contents (Table 2). As a result, the contribution of particulate chloride is weaker ($\sim$30% for sea spray and $\sim$10% for soil), and 2/3 of Cl^- are related to the presence of HCl at that season.

3.3. Impact of Saharan Dust in the Alps and Volcanic Eruptions in Greenland

[19] Saharan dust plumes can sporadically reach the Alps and disturb the snow chemistry [*Wagenbach et al.*, 1996]. Ninety-eight summer and four winter samples were identified (alkaline Ca^{2+}-rich layers) along the CDD core as contaminated by Saharan dust by *Preunkert et al.* [2001a].

[20] To calculate the HCl levels in these layers, we need to know the amount of Na^+ and Cl^- present in Saharan dust material reaching Alpine sites. *Talbot et al.* [1986] examined the water-soluble composition of aerosols collected in Saharan dust plumes present over the tropical North Atlantic for Na^+ (3704 ppm), K^+ (1663 ppm), and Cl^- (3158 ppm). Since Ca^{2+} was not measured by *Talbot et al.* [1986], we try to characterize the chemistry of Saharan dust by checking the linear relationships between Na^+, K^+, and Cl^- versus Ca^{2+} observed in the 98 summer CDD samples suspected to be contaminated by Saharan dust. These relationships ($[Na^+] = 0.071\ [Ca^{2+}] + 20.8$ with $R^2 = 0.66$; and $[K^+] = 0.035\ [Ca^{2+}] + 12.5$ with $R^2 = 0.56$)

indicate that Na^+ is 2 times more abundant than K^+ in these snow layers, which is in very good agreement with the composition reported by *Talbot et al.* [1986]. On the basis of Na^+ and Cl^- data from *Talbot et al.* [1986] and the observed Na^+/Ca^{2+} ratio of 0.071 in CDD dust events, we can expect a Cl^-/Ca^{2+} ratio close to 0.063. This value is twice lower than the slope of the correlation between Cl^- and Ca^{2+} levels ($[Cl^-] = 0.113\ [Ca^{2+}] + 34.6$ with $R^2 = 0.67$). Such a difference may be due to an additional uptake of chloride in the form of HCl by this alkaline aerosol during transport. On this basis we corrected all samples suspected to be influenced by Saharan dust from their terrigeneous contribution using Na^+/Ca^{2+} and Cl^-/Ca^{2+} ratios of 0.071 and 0.063, respectively.

[21] As discussed by *Fischer et al.* [1998] and *Preunkert et al.* [2001b], the SO_4^{2-} background level of Summit snow layers has been sporadically disturbed by well-identified volcanic eruptions. Denoted with a star in Figure 3, some of these events also appear to disturb the background Cl^- levels by a few tens of ng g^{-1}, in particular, in 1873 (the Grimsvotn eruption in Iceland) and at the beginning of the 20th century (several eruptions including the Katmai one in Alaska in 1912/1913). In the following, all of these snow layers were discarded in examining the long-term trend.

4. The Alpine HCl Trends at Col du Dôme

4.1. CDD Summer Trend

[22] To examine the long-term summer trend of HCl, we smoothed summer means reported in Figure 4 by using single spectrum analysis (SSA) with a time window of 5 years (Figure 6). As discussed in detail by *Preunkert et al.* [2001b], in spite of a very uncertain dating, the CDD snow layers located between 90.3 and 95.3 mwe depth closely correspond to the preindustrial condition at this site. An overall mean summer HCl level of 0.2 ± 2.7 ng g^{-1} is calculated for these preindustrial CDD ice layers. Out of 12 summer means, 8 exhibit negative values (from −1 to −3 ng g^{-1} with an uncertainty of 3.5 ng g^{-1}), and 4 are positive (from 1 to 6 ng g^{-1}), of which 2 are significantly different from zero with respect to their uncertainties. That suggests the existence of a natural HCl level in summer ranging between 0 and 6 ng g^{-1}. From 1925 to 1965, smoothed values fluctuated between 3 and 9 ng g^{-1} (Figure 6), significantly exceeding the mean preindustrial level of 0.2 ng g^{-1}. After 1965, HCl levels were sharply enhanced, reaching a plateau value of 16–18 ng g^{-1} between 1972 and 1980. In the following we examine the role of anthropogenic processes having disturbed the natural HCl level of summer ice at high-elevation Alpine sites.

4.1.1. Coal burning contribution

[23] Both S and Cl are present at significant levels in coal. During combustion most sulfur emitted to the atmosphere is in the form of SO_2, but a certain fraction of the S content is retained in ash. For chloride the amount of particulate versus HCl emissions is not well known and may depend of the combustion process [*McCulloch et al.*, 1999]. Also, a fraction of Cl can be retained in ash. Assuming that a similar fraction of Cl and S is retained in ash during the combustion and that Cl is mainly released into the atmosphere in the form of HCl, annual HCl emission (E_{Cl}) can be calculated from the Cl (C_{Cl}) and S (C_S) contents of employed coal and from annual S coal burning emissions (E_S) following

$$E_{Cl} = (C_{Cl}/C_S)E_S. \tag{4}$$

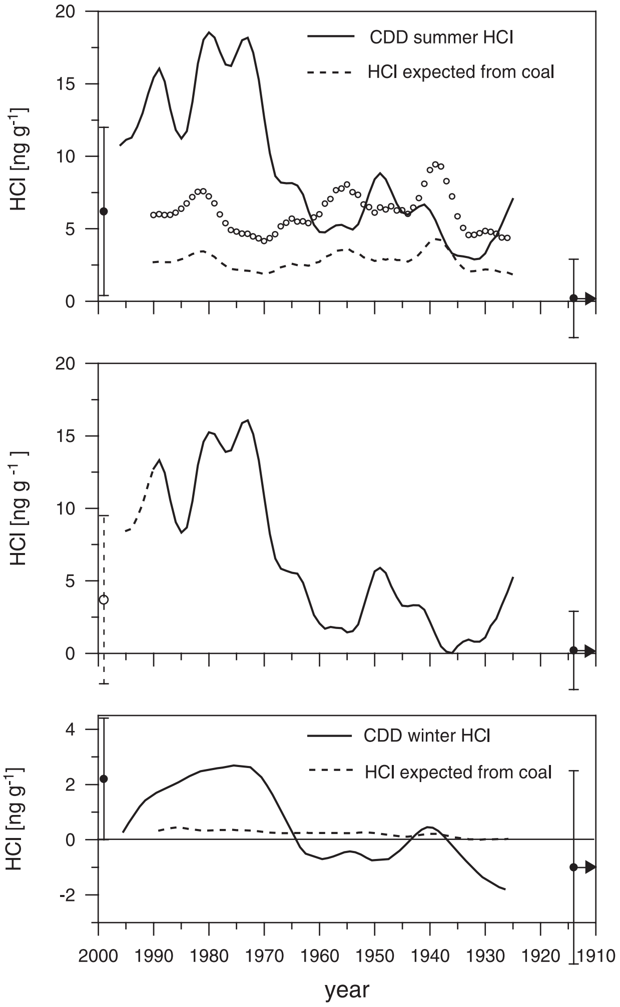

Figure 6. (top) Summer and (bottom) winter trends of HCl (solid lines) in the 1994 CDD ice core compared with the expected contribution of coal combustion (dashed lines). The arrows on the right side refer to the mean level calculated for the bottom part of the core. The circles on the left side refer to the mean level calculated for snow layers sampled in snow pits covering the 1998, 1999, and 2000 years. The dotted line refers to the coal contribution calculated if the residence times of HCl and sulfate are assumed to be identical (see section 4.1). (middle) Temporal trend of the non coal burning HCl contribution in summer.

[24] Comparing the long-term trend of the anthropogenic sulfate fraction (evaluated by subtracting the natural background SO_4^{2-} level of 80 ng g^{-1} from the total SO_4^{2-} level) in summer CDD layers with past SO_2 anthropogenic emissions in western Europe, *Preunkert et al.*, [2001b] derived a main influence of SO_2 emissions from regions located within 700–1000 km from the Alps with a major contribution from France, Spain, Italy, and Switzerland. Chlorine and sulfur contents of employed hard and brown coals have

been documented by *McCulloch et al.* [1999] and *Lefohn et al.* [1999]. For these four countries the mean chlorine and sulfur contents are 0.11 ± 0.01% and 0.7 ± 0.2% in hard coal, respectively. For brown coal the Cl and S content are 0.04 ± 0.02% and 1.5 ± 0.5%, respectively. *Lefohn et al.* [1999] also documented the annual sulfur emissions from hard and brown coal combustion in individual countries since 1850. Applying equation (4) to France, Italy, Spain, and Switzerland, we derive annual HCl emissions (E_{Cl}) related to coal combustion. The contribution of coal combustion to HCl levels in CDD ice can be then estimated from the level of anthropogenic $\mathrm{SO_4^{2-}}$ observed in summer CDD ice layers which are related to solid and liquid fuel combustion following

$$[\mathrm{HCl}]_{\mathrm{coal}} = E_{\mathrm{Cl}}([\mathrm{SO_4^{2-}}] - 80)/(E_{\mathrm{sulfate}} \times \delta), \qquad (5)$$

where E_{sulfate} is the total anthropogenic annual $\mathrm{SO_4^{2-}}$ emission, including solid and liquid fuel contribution (E_{sulfate} derived from *Mylona* [1996]), E_{Cl} is the annual chloride emission calculated from equation (4), and δ is the factor that refers to change of atmospheric $\mathrm{HCl/SO_4}$ ratio between emission and deposition at the site.

[25] Since the atmospheric fate of HCl and $\mathrm{SO_2}$ are not identical with respect to wet and dry deposition processes and considering the subsequent $\mathrm{SO_2}$ to $\mathrm{SO_4}$ conversion, the atmospheric $\mathrm{HCl/SO_4}$ ratio is not conservative after emissions and the δ value would be higher than unit. As seen in Figure 6, using a δ value of 1, we calculated a coal burning contribution close to 8 ng $\mathrm{g^{-1}}$ in 1955, whereas the HCl level in the corresponding snow layers was close to 5 ng $\mathrm{g^{-1}}$, suggesting a change of the $\mathrm{HCl/SO_4}$ ratio between emission and deposition by at least a factor of 1.6. This δ value represents a lower estimate since the assumption made here that no other sources contribute to the HCl CDD levels is not necessarily valid (see section 4.1.2). *Preunkert et al.* [2001a] proposed a change by a factor of 2.2 between emission and deposition for the fluoride to sulfate ratio, which may be relevant for HCl as well since a similar atmospheric lifetime for HCl and HF is realistic. That is also consistent with a mean HCl lifetime of 1–2 days in the boundary layer proposed by *Graedel and Keene* [1995], compared with a lifetime of 4 days for sulfate [*Chin et al.*, 1996]. Applying this δ value of 2.2 in equation (5), we calculated a mean coal burning contribution of 2.9 ± 0.6 ng $\mathrm{g^{-1}}$ to the HCl level of summer CDD layers deposited between 1925 and 1965. From 1965 to 1990 this contribution remained constant (2.6 ± 0.5 ng $\mathrm{g^{-1}}$; Figure 6) with respect to the one from 1925 to 1965. This is in accordance with stabilized consumption of hard and brown coal in France, Italy, Spain, and Switzerland.

4.1.2. Natural HCl inputs

[26] From 1925 to 1965 the residual (non coal burning) HCl fraction calculated by subtracting the coal burning contribution to the total level of HCl (Figure 6) is of 2.7 ± 1.7 ng $\mathrm{g^{-1}}$. Prior to 1965 the major anthropogenic HCl source is likely coal burning, and the residual HCl fraction would likely be of natural origin. Thus the examination of the bottom part of the CDD core as well as the trend between 1925 and 1965 suggests the significant contribution of a natural HCl source in summer at that site.

[27] On a global scale, main natural sources of HCl include volcanoes, biomass burning, and sea-salt dechlorination [*Keene et al.*, 1999]. It is unlikely that volcanoes contribute significantly to the HCl budget at high-elevation Alpine sites. For volcanic emissions, *Graedel and Keene* [1995] adopted an averaged global flux of 2 megatons (Mt) $\mathrm{yr^{-1}}$, which remains 2 times lower than the annual release from coal burning in 1990 (4.6 Mt $\mathrm{yr^{-1}}$) [*McCulloch et al.*, 1999]. Volcanic emissions take place far away from the Alps and even the Mt. Etna (Sicily) was found to have no significant impact on the CDD fluoride record [*Preunkert et al.*, 2001a]. It is therefore unlikely that volcanic emissions represent the main natural source of HCl over the Alps. The sea-salt dechlorination represents on a global scale a large source of HCl (50 Mt $\mathrm{yr^{-1}}$) [*Graedel and Keene*, 1995]. Due to larger amount of sea-salt aerosol and high levels of $\mathrm{HNO_3}$, $\mathrm{SO_2}$, and $\mathrm{N_2O_5}$ in winter than in summer, this source is likely more active in winter than in summer [*Erickson et al.*, 1999]. Given the low winter HCl levels in CDD ice (close to zero between 1925 and 1965, Figure 6), it is therefore unlikely that the natural sea-salt dechlorination represents a major source for HCl present in summer Alpine ice. Furthermore, as discussed in section 4.1.3, the recent change of HCl levels does not follow the course of the enhancement of the acidity, which would have strengthened the sea-salt dechlorination.

[28] Therefore, biomass burning, which on a global scale would emit up to 6.3 Mt $\mathrm{yr^{-1}}$ of HCl [*Lobert et al.*, 1999], may be a possible candidate. Using estimates from *Lobert et al.* [1999] for the 1980s, we calculated an annual biomass burning HCl emission of 0.02 Mt provided by France, Spain, Italy, and Switzerland. As argued by *Lobert et al.* [1999], very little quantitative information is available about long-term trend of biomass burning, and recent data tend to suggest that biomass burning may currently not be increasing at all. Assuming such an absence of temporal trend in biomass burning at temperate latitudes, the 0.02 Mt of HCl emitted annually by biomass burning are 6 times weaker than annual emissions from coal combustion (~0.12 Mt) in 1955. However, biomass burning emissions may have a larger impact on HCl summer levels because they are more intense during the dry season opposite to coal burning emissions, which were likely far more important in winter. The large interannual variability of residual HCl levels seen between 1925 and 1965 (also suggested by investigations made on the bottom part of the core) is consistent with the expected large interannual variability of this source. Note also that the large residual HCl levels seen in the late 1940s (Figure 6) correspond to a period of unusually warm summer seasons in countries around the Alps [*Boehm et al.*, 2001].

[29] *Sanhueza* [2001] proposed that the present-day chlorocarbons oxidation would produce up to 4.2 Mt of HCl per year in the background atmosphere, more than a half being related to the oxidation of methyl chloride. The author estimated that 50% of this HCl comes from anthropogenic sources of chlorocarbons. Since most of chlorocarbons are long-lived species (e.g., 1.5 years for $\mathrm{CH_3Cl}$), we would expect little interannual variability of this source. The residual HCl levels of summer snow layers deposited at CDD remained close to 1 ng $\mathrm{g^{-1}}$ over several years in the 1930s and late 1950s (Figure 6). Thus, if it exists, the

Table 4. Estimates of the HCl Fractions Related to Different Processes Contributing to the Mean Summer Snow Layers HCl Level Deposited at CDD in the 1980s (15.5 ng g^{-1})[a]

Sources	Summer Emission in western Europe, Mt[b]	HCl fraction in CDD Summer, ng g^{-1}	Global Emission, Mt yr^{-1}	References
Volcanoes	–	–	2	*Graedel and Keene* [1995]
Biomass Burning	0.02	2.7	<6.3	*Lobert et al.* [1999]
Coal Burning	0.04	2.6	4.6 ± 4.3	*McCulloch et al.* [1999]
Waste Burning	0.046	8.2–10.2	2.0 ± 1.9	*McCulloch et al.* [1999]
Sea-salt Dechlorination	–	–	50 ± 20	*Graedel and Keene* [1995]
Chlorocarbons Oxidation	0.01	0–2	4.2	*Sanhueza* [2001]

[a] Comparison with the respective annual emission rates of these processes on a global scale and for summer over western Europe (see section 4.1.4).

[b] Mt, megatons.

natural contribution of chlorocarbon oxidation to the HCl budget would not exceed 1 ng g^{-1} in summer CDD snow layers.

4.1.3. Other anthropogenic inputs

[30] Being close to 8 ng g^{-1} in 1965, HCl summer levels in CDD ice were enhanced to 17–18 ng g^{-1} between 1970 and 1980 and then decreased to 15 ng g^{-1} in 1990 (Figure 6). The present-day contribution of chlorocarbon oxidation would not exceed 2 ng g^{-1}, referring to the upper limit of 1 ng g^{-1} derived for the 1925–1965 time period and assuming a doubling of chlorocarbon emissions between 1950 and present [*Sanhueza*, 2001]. Thus the increase seen in Figure 6 would be related to another anthropogenic input. The residual HCl levels were rapidly enhanced between 1965 and 1975. This change does not follow the course of the change of acidity (not shown), which was enhanced from 2 μeq L^{-1} in the early 1950s to 5 μeq L^{-1} in 1965 and 8 μeq L^{-1} in 1975. Thus the recent HCl trend appears to be unrelated to an enhancement of the sea-salt dechlorination in response to the increase of the atmospheric acidity. Conversely, the change of HCl levels coincides rather well with the deployment of waste incineration whose PVC burning represents a large source of HCl. For 1983, *Lightowlers and Cape* [1988] estimated that France, Italy, Spain, and Switzerland together emitted 0.093 Mt of HCl from waste incineration, with more than a half (0.064 Mt) being emitted in France. Total amount of waste burned in France was insignificant in early 1960s, reached 2.7 Mt in 1971, 4.3 Mt in 1975, 5.8 Mt in 1985, and 8.7 Mt in 1989. After 1985 the waste amount burned in France continued to increase (9.6 Mt in 1998), but corresponding HCl emissions likely started to decrease as a result of a progressive set up of flue gas scrubbers fitted to incineration units, all units having been equipped in 1995. Using data from *McCulloch et al.* [1999], we calculated an HCl emission from France, Italy, Spain, and Switzerland of 0.064 Mt for 1990 with reduced emissions from France (from 0.024 Mt instead of 0.064 Mt in 1983) and Switzerland (from 0.0026 Mt instead of 0.012 Mt in 1983) and enhanced emissions from Spain (from 0.0022 Mt in 1983 [*Lightowlers and Cape*, 1988] to 0.017 Mt in 1990 [*McCulloch et al.*, 1999]). After 1995 the release of HCl from waste incineration continued to decrease due to the decreasing amount of burned PVC. Pit studies carried out at CDD indicate a mean HCl summer level of 6.2 ± 5.8 ng g^{-1} for 1998 to 2000 instead of 10 ng g^{-1} in 1995 (Figure 6). Thus the change of HCl levels in summer CDD snow layers covering the 1965–2000 time period is very consistent with the expected course of HCl emissions from waste incineration in western Europe.

4.1.4. Comparison of the various HCl source strengths in western Europe

[31] In Table 4 we summarized the estimated contribution of biomass burning, coal combustion, waste incinerator, and chlorocarbon oxidation to the summer budget of HCl in CDD snow layers deposited in the 1980s. In the 1980s the mean HCl level of CDD snow layers was close to 15.5 ng g^{-1}, of which 2.6 ng g^{-1} would be related to coal burning emissions. The HCl fraction related to waste incineration plus biomass burning emissions is close to 12.9 ng g^{-1}. Assuming a mean contribution of 2.7 ± 1.7 for biomass burning (i.e., similar to the one calculated for the 1925–1960 time period), that indicates that in the 1980s the waste incineration contribution reached 10 ng g^{-1} if the chlorocarbon oxidation was neglected.

[32] In Table 4 we report annual global emissions as well summertime emissions at the scale of western Europe (France, Italy, Spain, and Switzerland). For the latter we assumed that biomass burning emissions mainly take place in summer, coal burning emissions are two times larger in winter than in summer, and waste incineration emissions are well distributed over the year. Given the lifetime of several months of chlorocarbons and referring to a proposed lifetime of 1–2 months for HCl in the free troposphere [*Graedel and Keene*, 1995], we have assumed that the HCl production from the chlorocarbon oxidation is homogeneously distributed over the world.

[33] The contribution of biomass burning and coal combustion to the HCl budget at CDD in summer are similar, which remains consistent within a factor of 2 with the estimates of summer emissions from these two sources over western Europe (Table 4). Note, however, that the emission of 0.02 Mt from biomass burning is though to represent an upper limit [*Lobert et al.*, 1999]. The contribution from waste incineration is found to be 3–4 times larger than the coal burning emissions, whereas summer emissions from waste incineration are estimated to be similar to the coal burning ones. Although the HCl production from the chlorocarbon oxidation is 2–4 times weaker than sources located at the surface, due to an HCl lifetime of 1–2 months in the free troposphere compared with 1–2 days in the boundary layer [*Graedel and Keene*, 1995], we would expect a larger impact of this process, which acts upon the whole troposphere. Since the chlorocarbon atmospheric burden is reasonably well known, such a discrepancy

suggests that estimates of this source have overestimated the hydrochloric production in the employed chemical schemes.

4.2. CDD Winter Trend

[34] Because of the lack of some individual means (Figure 4), we examined the winter trend by applying a robust spline smoothing [*Bloomfield and Steiger*, 1983]. The HCl winter means at CDD are mostly not significantly different from zero with respect to uncertainties (Figure 4). The smoothed profile (Figure 6) suggests that, if it exists, a trend mainly occurred after 1965. The contribution of coal combustion to the HCl level of winter CDD ice can be estimated from equation (5) using the natural background sulfate level of 20 ng g^{-1} (instead of 80 ng g^{-1} for summer) [*Preunkert et al.*, 2001b]. E_{sulfate} and E_{Cl} values used in equation (5) were calculated by assuming that all countries of western and eastern Europe contribute to the impurities content of winter CDD snow layers as suggested by *Preunkert et al.* [2001b]. As seen in Figure 6, the coal burning emissions only account for 0.3 ng g^{-1} (i.e., <15%) of the HCl budget of winter CDD snow layers deposited between 1970 and 1980. Referring to the summer to winter ratio of anthropogenic sulfate levels seen in CDD (close to 10) [*Preunkert et al.*, 2001b], the 15 ng g^{-1} of residual HCl in summer between 1970 and 1980 would correspond to a winter level of 1.5 ng g^{-1}, which is consistent with the observed winter levels at that time (Figure 6). Note, however, that the mean winter HCl level observed over very recent years (1998–2000) (2.2 ± 0.6 ng g^{-1}) exceeds what is expected (~0.6 ng g^{-1}) with regard to the corresponding level in summer (6.2 ± 5.8 ng g^{-1}). Thus, although needing to be confirmed by further studies, the HCl winter trend after 1965 suggests a limited contamination of the free troposphere by waste incineration emissions.

[35] At the low level of 1–2 ng g^{-1} encountered, we may consider stratospheric HCl as a potential source to the inferred winter snow HCl levels as well. Since most of the modern stratospheric HCl inventory can be attributed to the CFC degradation, a systematic increase of this contribution is expected after the 1960s as well. We estimated the maximum fraction of stratospheric HCl deposited at high Alpine glacier sites via the cosmogenic ^{36}Cl radioisotope. ^{36}Cl is mainly produced in the stratosphere and mixed downward into the troposphere in the form of $H^{36}Cl$. Neglecting any tropospheric ^{36}Cl input (including re-emitted bomb ^{36}Cl; see section 2), an upper limit of the stratospheric Cl concentrations at this site ($[\mathrm{Cl}_{\mathrm{stratosphere}}]$) may be simply calculated as

$$[\mathrm{Cl}_{\mathrm{stratosphere}}]_{\mathrm{CDD}} = (Q_{\mathrm{HCl}}/\tau P)[^{36}\mathrm{Cl}]_{\mathrm{CDD}}, \qquad (6)$$

with $[^{36}\mathrm{Cl}]_{\mathrm{CDD}}$ denoting the mean ^{36}Cl concentration in CDD firn, Q_{HCl} is the stratospheric HCl inventory, P is the ^{36}Cl production rate, and τ is the mean residence time of ^{36}Cl in the stratosphere.

[36] We derived a stratospheric HCl inventory Q of 4×10^{11} grams from the vertical HCl profile given by *Zander et al.* [1990] for 1985 and deployed the global production rate (P) from latest compilation by *Masarik and Beer* [1999] of 3×10^{23} atoms per year. Using the global instead of the stratospheric ^{36}Cl production value mainly compensates for the tropospheric fraction contributing to the mean ^{36}Cl ice core level. For the latter, 700 atoms g^{-1} are obtained referring to recent data reported by *Synal et al.* [1997] from Fischerhorn (an Alpine ice core drill site with comparably high snow accumulation rate as at CDD) and by correcting these data from a small bomb-produced ^{36}Cl excess via Greenland records [*Synal et al.*, 1990] extending into the prebomb era. Adopting a mean residence time τ of 1 year, we thus arrive at a typical Cl level at CDD derived from the stratosphere of around 0.9 ng g^{-1}. This crude estimate may be uncertain at least by a factor of 2, mainly arising from the production rate and the systematically different vertical profiles of HCl and ^{36}Cl in the stratosphere. We conclude therefore that $[\mathrm{HCl}]_{\mathrm{stratosphere}}$ at CDD will be <1.8 ng g^{-1}. Thus we cannot totally exclude the possibility that the stratospheric changes related to the changing load of CFC in the stratosphere have also contributed to the change of HCl in winter snow layers after 1965.

5. The HCl Greenland Records

5.1. The Natural HCl Input

[37] The level of HCl in spring and summer Summit snow layers remained close to 4 ng g^{-1} prior to 1910 and was then enhanced to some 10 ng g^{-1} after 1970 (Figure 7). With respect to the situation at CDD, such a more moderate change over the 20th century indicates a more important contribution of natural HCl emissions there. With the aim to evaluate the representativeness of the Summit profile at the scale of the Greenland ice cap for this short-lived species, we examined the long-term HCl trend in another Greenland ice core. *Fischer* [1997] investigated the chemical composition of snow layers deposited at another Greenland site (B18, located 400 km north from Summit) since 1500 A.D. on a mean biannual time resolution. Calculating HCl levels from Cl^-, $-Na^+$, and Ca^{2+} by using equation (2), we obtained the long-term trend reported in Figure 8. The smoothed HCl curve at B18 exhibits similar changes than those seen at Summit with a preindustrial level close to 6 ng g^{-1} and an increase by a factor of 2 in the 1970s. Thus the HCl long-term Summit trend seen can be considered as well representative for the entire high-elevation Greenland sites.

[38] In spring we can assume that biomass burning is not a significant natural HCl contributor for Greenland snow layers. For summer, *Legrand and De Angelis* [1996] showed that the NH_4^+ level of summer Summit snow layers is significantly influenced by biomass burning emissions from the boreal zone. *Savarino and Legrand* [1998] pointed out a higher frequency of biomass burning at the turn of the 19th century. Since no change of the HCl levels of summer Summit snow layers deposited at that time can be detected (Figure 7), we conclude that biomass burning is not the major natural source contributing to the HCl budget of preindustrial Greenland snow layers.

[39] In addition to biomass burning, the two other possible HCl natural sources are natural sea-salt dechlorination and passively degassing volcanoes. On a global scale the volcanic source of HCl is estimated to be in the range of 2 Mt per year [*Graedel and Keene*, 1995] and remains weak compared to sea-salt dechlorination emissions. However, for Greenland this contribution may be far larger due the rather high volcanic activity taking place in the high north-

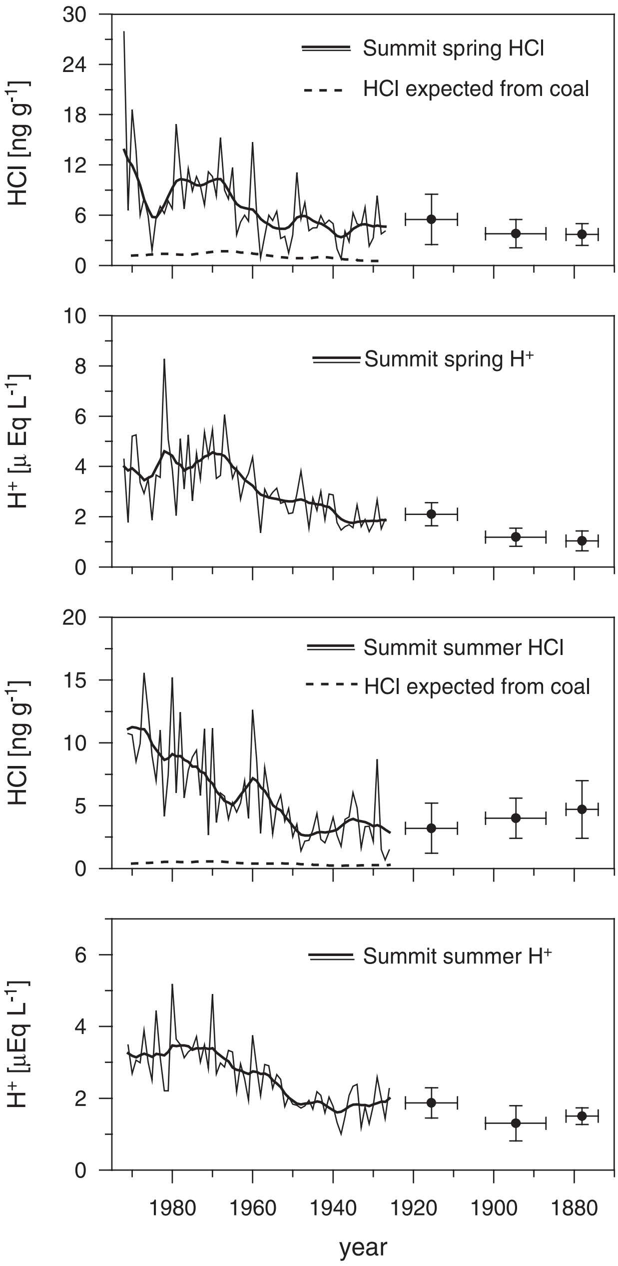

Figure 7. Summit HCl and acidity records over the 1870–1993 time period for (top) spring and (bottom) summer means. The solid smoothed curves represent the first single spectrum analysis component with a 5-year time window. The three crosses reported on the right side refer to multiple year means (1873–1881, 1886–1901, and 1908–1922) (horizontal bars are covered time periods, and vertical bars refer to standard deviation). The dashed lines reported along with the HCl trends refer to the contribution of coal burning. The acidity has been calculated by checking the ionic balance following *Legrand and De Angelis* [1996].

ern latitude belt. *Legrand et al.* [1997] estimated that 12 ng g^{-1} of preindustrial sulfate level at Summit are due to these passive quasi-permanent volcanic emissions. On the basis of this value and assuming a mean SO_2 to HCl mass ratio in passive volcanic emissions ranging from 1.8 to 18 (i.e., a sulfate to chloride mass ratio of 2.7–27) [*Symonds et al.*, 1988], we calculate a chloride contribution of this source between 4.5 and 0.45 ng g^{-1} in Summit snow layers. This estimate does not account for the scavenging process in the water-rich volcanic plumes and for the fact that HCl is some 300 times more soluble in water than SO_2. For the 1912 Katmai eruption, which injected the debris within the stratosphere, *De Angelis and Legrand* [1994] found that the HCl deposition of HCl at Summit was 3 times lower than the sulfate one with respect emissions. Therefore the passive volcanic emissions would only account for 1.5–0.15 ng g^{-1} to the natural HCl level at Summit, and very

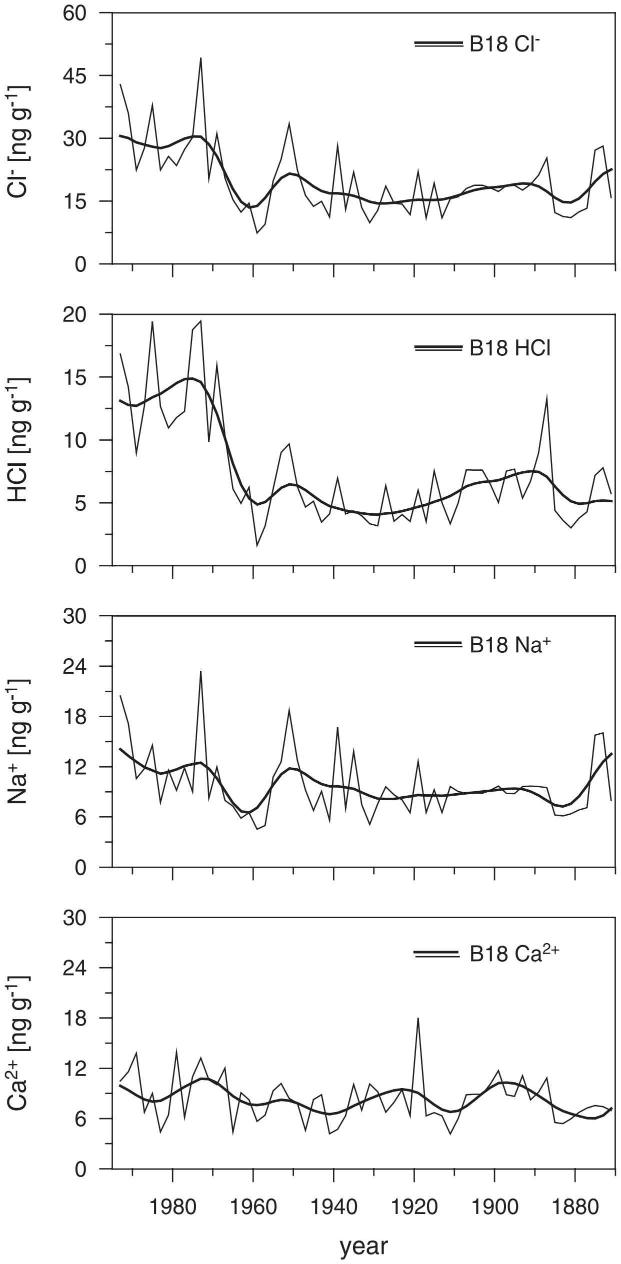

Figure 8. Records of chloride, HCl, sodium, and calcium at the B18 north Greenland site. Raw chloride, sodium, and calcium data are from *Fischer* [1997]. HCl levels were evaluated in a same way than the one applied for the Summit snow layers.

likely, the natural HCl level of 4 ng g^{-1} is mainly related to the sea-salt dechlorination.

5.2. The Anthropogenic Input

[40] At Summit the HCl level in spring snow layers, close to 3.7 ± 1.5 ng g^{-1} between 1870 and 1900, was enhanced to 5.5 ± 3.0 ng g^{-1} between 1920 and 1950 (Figure 7). The level was then rapidly enhanced up to 10 ng g^{-1} in the late 1970s. Examining the source region apportionment for sulfate in the Summit spring snow layers, *Preunkert et al.* [2001b] concluded that the source regions influencing the Greenland ice cap in spring include Eurasia (eastern Europe, Russia, Japan, and Korea) and North America. On the basis of this fact the coal burning contribution was calculated using equation (5) by considering a preindustrial value of 38 ng g^{-1} [*Preunkert et al.*, 2001b], and a δ value of 2.2 may account for up to 1.2 ng g^{-1} in spring Summit layers deposited in the late 1960s. In contrast to the case of western Europe where coal burning and waste incineration HCl emissions are similar in amplitude, annual HCl emissions from Eurasia and North America in 1990 are dominated by coal combustion (~1.42 Mt) against only 0.34 Mt from waste incineration [*McCulloch et al.*, 1999]. Thus growing emissions from coal burning and waste incineration may have accounted for ~1 ng g^{-1} to the observed trend of HCl in spring Summit snow layers. Due to a lower snow accumulation at Summit than at CDD, the estimated upper limit of the stratospheric HCl contribution in 1985 would be slightly higher there (~3 ng g^{-1} instead of 1.8 ng g^{-1} at CDD; see section 4.2). As seen in Figure 7, the spring Summit trend of 6 ng g^{-1} mainly took place between 1955 and 1970, whereas a significant contribution of stratospheric HCl is expected in the 1980s. In contrast to spring levels, summer HCl levels remained unchanged and close to 4 ng g^{-1} until 1950 and were then increased by a factor of 2 in 1980 (Figure 7). We estimated that the coal burning contribution might account for up to 0.5 ng g^{-1} in summer Summit layers deposited in the late 1960s. Finally, the contribution of stratospheric HCl is expected to be lower in summer with respect to the spring situation in relation with less frequent intrusion of stratospheric air masses within the troposphere at that season.

[41] Over the 20th century the acidity of spring Summit layers have been enhanced from 1 ± 0.4 μeq L^{-1} at the beginning of the century to 2.3 ± 0.3 μeq L^{-1} between 1920 and 1950. In 1970 the acidity was close to 4.6 μeq L^{-1} (Figure 7). Such a change of the acidity of Greenland snow layers is related to the acidification of precipitation at high northern latitudes in response to enhanced emissions of SO_2 and NO_x [*Legrand and De Angelis*, 1996]. Note that the changes of acidity developed at the same time as the increase of HCl levels (Figure 7). In summer the acidity remained close to 1.7 μeq L^{-1} until 1950 and then was increased by a factor of 2 in 1980. As for spring snow layers, the change of the acidity is similar to the HCl trend in summer. Following our conclusion (section 5.1) that sea-salt dechlorination is the most likely source of HCl in preindustrial Greenland snow layers, the HCl trends that follow the change of the acidity over the 20th century supports the idea that the dominant acid displacement for the sea-salt dechlorination is controlled by sulfuric and nitric acids [*Sievering et al.*, 1995]. Referring to the change by a factor 2–3 between the preindustrial time and the 1990s, the estimate of 50 Mt of HCl annually emitted at present from sea salt [*Graedel and Keene*, 1995] would imply that in the natural atmosphere this process produces some 17–25 Mt of HCl per year.

[42] More recently, *Erickson et al.* [1999] suggested that the acid displacement processes can only produce 7.2 Mt of HCl per year (instead of 50 Mt). Other processes that are not well known (photolysis of dissolved organic compounds and free radical reactions) [see *Keene et al.*, 1999, and references therein] have been proposed to account for the remaining HCl production. If correct, the HCl Greenland trend would suggest that these processes that are not well known have been enhanced by a factor of 2 over the 20th century, similar to the enhancement of the acidification of the atmosphere.

6. Conclusions

[43] This study of Cl^-, Na^+, and Ca^{2+} present in precipitation deposited at a high-elevation Alpine site and over Greenland revealed the complexity to calculate the amount of HCl present there. It is shown that an accurate evaluation of this HCl fraction requires a detailed examination of cations in order to evaluate the amount of chloride purely related to halide emissions (sea spray, evaporite, and possibly manure-fertilized field) and soil weathering input, which together represent some 80% of total Cl^-. The long-term trend of HCl level in a high-elevation Alpine ice core suggests that in summer, although being highly variable from year to year, biomass burning is on average a significant natural source of HCl over the Alps. Coal burning emissions represented an additional (similar in intensity) source of HCl for these regions in summer throughout the 20th century. The main anthropogenic input comes from waste incineration, which had an impact of 3–4 times larger than coal burning at the scale of western Europe in the 1970s and 1980s. The contribution of chlorocarbon oxidation appears far lower than expected stimulating further investigation of the atmospheric fates of these species. Although needing to be confirmed by other ice core studies, the increase of winter levels after 1965 may be due to a limited contamination of the free troposphere by HCl waste incineration emissions and possibly to stratospheric HCl changes related to CFC degradation. The presence of HCl in Greenland ice cores is essentially related to sea-salt dechlorination, which was enhanced by a factor of 2 over the 20th century. If the recent finding that the acid displacement of sea salt by SO_2 and NO_x only accounts for a minor part of the total sea-salt dechlorination is correct, the Greenland data suggest that major (unknown) dominant sea-salt dechlorination processes have also been enhanced by a factor of 2 over the 20th century.

[44] **Acknowledgments.** This work has been supported by the European Environment and Climate program ALPCLIM. Funding was provided by the European Community via contracts ENV4-CT97 (ALPCLIM) and ENV4-CT96-5051 (Environment and Climate Research Training), the Centre National de la Recherche Scientifique (programme PNCA), and the Ministry for Science and Research of Baden-Württemberg within the collaboration programme between Region Rhône-Alpes and Baden-Württemberg.

References

Baltensperger, U., H. W. Gaeggeler, D. T. Jost, M. Lugauer, M. Schwikowski, E. Weingartner, and P. Seibert, Aerosol climatology at the high-alpine site Jungfrauchjoch, Switzerland, *J. Geophys. Res.*, *102*, 19,707–19,715, 1997.

Bloomfield, P., and W. L. Steiger, *Last Absolute Deviations: Theory, Applications and Algoritms*, Birkhauser, Boston, Mass., 1983.

Boehm, R., I. Auer, M. Brunetti, M. Maugeri, T. Nanni, and W. Schöner, Regional temperature variability in the European Alps: 1760–1998 from homogenized instrumental time series, *Int. J. Climatol.*, *21*, 1779–1801, 2001.

Chin, M., D. J. Jacob, G. Gardner, M. S. Foreman-Fowler, and P. A. Spiro, A global three-dimensional model of tropospheric sulfate, *J. Geophys. Res.*, *101*, 18,667–18,690, 1996.

De Angelis, M., and M. Legrand, Origins and variations of fluoride in Greenland precipitation, *J. Geophys. Res.*, *99*, 1157–1172, 1994.

De Angelis, M., and M. Legrand, Preliminary investigations of post depositional effects on HCl, HNO_3, and organic acids in polar firn layers, in *Ice Core Studies of Global Biogeochemical Cycles*, *NATO ASI Ser., Ser. I*, vol. 30, edited by R. J. Delmas, pp. 361–381, Springer-Verlag, New York, 1995.

De Angelis, M., J. P. Steffensen, M. Legrand, H. Clausen, and C. Hammer, Primary aerosol (sea salt and soil dust) deposited in Greenland ice during the last climatic cycle: Comparison with East Antarctic records, *J. Geophys. Res.*, *102*, 26,681–26,698, 1997.

Eichler, A., M. Schwikowski, and H. Gäggeler, An Alpine ice-core record of anthropogenic HF and HCl emissions, *Geophys. Res. Lett.*, *27*, 3225–3228, 2000.

Erickson, D. J., III, C. Seuzaret, W. C. Keene, and S. L. Gong, A general circulation model based calculation of HCl and $ClNO_2$ production from sea salt dechlorination: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, *104*, 8347–8372, 1999.

Fischer, H., Spatial variability of ice core records from North-East Greenland: Reconstruction of climatic and atmospheric chemistry long-term trends since 1500 AD, Ph.D. dissertation, 135 pp., Univ. of Heidelberg, Heidelberg, Germany, 1997.

Fischer, H., D. Wagenbach, and J. Kipfstuhl, Sulfate and nitrate firn concentrations on the Greenland ice sheet, 1, Large-scale geographical deposition changes, *J. Geophys. Res.*, *103*, 21,927–21,934, 1998.

Graedel, T. E., and W. C. Keene, The tropospheric budget of reactive chlorine, *Global Biogeochem. Cycles*, *9*, 47–78, 1995.

Graedel, T. E., and W. C. Keene, The budget and cycle of Earth's natural chlorine, *Pure Appl. Chem.*, *68*, 1689–1697, 1996.

Kahl, J. D., D. A. Martinez, H. Kuhns, C. I. Davidson, J. L. Jaffrezo, and J. M. Harris, Air mass trajectories to Summit: A 44-year climatology and some episodic events, *J. Geophys. Res.*, *102*, 26,861–26,875, 1997.

Keene, W. C., et al., Composite global emissions of reactive chlorine from anthropogenic and natural sources: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, *104*, 8429–8440, 1999.

Lefohn, A. S., J. D. Husar, and R. B. Husar, Estimating historical anthropogenic global sulfur emission patterns for the period 1850–1990, *Atmos. Environ.*, *33*, 3435–3444, 1999.

Legrand, M., and M. De Angelis, Light carboxylic acids in Greenland ice: A record of past forest fires and vegetation emissions from the boreal zone, *J. Geophys. Res.*, *101*, 4129–4145, 1996.

Legrand, M., and R. J. Delmas, Formation of HCl in the Antarctic atmosphere, *J. Geophys. Res.*, *93*, 7153–7168, 1988.

Legrand, M., and P. Mayewski, Glaciochemistry of polar ice cores: A review, *Rev. Geophys.*, *35*, 219–243, 1997.

Legrand, M., C. Lorius, N. I. Barkov, and V. N. Petrov, Vostok (Antarctica) ice core: Atmospheric chemistry changes over the last climatic cycle (160,000 years), *Atmos. Environ.*, *22*, 317–331, 1988.

Legrand, M., M. De Angelis, and F. Maupetit, Field investigation of major and minor ions along Summit (central Greenland) ice cores by ion chromatography, *J. Chromatogr.*, *640*, 251–258, 1993.

Legrand, M., C. Hammer, M. De Angelis, J. Savarino, R. Delmas, H. Clausen, and S. J. Johnsen, Sulfur-containing species (methanesulfonate and SO_4) over the last climatic cycle in the Greenland Ice Core Project (central Greenland) ice core, *J. Geophys. Res.*, *102*, 26,663–26,679, 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.

Lobert, J. M., W. C. Keene, J. A. Logan, and R. Yevich, Global chlorine emissions from biomass burning: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, *104*, 8373–8389, 1999.

Masarik, J., and J. Beer, Simulation of particle fluxes and cosmogenic nuclides production in the Earth's atmosphere, *J. Geophys. Res.*, *104*, 12,099–13,112, 1999.

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*, 12,839–12,847, 1993.

McCulloch, A., M. L. Aucott, C. M. Benkovitz, T. E. Graedel, G. Kleiman, P. M. Midgley, and Y.-F. Li, Global emissions of hydrogen chloride and chloromethane from coal combustion, incineration and industrial activities: Reactive Chlorine Emissions Inventory, *J. Geophys. Res.*, *104*, 8391–8403, 1999.

Mylona, S., Sulphur dioxide emissions in Europe 1880–1991 and their effect on sulphur concentrations and deposition, *Tellus, Ser. B*, *48*, 662–689, 1996.

Preunkert, S., and D. Wagenbach, An automatic recorder for air/firn transfer studies of chemical aerosol species at remote glacier sites, *Atmos. Environ.*, *32*, 4021–4030, 1998.

Preunkert, S., D. Wagenbach, M. Legrand, and C. Vincent, Col du Dôme (Mt. Blanc Massif, French Alps) suitability for ice core studies in relation with past atmospheric chemistry over Europe, *Tellus, Ser. B*, *52*, 993–1012, 2000.

Preunkert, S., M. Legrand, and D. Wagenbach, Causes of enhanced fluoride levels in Alpine ice cores over the last 75 years: Implications for the atmosphere fluoride budget, *J. Geophys. Res.*, *106*, 12,619–12,632, 2001a.

Preunkert, S., M. Legrand, and D. Wagenbach, Sulfate trends in a Col du Dôme (French Alps) ice core: A record of anthropogenic sulfate levels in the European midtroposphere over the twentieth century, *J. Geophys. Res.*, *106*, 31,991–32,004, 2001b.

Sanhueza, E., Hydrochloric acid from chlorocarbons: A significant global source of background rain acidity, *Tellus, Ser. B*, *53*, 122–132, 2001.

Savarino, J., and M. Legrand, High northern latitude forest fires and vegetation emissions over the last millennium inferred from the chemistry of a central Greenland ice core, *J. Geophys. Res.*, *103*, 8267–8279, 1998.

Sievering, H., E. Gorman, T. Ley, A. Pszenny, M. Springer-Young, J. Boatman, Y. Kim, C. Nagamoto, and D. Wellman, Ozone oxidation of sulfur in sea-salt aerosol particles during the Azores marine aerosol and gas exchange experiment, *J. Geophys. Res.*, *100*, 23,075–23,081, 1995.

Simeonov, V., H. Puxbaum, S. Tsakovski, C. Sarbu, and M. Kalina, Classification and receptor modeling of wet precipitation data from central Austria (1984–1993), *Environmetrics*, *19*, 137–152, 1999.

Stanzick, A., Spatio-temporal variations of ^{10}Be, ^{210}Pb, and ^{36}Cl in the Greenland firn cover: Air-firn transfer and recent trends (in German), Ph.D. dissertation, 118 pp., Univ. of Heidelberg, Heidelberg, Germany, 2001.

Symonds, R. B., W. Rose, and M. H. Reed, Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, *Nature*, *334*, 415–418, 1988.

Synal, H. A., J. Beer, G. Bonani, M. Suter, and W. Wolfli, Atmospheric transport of bomb produced ^{36}Cl, *Nucl. Instrum. Methods Phys. Res.*, *52*, 483–488, 1990.

Synal, H. A., J. Beer, U. Schotterer, M. Suter, and L. Thompson, Bomb produced ^{36}Cl in ice core samples from mountain glaciers, in *Glaciers From the Alps: Climate and Environmental Archives*, Paul Scherrer Inst., Wengen, Switzerland, 1997.

Talbot, R. W., R. C. Harriss, E. V. Browell, G. L. Gregory, D. I. Sebacher, and S. M. Beck, Distribution and geochemistry of aerosols in the tropical North Atlantic troposphere: Relationship to Saharan dust, *J. Geophys. Res.*, *91*, 5173–5182, 1986.

Wagenbach, D., S. Preunkert, J. Schaefer, W. Jung, and L. Tomadin, Northward transport of Saharan dust recorded in a deep Alpine ice core, in *The Impact of African Dust Across the Mediterranean*, edited by S. Guerzoni and R. Chester, pp. 291–300, Kluwer Acad., Norwell, Mass., 1996.

Whitlow, S., P. Mayewski, and J. Dibb, A comparison of major chemical species input timing and accumulation at South Pole and Summit, Greenland, *Atmos. Environ.*, *26*, 2045–2054, 1992.

Zander, R., M. R. Gunson, J. C. Foster, C. P. Rinsland, and J. Namkung, Stratospheric $ClONO_2$, HCl, and HF concentration profiles derived from atmospheric trace molecule spectroscopy experiment Spacelab 3 observations: An update, *J. Geophys. Res.*, *95*, 20,519–20,525, 1990.

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