

# Sulfate and nitrate firn concentrations on the Greenland ice sheet

## 2. Temporal anthropogenic deposition changes

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**Abstract.** Intercomparison of three new chemical ice core records from northern Greenland (covering the time span from approximately 1500 A.D. to present) with previously published records for southern and central Greenland reveals a uniform timing of anthropogenic changes in sulfate and nitrate firn concentrations over the entire ice sheet. The anthropogenic sulfate increase started around 1890, was interrupted by a transient decrease in the 1930s, and has resumed a major increase since 1950. Since the late 1970s though, a significant 30% decline in Greenland sulfate firn levels can be documented. The maximum anthropogenic increase in northern Greenland sulfate firn concentrations (up to 200-230 ppb) is 2-3 times larger than in southern and central Greenland. Nitrate records show an essentially steady increase since 1950 and, documented for the first time, a slight reduction during most recent years. Maximum nitrate firn levels of 100-130 ppb exceed the preindustrial background by 100% all over the Greenland ice sheet. Comparison with anthropogenic SO<sub>2</sub> and NO<sub>x</sub> emission records indicates that the major increase in sulfate firn concentrations since 1950 can be attributed to Eurasian sources, while firn levels during the first half of this century appear to be dominated by North American emissions. A stronger North American source contribution is indicated over the entire 20th century in the case of nitrate. Applying a macroscopic deposition model separate time series for wet and dry deposition were derived which revealed a close correspondence of wet deposited sulfate with the timing of U.S. emissions, while the temporal evolution of Eurasian emissions is mainly reflected in the dry sulfate deposition record. During this century wet sulfate deposition increased by a factor of two while the total dry sulfate deposition flux increased by more than 500%. Wet and dry nitrate deposition both increased by 100% during the same period.

### 1. Introduction

The extensive combustion of fossil fuels since the beginning of the industrial revolution has led to a significant perturbation of atmospheric levels of sulfur and nitrogen species in the northern hemisphere. The occurrence of the Arctic haze phenomenon, which is attributed to the long-range transport of Eurasian industrial emissions to the Arctic basin in winter [Barrie, 1986], shows that even remote Arctic regions are subject to anthropogenic changes. Because of the long-range transport of anthropogenically derived aerosols and their water-reactive precursor gases, chemical ice core records from the Greenland ice sheet represent a unique archive for the reconstruction of such changes beyond the time span covered by direct atmospheric measurements. Investigations by Neftel

*et al.* [1985] and Mayewski *et al.* [1990] documented for the first time a 100% increase in nitrate and sulfate concentrations in southern Greenland ice cores since the turn of the century. However, interpretation of such ice core records in terms of atmospheric concentration changes is not straightforward due to the still insufficient understanding of the air/snow transfer processes involved. Moreover, the speciation and relevance of different organic and inorganic nitrate precursor gases to Greenland nitrate firn levels is mostly unknown so far [Dibb *et al.*, 1998]. The intercomparison of ice core records from different climatological regions of the Greenland ice sheet is hampered furthermore by geographically varying deposition conditions (this includes spatial trends in scavenging efficiency [Davidson *et al.*, 1989], seasonality in precipitation frequency [Chen *et al.*, 1997], relative contributions of wet and dry deposition fluxes [Fischer and Wagenbach, 1996; Fischer *et al.*, this issue] and remobilization of gaseous species from the firn column [McConnell *et al.*, 1997; Fischer *et al.*, this issue]). This geographical variability of air/snow transfer conditions may add substantial uncertainty to the identification of source regions and transport pathways of anthropogenic species deposited onto the Greenland ice sheet [Mayewski *et al.*, 1990; Whitlow *et al.*, 1992].

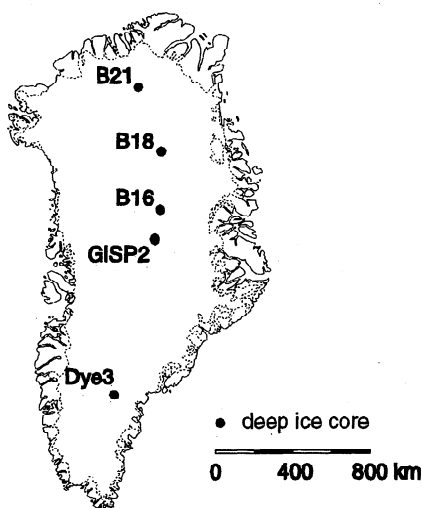
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In this study we try to resolve this problem by an intercomparison of sulfate and nitrate ice core records covering the last 200-600 years from climatologically diverse regions over the Greenland ice sheet. The ice cores investigated in this study (B16, B18, B21) were drilled in the years 1993-1995 along the North Greenland Traverse (NGT) and were supplemented by previously published sulfate, nitrate and accumulation records in ice cores from central (Summit-GISP2) and southern Greenland (D20) [Mayewski *et al.*, 1990; Mayewski *et al.*, 1993; Meese *et al.*, 1994]. The geographical distribution of the drill sites (shown in Figure 1) extends over an area from 65°N to 80°N and covers a change in snow accumulation rate from 46 to 10 cm water equivalent (WE) per year.

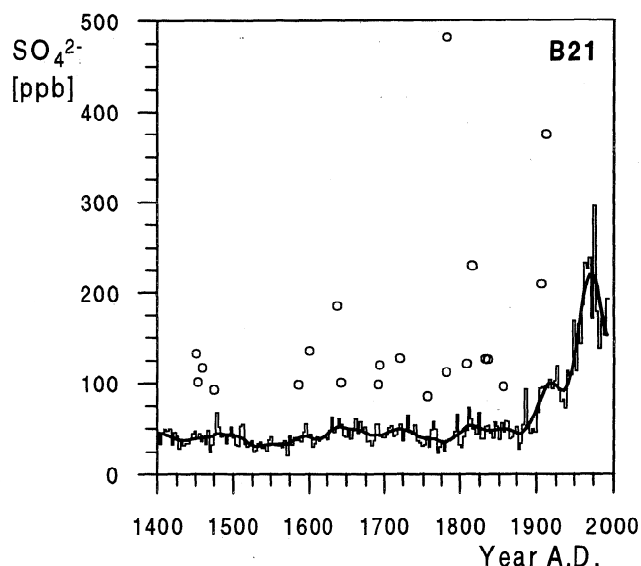
Making use of a comparable change in snow accumulation rate in two geographically highly resolved surface studies and by developing an easy macroscopic deposition model [Fischer and Wagenbach, 1996; Fischer *et al.*, this issue], we were able to show that geographical variations in recent nitrate and sulfate firn concentrations on the ice sheet can be explained largely by accompanying changes in the relative contribution of wet and dry deposition fluxes which are controlled by the local snow accumulation rate. Accordingly, comparison of long-term glacio-chemical records from different regions on the ice sheet must take this accumulation dependence into account in order to determine the relative contributions made by different anthropogenic source regions located west and east of the Greenland ice sheet.

## 2. Methods

Sampling and ion chromatographic analyses of the NGT ice cores are described in detail in part 1 of Fischer *et al.* [this issue]. The temporal resolution of the deep ice core samples was approximately 1-4 years for B16, B18 and 1-2 years for B21, GISP2. The D20 data already existed in formally resampled 1 year resolution. Dating of the NGT ice cores was performed by identification of historic volcanic horizons in quasi-continuous  $\text{SO}_4^{2-}$  [Fischer *et al.*, 1998] and high-



**Figure 1.** Geographical location of the drill sites of the new ice cores B16, B18 and B21 drilled along the North Greenland Traverse as well as the ice cores D20 and GISP2 investigated in this study.



**Figure 2.** Example of the time series analysis performed on the sulfate record of core B21. Circles indicate raw data points excluded from further analysis by the robust running median method, the thin step line shows 3-year intervals of the reduced data set, and the thick line represents the trend reconstruction derived by singular spectrum analysis/Monte Carlo singular spectrum analysis.

resolution DC-conductivity profiles [Werner, 1995] in combination with annual layer counting from high-resolution  $\gamma$ -ray attenuation density measurements [Wilhelms, 1996] and continuous flow analysis  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  statigraphies [Sommer, 1996]. The maximum dating error is less than  $\pm 3$  years over the entire length of the cores.

To deduce representative sulfate and nitrate background concentrations in each core, the following data reduction and time series analysis has been applied (as also depicted in Figure 2):

1. Episodic events like volcanic horizons in the sulfate records were removed from the raw data set by a robust running median method. All data points  $i$  with concentrations  $Y_i$  exceeding the running median  $\text{RM}_i$  of window length  $N$  by  $k$  times the running median of absolute deviations  $\text{MAD}_i$  [Bloomfield and Steiger, 1983] were excluded from the data set (open circles in Figure 2) and replaced by the running median at this point:

$$Y_i = Y_i \quad ; \quad \text{RM}_i - k \text{MAD}_i \leq Y_i \leq \text{RM}_i + k \text{MAD}_i$$

$$Y_i = \text{RM}_i \quad ; \quad Y_i > \text{RM}_i + k \text{MAD}_i$$

with

$$\text{RM}_i = \text{median}(Y_{i-(N-1)/2}, \dots, Y_{i+(N-1)/2})$$

$$\text{MAD}_i = \text{median}(|Y_{i-(N-1)/2} - \text{RM}_i|, \dots, |Y_{i+(N-1)/2} - \text{RM}_i|)$$

Depending on the temporal sample resolution of each core, the values of  $N$  and  $k$  were chosen to be 61 and 5 for D20, GISP2, and B21 and 21 and 4 for B16 and B18. At the boundaries of the data sets ( $(N-1)/2$  data points) the window length  $N$  was gradually lowered leading to less sensitive outlier identification for these points.

2. For direct comparison all records were formally collapsed into water-weighted 3-year averages after data reduction (thin step line in Figure 2).

3. Trend analysis was performed by singular spectrum analysis (SSA) [Vautard *et al.*, 1992] supplemented by a Monte Carlo significance test (MCSSA) introduced by Allen and Smith [1994]. The latter allows the separation of significant reconstructed signal components from red noise. The embedding dimension  $M$  in the SSA, representing the maximum considered time lag of the autocorrelation function, was chosen to be 25 corresponding to a maximum time lag of 75 years. For the sulfate data the sum of the first four (thick line in Figure 2), for nitrate the sum of the first three, reconstructed components were identified as trend components which were significant from red noise on the 95% level. Due to the short time span covered by the D20 record (only 73 3-year intervals) compared to the embedding dimension (25 3-year intervals), only the first two reconstructed components were significant on the 95% level in this record. For the sake of a consistent degree of smoothing, however, the same number of reconstructed components are given in Figure 4 for all cores. Note also that the trend reconstructions commonly become more and more sensitive to the data points near the boundaries of the data set. This, together with the less sensitive outlier identification for these data points, might be responsible for some of the slight variations in the phase and absolute level of most recent sulfate trend concentrations between the different cores shown in Figure 4.

In order to take the fivefold increase in snow accumulation rate over the investigated area into account, a simple macroscopic deposition model, as outlined in part 1 of Fischer *et al.* [this issue], was applied. This allowed the reconstruction of separate time series for wet and dry deposition. In the case of the irreversible deposition of conservative species like sulfate the average firm concentration  $C_{\text{firm}}$  at a given position can be described as the sum of the average fresh snow concentration  $C_{\text{snow}}$  and the average total dry deposition flux  $J_{\text{dry}}^{\text{tot}}$  which is diluted by the average snow accumulation  $A$ :

$$C_{\text{firm}} = C_{\text{snow}} + \frac{J_{\text{dry}}^{\text{tot}}}{A} \quad (1)$$

In our simple macroscopic model for the reversible deposition of gaseous nitrate precursors, nitrate firm concentrations are described as a budget between nitrate deposition and volatilization leading to

$$C_{\text{firm}} = C_{\text{snow}} + \left( J_{\text{dry}}^{\text{tot}} - \lambda \cdot \Delta z \cdot C_{\text{snow}} \right) \frac{1}{A} - \lambda \cdot \Delta z \cdot J_{\text{dry}}^{\text{tot}} \frac{1}{A^2} \quad (2)$$

with a characteristic nitrate evasion velocity  $v_{\text{evasion}} = \lambda \Delta z$  (where  $\lambda$  is the rate constant of the first-order nitrate loss process and  $\Delta z$  is the thickness of the box where nitrate loss occurs). No assumptions are made concerning microscopic deposition and reevaporation processes or the actual speciation of gaseous nitrate precursors in the Greenland atmosphere.

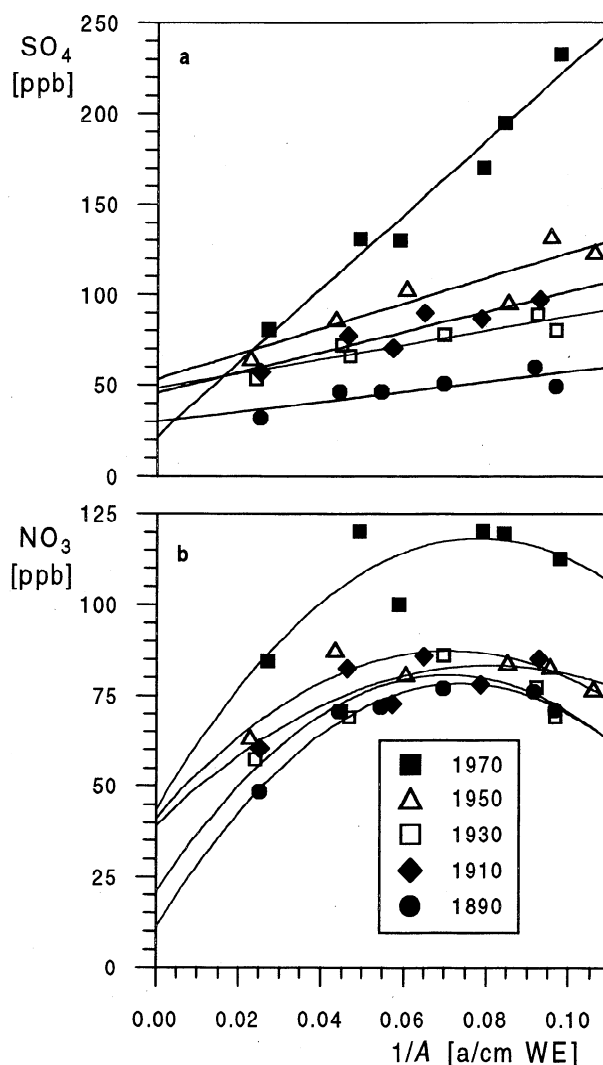
For continuous application of this model on the time series, running 15-year averages in the reduced sulfate and nitrate firm concentrations as well as snow accumulation rate were calculated for all cores. According to equations (1) and (2), we applied a first- and second-order polynomial fit in inverse snow accumulation rate to corresponding 15-year intervals in sulfate and nitrate firm concentrations of the five cores, respectively.

From the polynomial coefficients the average fresh snow concentration  $C_{\text{snow}}$ , the average total dry deposition flux  $J_{\text{dry}}^{\text{tot}}$  and in the case of nitrate the evasion velocity  $v_{\text{evasion}}$  were derived. To illustrate this calculation, examples of the regressions of sulfate and nitrate firm concentration versus inverse accumulation rate are plotted in Figure 3 for the 15-year intervals centered around the years 1970, 1950, 1930, 1910, and 1890.

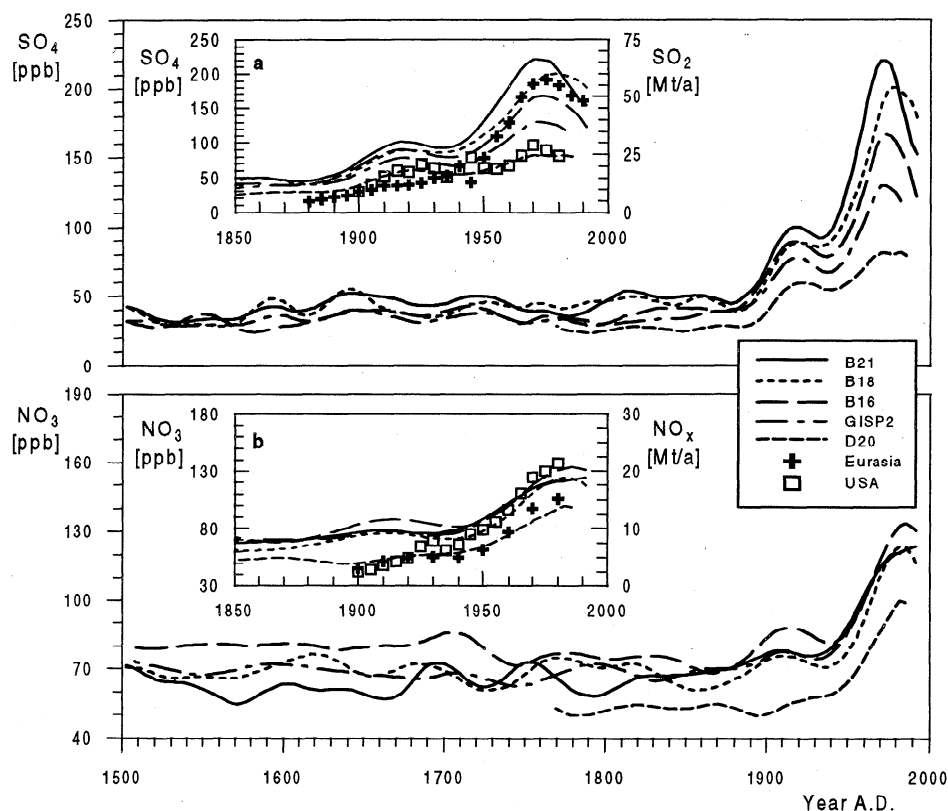
### 3. Results

#### 3.1. Sulfate

Sulfate trend reconstructions (as determined by SSA/MCSSA) for the cores B16, B18, B21, D20, and GISP2 are plotted in Figure 4a. The trend components show a high covariance between all five cores over the preindustrial period and especially since the onset of anthropogenic forcing of sulfate aerosol concentrations over the Greenland ice sheet.



**Figure 3.** (a) Linear regression of average sulfate firm concentrations versus inverse snow accumulation rate of the 15-year intervals centered around the years 1970, 1950, 1930, 1910, and 1890 A.D. according to equation (1). (b) Second-order polynomial regression for nitrate firm concentrations according to equation (2).



**Figure 4.** Trend reconstructions for the cores D20, GISP2, B16, B18, and B21. Plotted are (a) the sum of the first four significant reconstructed components derived by SSA/MCSSA for the sulfate record of each core and (b) the sum of the first three significant reconstructed components for the nitrate records. Also indicated in the enlargements are emission records for the United States (squares) and Europe/USSR (crosses) as taken from Gschwandtner *et al.* [1986], Mylona [1996] and Hov *et al.* [1987].

Preindustrial background concentrations, as represented by the long-term trends, range from ~30 ppb in the south to ~50 ppb in the north of the ice sheet and vary temporally by approximately  $\pm 25\%$ , probably associated with the long-term variation of natural sulfate sources (e.g., marine biogenic emissions or noneruptive volcanic exhalations). The common features of the anthropogenic increase in all cores are: (1) an initial strong increase by up to 3 ppb/a starting around 1880-1890 concurrent with the major start of the industrialization, (2) a transient drop during the 1930s, possibly linked to the economic crisis in that decade; (3) a major increase in sulfate background levels starting around 1945 with growth rates of up to 5 ppb/a; sulfate firn concentrations reached their maximum during the late 1970s; (4) a significant decline during recent decades to values comparable to levels formerly encountered around 1960. This decline most probably is due to the sulfur emission controls established in western Europe and the United States (see also the comparison with emission estimates below) together with the decline in industrial production in the former USSR.

### 3.2. Nitrate

Preindustrial nitrate levels of approximately 50-80 ppb (as depicted by the trend components in Figure 4b) vary by only  $\sim \pm 15\%$  and, unlike sulfate, do not show such a clear covariation between the different records. However, with increasing anthropogenic influence of the atmospheric nitrate

levels, a very high covariance in the temporal pattern of nitrate firn concentrations emerges between all cores. In general, higher nitrate levels are found in central Greenland compared to southern and northern Greenland locations. The common features of the anthropogenic rise in nitrate firn concentrations are: (1) a slight increase since approximately 1890 by up to 1 ppb/a; (2) a weak depletion during the 1930s; (3) a significant increase since 1950 by up to 2 ppb/a, which extends to the 1990s, and (4) for the first time, a weak decline during most recent years is recorded in our new northern Greenland ice cores.

## 4. Discussion

### 4.1. Comparison With Anthropogenic Emission Estimates

Having established a spatially representative history of the anthropogenic influence on sulfate and nitrate firn concentrations over the Greenland ice sheet, it is tempting to identify possible source regions of such pollutions relevant for the Greenland atmosphere. Emission estimates taken from Gschwandtner *et al.* [1986] for SO<sub>2</sub> and NO<sub>x</sub> emitted in the United States, from Mylona [1996] for SO<sub>2</sub> emissions in Europe and the former USSR as well as from Hov *et al.* [1987] for NO<sub>x</sub> emitted in Europe are plotted in the enlargements in Figure 4.

The major peak in sulfate firn concentrations occurring in the 1970s in all ice cores is also found in SO<sub>2</sub> emissions in

Europe and the USSR but is not as pronounced in U.S. estimates. This points to a major influence of Eurasian anthropogenic sources on the sulfate level in Greenland firn for the second half of this century, although U.S.  $\text{SO}_2$  emissions of approximately 28 Mt/a [Gschwandtner et al., 1986] comprise around 50% of the Eurasian output during that time. However, pollution plumes from North American source regions are subject to strong precipitation scavenging when transported over the Atlantic, while the atmospheric lifetimes of pollutants transported to the Arctic basin from Eurasian sources in winter are longer during the polar night due to lower photooxidation rates and low precipitation scavenging for these rather dry air masses. Thus  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  removal from pollution plumes originating in the United States is expected to be much more efficient than from polluted air masses advected to the Arctic from Eurasia [Barrie, 1986].

In contrast, European  $\text{SO}_2$  emissions were only two thirds of U.S. sources at the beginning of this century and experienced lower increase rates during the first decades of this century compared to U.S. emission records. The relatively strong increase in Greenland sulfate concentrations starting at around 1890 therefore most likely reflects the influence of U.S. emissions on the Greenland sulfate firn level during the first half of this century. This assumption is also supported by the transient decrease in Greenland sulfate firn concentrations during the 1930s, which is found in U.S. emission estimates but not in Eurasian ones. Note here, that because of the smoothing inherent in the trend reconstruction, average sulfate concentrations in Figure 4 start to decline already in the 1920s. Looking at the unsmoothed triannual data set in Figure 2, this decline is clearly caused by significantly lower sulfate concentrations during the 1930s and may therefore be attributed to the economic decline during this decade.

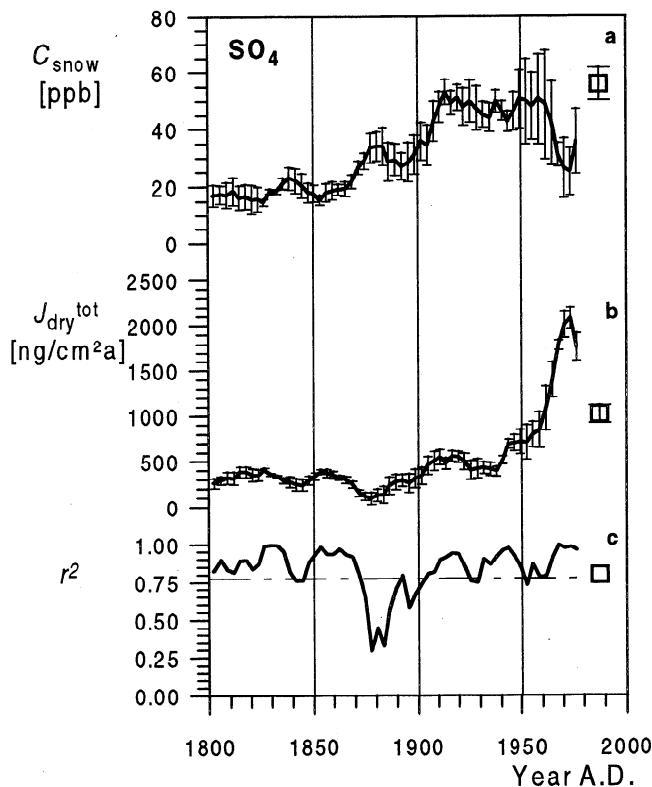
In the case of nitrate the very similar temporal evolution of Eurasian and U.S.  $\text{NO}_x$  emission estimates, which both show a major increase since 1950, does not allow a conclusive source identification. Under the assumption of similar atmospheric lifetimes and long-range transport pathways of anthropogenic sulfur and nitrogen species, the lower Eurasian  $\text{NO}_x$  emissions (amounting to approximately 70% of U.S. values in the year 1980) point to a relatively higher North American influence on recent nitrate levels in Greenland compared to sulfate. The slight decrease in U.S.  $\text{NO}_x$  emissions during the 1930s, not found in European emission estimates, is also imprinted in the Greenland ice core records, thus supporting significant contributions of U.S. emissions to Greenland nitrate firn concentrations in the first half of this century.

#### 4.2. Temporal Evolution of Wet and Dry Deposition Fluxes

In view of the extraordinary covariance in the trend reconstructions of nitrate and especially sulfate firn concentrations between the different cores since the beginning of this century, we conclude that the source mix of anthropogenic polluted air masses transported from Eurasia and the United States is rather uniform over the entire ice sheet both for sulfate and for nitrate. However, comparison of the absolute concentration of concurrent sulfate levels in the five cores reveals systematic geographic variations with sulfate levels strongly increasing from south to north. In

contrast, higher nitrate firn concentrations are found in central Greenland than on the southern and northern ice sheet. These geographical variations can be attributed largely to the corresponding accumulation changes (as demonstrated by Fischer et al., [this issue]) leading to different relative contributions of wet and dry deposition fluxes as well as systematic geographical variations in the net loss of nitrate from the firn column. Surprisingly, the increase in sulfate concentrations during the 1970s relative to the preindustrial level changes from a factor of 2.5 in southern Greenland to approximately 5 in northern Greenland. Since average snow accumulation rates in our ice cores changed by less than 20% over the last 100 years [Fischer et al., 1998], equation (1) implies that temporal anthropogenic changes during this century are not equally reflected in wet and dry deposited sulfate on the Greenland ice sheet.

In order to investigate these temporal deposition changes and their possible causes in more detail, empirical time series for  $C_{\text{snow}}$  (which can be regarded as proxy for wet deposition changes since the snow accumulation remained essentially constant) and  $J_{\text{dry}}^{\text{tot}}$  were continuously determined according to equation (1) from linear regression of 15-year averages in sulfate firn concentration versus inverse accumulation rate for the time span 1785-1976, which is covered by all cores (see Figure 5a and 5b). To extend the time span, model values for the interval 1983-1992, as derived from our surface study in



**Figure 5.** Model results for sulfate: (a) average fresh snow concentration  $C_{\text{snow}}$  and (b) average total dry deposition flux  $J_{\text{dry}}^{\text{tot}}$ . Displayed are the linear regression parameters (thick line) in inverse accumulation rate together with their standard errors (error bars). Also displayed are the results of the high-resolution surface study (open square) by Fischer et al. [this issue]. (c) coefficient of determination  $r^2$  of the linear fit (thick line) together with its 5% significance level (dashed line).

high geographical resolution [Fischer *et al.*, this issue], are indicated in Figure 5 as well. Note, that by inserting corresponding 15-year snow accumulation averages in the regression, possible systematic but rather small temporal accumulation effects on firn concentrations are taken into account.

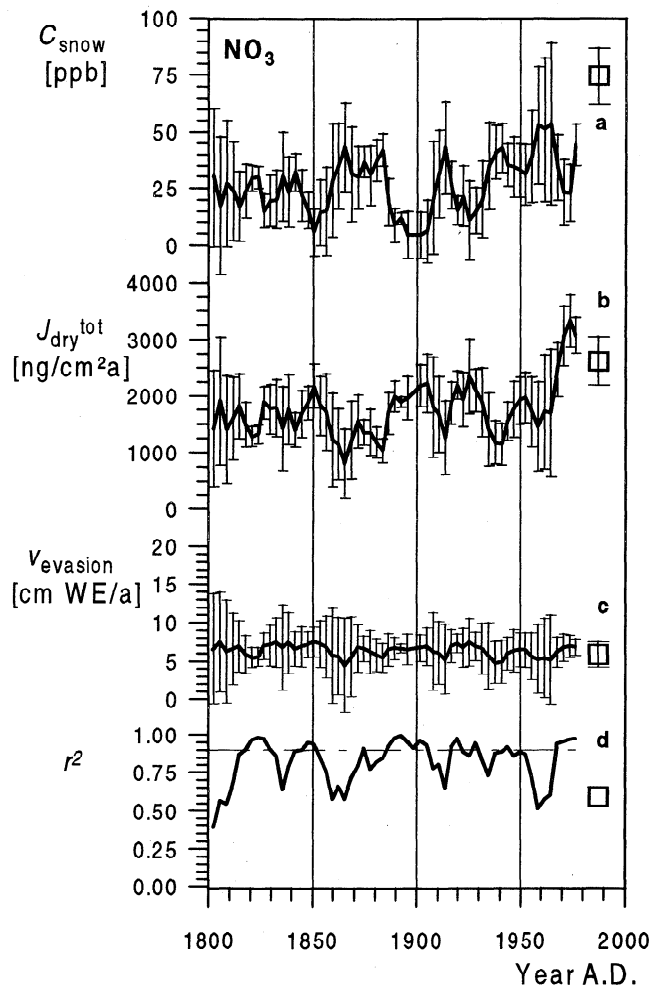
In Figure 5c the coefficient of determination  $r^2$  of the fit is plotted as well. This parameter can be interpreted as a measure of linearity and therefore indicates whether the deposition model according to equation (1) is applicable at all (however, one has to keep in mind that with only five data points available for each 15-year interval the statistical definition of the linear regression is not optimal). As clearly seen in Figure 5c,  $r^2$  is close to 1 and significantly different from zero on the 5% level for most of the time span covered by all cores. Thus a linear relationship between average firn concentration and inverse snow accumulation rate is reasonable to assume and accounts for most of the data variance. This implies that the geographical variation in sulfate firn concentrations can be explained largely by the change in snow accumulation rate over most of the time span investigated.

Comparing the records of wet and dry sulfate deposition in Figure 5a and 5b reveals significant differences in their temporal evolution.  $C_{\text{snow}}$  doubles from approximately 20 ppb at 1850 to 40 ppb in 1915 but remains relatively constant afterwards. In contrast, the total dry deposition flux rises slowly at the beginning of this century but increases strongly since 1950 by a factor of 5-6 compared to preindustrial values and is responsible for the major growth observed in Greenland sulfate firn concentrations during this century. The transient drop in fresh snow concentrations during the 1970s to values as low as during preindustrial conditions is accompanied by the concurrent maximum in the dry deposition flux. This feature could be caused either by a geographical net variation with higher atmospheric sulfate concentrations over the northern ice sheet during this period (possibly related to a higher influence of Arctic haze air masses), which causes an overestimation of  $J_{\text{dry}}^{\text{tot}}$  and an underestimation of  $C_{\text{snow}}$  in our linear model (see also Figure 3), or else by the statistically weak definition of the regression line by only five data points. If we assume a fresh snow concentration of 40-50 ppb for these years as over most of the century,  $J_{\text{dry}}^{\text{tot}}$  would be lower by only ~ 10% according to equation (1). Thus the temporal rise factor of dry sulfate deposition during the 1970s would still be more than twice the relative increase in fresh snow concentration.

Comparison of the  $\text{SO}_2$  emission scenarios with the derived time series of wet and dry sulfate deposition suggests that wet deposition generally reflects the temporal evolution in U.S. estimates, while the European/USSR emissions are mirrored more closely by the dry deposition record. Keeping the uncertainty in the regression in mind, we may conclude that this difference reflects a preferred sampling of air masses advected from southwesterly directions by wet deposition and from northeasterly directions by dry deposition, respectively. The average fresh snow concentration  $C_{\text{snow}}$  essentially represents a precipitation-weighted picture of the atmospheric aerosol concentration and is only representative of air masses connected to substantial snowfall on the ice sheet. Such air masses are closely linked to the cyclonic activity over the North Atlantic [Chen *et al.*, 1997] and are most often transported onto the interior of the ice sheet from

southwesterly directions [Fischer *et al.*, 1995]. Accordingly, a mainly North American origin of the wet scavenged pollutant load is expected. Air masses advected onto the Greenland ice sheet from the Arctic basin, which are polluted by Eurasian emission sources in winter/spring [Barrie, 1986], are relatively dry and therefore not efficiently scavenged by precipitation events over the ice sheet (as also reflected in the pile-up of  $\text{SO}_2$  and sulfate aerosol over the Arctic basin during Arctic haze events). Dry deposition is essentially an image of the temporal mean of atmospheric sulfate aerosol concentrations, and accordingly these air masses should be preferentially reflected in  $J_{\text{dry}}^{\text{tot}}$ .

In the case of nitrate, no significant discrepancy in the increase by a factor of approximately 2 since the preindustrial period exists between the five records plotted in Figure 5b. No distinct difference in the temporal evolution of wet and dry deposition, as determined from a second-order polynomial fit according to equation (2), can be found in Figure 6a and 6b as well. Note, however, that the statistical significance of this fit



**Figure 6.** Model results for nitrate: (a) average fresh snow concentration  $C_{\text{snow}}$ , (b) average total dry deposition flux  $J_{\text{dry}}^{\text{tot}}$  and (c) evasion velocity  $v_{\text{evasion}}$  derived from the second-order polynomial fit (thick line) in inverse snow accumulation together with their propagated standard errors (error bars). Also displayed are the results of the high-resolution surface study (open square) by Fischer *et al.* [this issue]. (d) coefficient of determination  $r^2$  of the fit (thick line) together with its 5% significance level (dashed line).

is strongly limited in the case of only five data points ( $r$  is significantly different from zero on the 5% level only if  $r^2$  in Figure 6d is larger than 0.9) and may be subject to significant error, as reflected in the high noise in the  $C_{\text{snow}}$  and  $J_{\text{dry}}^{\text{tot}}$  records. Furthermore,  $C_{\text{snow}}$  and  $J_{\text{dry}}^{\text{tot}}$  show a strong anticorrelation throughout the last 200 years which can be attributed to the insufficient definition of the fit. With respect to this uncertainty, we refrain from speculating about the significance of the recent peak in dry nitrate deposition seen in Figure 6b. Expansion of the database with further long-term nitrate records from other positions on the ice sheet, currently under way in our lab, may resolve this problem.

The evasion velocity connected with the remobilization process plotted in Figure 6c remains essentially constant throughout the time span investigated with values around 5–8 cm WE/a as also found for recent conditions in our high-resolution surface study [Fischer *et al.*, this issue]. This supports the hypothesis, that  $v_{\text{evasion}}$  is a parameter typical for the loss process encountered in the dry snow zone of the Greenland ice sheet and is mainly controlled by the internal structure and the ongoing recrystallization of the snowpack.

## 5. Summary and Conclusions

Comparison of five highly covariant long-term ice core records for sulfate and nitrate concentrations in Greenland firn allowed us to reconstruct a detailed and spatially representative history of anthropogenic change over the ice sheet. Sulfate firn concentrations were 100% higher during the 1970s than preindustrial levels in southern Greenland but up to 500% higher in the northern part of the ice sheet. Recent nitrate levels are 100% higher than preindustrial concentrations throughout the ice sheet. An approximately 30% decline in sulfate firn concentrations and, for the first time, slight indications for a nitrate decrease during recent years are revealed. The sulfate decrease may be attributed to the effect of sulfur emission reduction measures in Europe and the United States and possibly the decline in industrial production in the former USSR. The very weak nitrate decline, however, shows that denoxification measures of industrial and vehicle emissions are still not sufficient to have a major effect on nitrate precursor levels in anthropogenically polluted air masses over the Greenland ice sheet. Comparison of the concentration records with emission estimates for the United States and Eurasia suggests that sulfate firn concentrations were essentially controlled by North American emissions in the first half of this century while the major increase in sulfate levels since 1950 has been primarily governed by Eurasian sources. The temporal evolution of  $\text{NO}_x$  emission estimates for Europe and the United States are very similar, preventing an unambiguous identification of source areas for anthropogenic nitrate species. However, higher  $\text{NO}_x$  emissions in the United States compared to Europe point to a higher influence of US sources on Greenland nitrate levels during this century.

By continuously applying a macroscopic model for the irreversible deposition of particulate sulfate aerosol as well as the reversible deposition of gaseous nitrate species, separate series of wet and dry deposition fluxes can be extracted. This shows that the geographically varying extent of the anthropogenic change in sulfate firn concentrations can be attributed largely to the temporal changes in wet and dry deposition which, depending on the snow accumulation rate, contribute different amounts to the total sulfate deposition in

different climatological regions on the ice sheet. In particular, no major geographical variations in average air concentrations are indicated by the model outcome. Comparison of the temporal sulfate deposition records with anthropogenic  $\text{SO}_2$  emission records points to a preferred sampling of polluted air masses of North American origin by wet deposition and from Eurasian sources by dry deposition, reflecting the different precipitation probability of these air masses over the Greenland ice sheet. Thus the atmospheric information archived in ice core records from climatological different regions on the ice sheet is specifically filtered by wet and dry deposition, depending on the snow accumulation rate encountered in the drill site region.

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