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Strong similarities in seasonal concentration ratios of SO_4^{2-}, NO_3^- and NH_4^+ in precipitation between Sweden and the northeastern US*

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ABSTRACT

We analyzed 21-year long records of precipitation chemistry from central Scandinavia and the northeastern US to compare seasonal variations of three major pollutant ions, SO_4^{2-}, NO_3^- and NH_4^+. Seasonal variations in concentrations of the individual ions were distinctly different between the two regions. However, despite these differences, we found strong and unexpected similarities between the two regions in seasonal variations of the concentration ratios NO_3^-/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/SO_4^{2-}. A preliminary analysis suggests that these similarities are due to similarities between the two regions in chemical transformation and removal processes affecting SO_4^{2-} and NO_3^- in the atmosphere, and to a coupling between NH_4^+ and SO_4^{2-} aerosol in long-range transport. Ion ratios appear to be less sensitive to seasonal variations in SO_2 and NO_x emissions compared to individual ion concentrations.

1. Introduction

The chemical composition of precipitation in both the northeastern US and central Scandinavia is influenced strongly by anthropogenic emissions of sulfur and nitrogen (Bolin et al., 1971; National Research Council, 1978, 1983; Buijsman et al., 1987). However, there are distinct differences in annual average concentrations of several major pollutant ions between the two regions. For example, average yearly concentrations of SO_4^{2-} and NH_4^+ in precipitation of central Scandinavia are 1.4 and 2.2 times larger, respectively, than those in the northeastern US, while concentrations of NO_3^- are not significantly different ($p > 0.2$, t-test; Table 1) (Likens et al., 1984; Rodhe and Granat, 1984; Rodhe and Rood, 1986; Dana and Easter, 1987). Average yearly concentration ratios for NO_3^-/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} also differ between the two regions (Table 1). Furthermore, seasonal variations in concentrations of SO_4^{2-} appear to be substantially different between central Scandinavia and the northeastern US (National Research Council, 1983; also compare Rodhe and Granat, 1984 versus Dana and Easter, 1987). We will here use 21-year records of precipitation chemistry from central Scandinavia and the northeastern US to compare, in more detail, seasonal variations in concentrations and ratios of SO_4^{2-}, NO_3^- and NH_4^+ between the two regions. We will also compare these seasonal variations to seasonal changes in amounts of precipitation and emissions of SO_2 and NO_x.

2. Methods

We used long-term records of volume-weighted, monthly precipitation chemistry for the period 1965 to 1985 (21 years), from four stations in central Sweden which are part of the

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Table 1. *Arithmetic mean of annual, volume-weighted concentrations (μeq/l) and ratios of SO_4^{2-}, NO_3^- and NH_4^+ from monitoring sites at the Hubbard Brook Experimental Forest and central Sweden during 1965–85*

	Hubbard Brook Concentration (μeq/l)	Sweden Concentration (μeq/l)
SO_4^{2-}	51.1 (2.03)	70.8 (2.53)
NO_3^-	24.8 (0.73)	23.4 (1.09)
NH_4^+	10.3 (0.49)	22.9 (1.06)
	Equivalent ratio	Equivalent ratio
NO_3^-/SO_4^{2-}	0.50 (0.02)	0.34 (0.02)
NH_4^+/NO_3^-	0.42 (0.02)	0.99 (0.03)
NH_4^+/SO_4^{2-}	0.20 (0.01)	0.33 (0.02)

The values are averages of volume-weighted means for each year during the period ($n = 21$). Standard errors are given in parentheses. Other published long-term averages (e.g., Likens et al., 1984; Granat, 1978) may differ slightly because they represent different time periods and/or were calculated by different averaging methods.

European Air Chemistry Network (EACN; Rodhe and Granat, 1984), and one at the Hubbard Brook Experimental Forest (HBEF; Likens et al., 1984) in the northeastern US (Fig. 1). We based our analysis on ion concentrations since concentration fields are normally more uniform and less influenced by local meteorology than are deposition fields (Granat, 1978). We excluded H^+ because concentrations of H^+ in Sweden were affected in early years by local contamination from Ca^{2+} rich dust; SO_4^{2-}, NO_3^- and NH_4^+ were not affected similarly.

Similar types of bulk precipitation collectors were used at all sites throughout most of the study. Details on sampling and analytical methods are given in Likens et al. (1984) and Rodhe and Granat (1984). At HBEF, weekly samples were collected and monthly ion concentrations were weighted by precipitation volume. In Sweden, we used monthly samples during 1965–85 for stations FO15 and RK42, during 1967–85 for station SN80 and during 1972–85 for station HA129. Because the stations showed similar temporal variations in chemistry, we combined monthly data to produce arithmetic averages representative for central Sweden. Monthly concentrations of SO_4^{2-}, NO_3^- and NH_4^+ showed highly significant ($p < 0.002$) between-station correlations, with Pearson correlation coefficients generally exceeding 0.5 (range: 0.3–0.7). The difference in sampling period between Swedish (monthly) and US (weekly) stations was considered. Clearly, biological activity could affect NH_4^+ in rain samples. Based on our tests, 5 samples were removed from the Swedish record for this reason. In our judgement, however, the remaining Swedish data were not affected seriously by such biological activity. Galloway et al. (1976, 1979) reported no significant change in the chemistry of precipitation samples collected in Ithaca, NY, when the samples were stored for up to 8 months at 4°C.

In Sweden, bulk collectors were used during 1965–81, and wet-only collectors were used after 1981. Comparison of 114 months where both types of collectors were used simultaneously suggested that change of collector type had little (<10%) effect on concentrations of SO_4^{2-}, NO_3^- and NH_4^+. The contribution of sea-salt to average yearly SO_4^{2-} concentrations is <5% at any of the Swedish sites, and is negligible at HBEF (Hedin et al., 1987).

To minimize effects of any long-term trends in concentrations (e.g., Likens et al., 1984) on the seasonal variations, each monthly concentration value (or ion ratio) was expressed relative to the average concentration (or ratio) of that year. Monthly volume-weighted concentrations for each year were divided by the average arithmetic concentration for that year (sum of monthly volume weighted concentrations divided by 12). Similarly, the ratio of ion concentrations (e.g., NO_3^-/SO_4^{2-}) for each month was divided by the average arithmetic concentration ratio for that year.

Both the HBEF and the Swedish stations are located at similar distances (ca. 1000 km) downwind of major source areas of SO_2 and NO_x. Monthly data on emissions of SO_2 and NO_x for the US were taken from EPA regions 1, 2, 3 and 5, (Knudson, 1986) which are generally upwind of the HBEF sampling site (National Research Council, 1983), and cover the period 1975–84. Monthly data from before 1975 were not available. To minimize effects of any long-term change in emission amounts on the estimates of

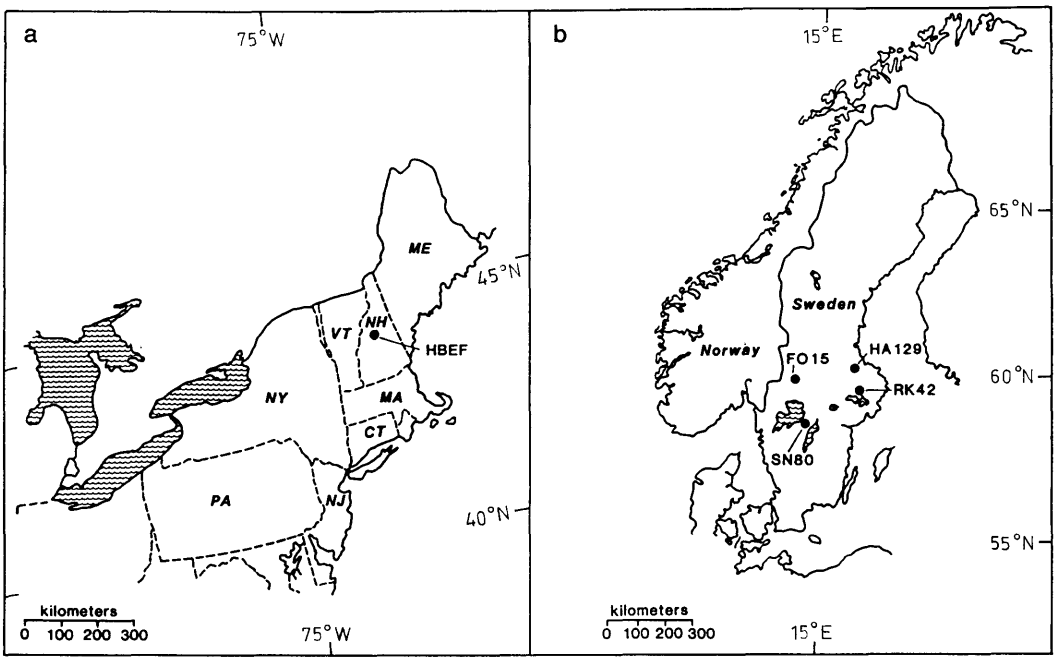

Fig. 1. (a) Location of the sampling station at the Hubbard Brook Experimental Forest (HBEF) in the northeastern USA. (b) Location of the four sampling stations in central Sweden: FO15, HA129; SN80; and RK42.

seasonal variations in emissions, each monthly emission estimate was expressed relative to the average monthly emission for that year. Thus, for each year, monthly emission values were divided by the mean (arithmetic) monthly emission for that year. Our conclusions are not dependent on the exact EPA regions chosen because, although absolute emission amounts vary substantially depending on region, the seasonal variations in emissions are similar between regions in the northeastern US (Knudson, 1986). Furthermore, comparisons between the periods 1975–79 and 1980–84 suggested that seasonal patterns in SO_2 and NO_x emissions have remained stable with time. Unfortunately, data on monthly emissions for specific years are not available for Europe. However, there have been several estimates of relative seasonal variations in SO_2 and NO_x emissions for the EMEP grid in Europe, including the western part of the USSR (OECD, 1977; EMEP/MSCW, 1987). These emissions data have been used in this analysis. Although absolute emissions have changed over time, the relative magnitude of these seasonal variations are thought to have remained stable (A. Eliassen, personal communication).

Monthly concentrations of SO_4^{2-} and NO_3^- were expressed per unit emission of SO_2 and NO_x (normalized to emissions) by dividing the monthly long-term average concentrations by the corresponding monthly emission values (i.e., SO_4^{2-}/SO_2 and NO_3^-/NO_x). Similarly, the ratio of NO_3^-/SO_4^{2-} was normalized to emissions by dividing the monthly long-term average concentration ratio by the corresponding monthly ratio of emissions (NO_x/SO_2).

3. Results

A comparison of seasonal variations in concentrations of SO_4^{2-}, NO_3^- and NH_4^+ between HBEF and Sweden revealed marked differences between the two regions (Fig. 2a–c). Concentrations of SO_4^{2-} and NH_4^+ at HBEF are high in the summer and low in the winter (Fig. 2a, c). In

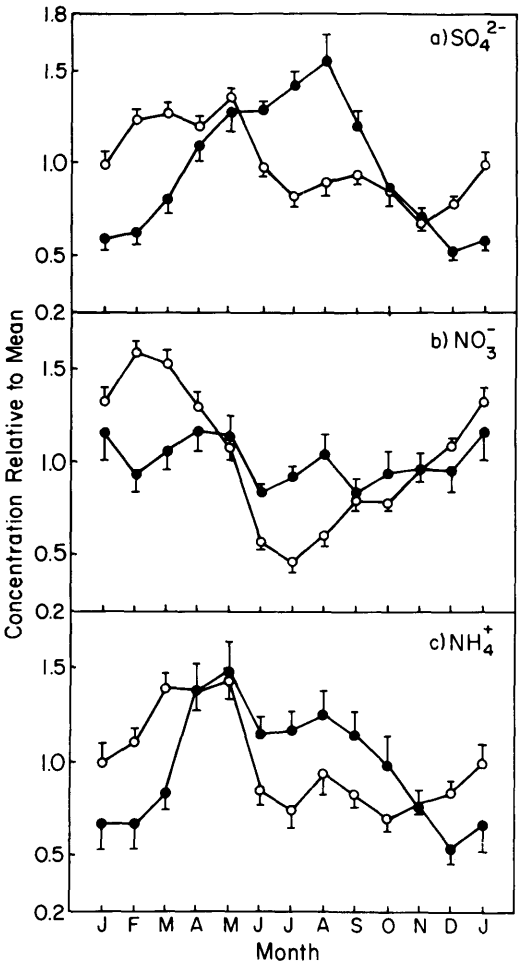

Fig. 2. Seasonal variations at HBEF (●) and Sweden (○) of monthly average concentrations of SO_4^{2-} (a), NO_3^- (b), and NH_4^+ (c) during 1965–85. Standard errors are given. Concentrations are expressed relative to the average concentration of each year.

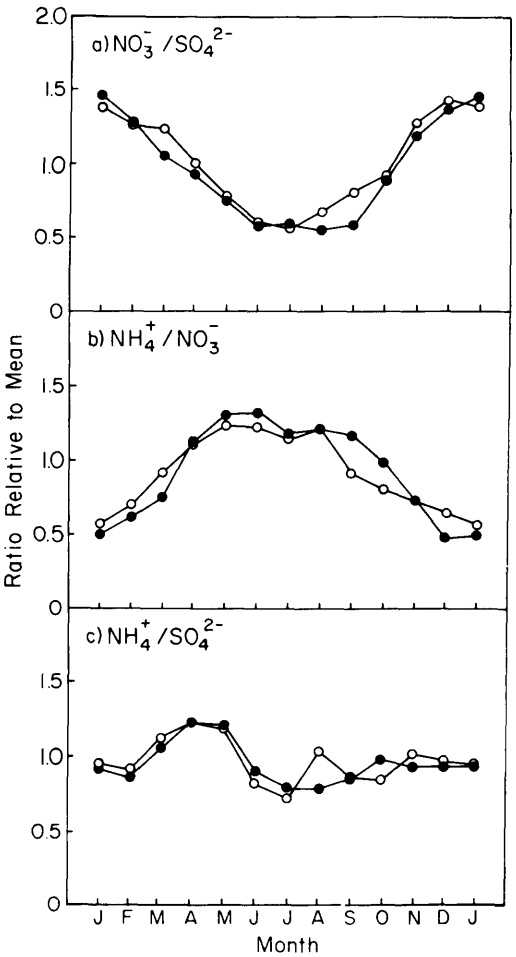

Fig. 3. Seasonal variations at HBEF (●) and Sweden (○) of monthly median ion ratios of NO_3^-/SO_4^{2-} (a), NH_4^+/NO_3^- (b), and NH_4^+/SO_4^{2-} (c) during 1965–85. Ratios are expressed relative to the average ion ratio for each year. Most variables are approximately normally distributed, however we present medians because some points are influenced by extreme outliers.

sharp contrast, concentrations of SO_4^{2-} and NH_4^+ in Sweden are high in the spring, and low in the autumn (Fig. 2a, c). Concentrations of NO_3^- at HBEF do not vary systematically with season (Fig. 2b), while in Sweden high concentrations occur in late winter and low concentrations occur in summer (Fig. 2b).

However, when concentration ratios between the 3 pollutant ions are considered, we find striking seasonal similarities between HBEF and Sweden (Fig. 3). Seasonal variations of each of the concentration ratios, NO_3^-/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/SO_4^{2-}, are similar both in shapes and in relative amplitudes at HBEF and in Sweden (Fig. 3). The NO_3^-/SO_4^{2-} and NH_4^+/NO_3^- ratios show strong variations during the year in both regions, with highest concentrations of SO_4^{2-} relative to NO_3^- and NH_4^+ relative to NO_3^- in summer (Fig. 3a, b). In contrast, the NH_4^+/SO_4^{2-} concentration

ratio does not show any distinct seasonal pattern (Fig. 3c), with the possible exception for a slight peak in spring.

The seasonal variations in these three concentration ratios (Fig. 3) are robust features of the long-term records from HBEF and Sweden. These variations can be derived directly from the seasonal variations in concentrations of the individual ions (Fig. 2), and are not artifacts of any mathematical treatment. Comparisons of the seasonal variations in each ion ratio between early, middle and late parts of the records (1965–71, 1972–78, and 1979–85), did not indicate any systematic changes with time at either site (e.g., Fig. 4a). For each concentration ratio at each site, a two-way ANOVA considering the factors month and period (early, middle versus late part of record) suggested that the period did not add significantly to the variance in the concentration ratio (in all cases $p > 0.95$). Furthermore, analysis of data from the MAP3S (Dana and Easter, 1987) and the EACN (Rodhe and Granat, 1984) networks suggested that these variations in concentration ratios are representative for larger areas of the northeastern US and Scandinavia.

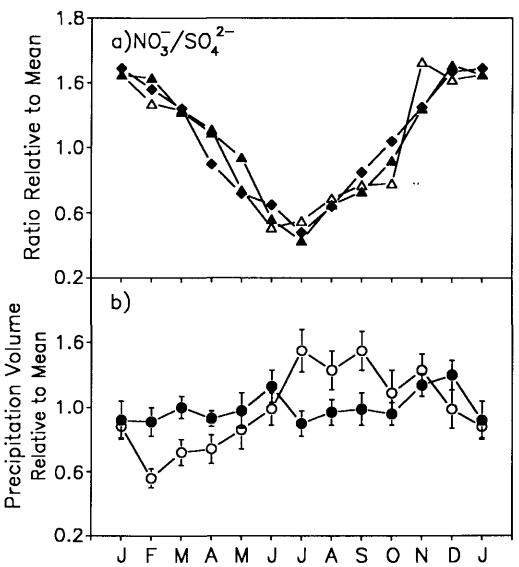

Fig. 4. (a) Seasonal variations of the monthly median ion ratio NO_3^-/SO_4^{2-} at Sweden during the periods 1965–71 (▲), 1972–78 (△) and 1979–85 (◆). (b) Seasonal variations in monthly precipitation volumes at HBEF (●) and Sweden (○) during 1965–85. Values are expressed relative to the average precipitation volume for each year. Error bars represent standard errors.

4. Analysis and discussion

The close similarity between the northeastern US and Scandinavia in seasonal variations of the concentration ratios NO_3^-/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} is surprising given the marked differences in seasonal variations of the individual ions (Fig. 2), and given other differences between the two regions such as latitude and seasonal variations in amounts of precipitation and emissions. Before discussing this similarity in seasonal concentration ratios, we will examine why the seasonal variations in individual ion concentrations (Fig. 2) are so different between the two regions. Although several factors may contribute, we will here explore two major factors which show distinctly different seasonalities between central Scandinavia and the northeastern US, and which may both affect ion concentrations (Likens et al., 1984; Granat, 1978; Lindberg, 1982; Oppenheimer, 1985): i.e., amounts of precipitation and emissions of SO_2 and NO_x.

Monthly amounts of precipitation show a distinct seasonal variation in central Scandinavia with a maximum in late summer, but vary little during the year at the HBEF (Fig. 4b). However, several lines of evidence suggest that precipitation amount is not the major determinant of the observed seasonal differences in ion concentrations (Fig. 2) between Sweden and the HBEF. First, if precipitation amount were the major determinant, we would expect that ion ratios other than NO_3^-/SO_4^{2-}, NH_4^+/NO_3^-, and NH_4^+/SO_4^{2-} also would show close seasonal similarity between the two regions. However, concentration ratios between elements originating from sea-salt or terrestrial sources and SO_4^{2-} (e.g., Cl^-/SO_4^{2-} or Mg^{2+}/SO_4^{2-}) do not bring seasonal coincidence between Sweden and HBEF. Second, analysis of years from Sweden with markedly dissimilar seasonal variations in amounts of precipitation (4 years with weak seasonal variation: wet winter and dry summer versus 4 years with strong seasonal variation: dry

winter and wet summer) showed no major differences in the seasonal patterns of SO_4^{2-}, NO_3^- or NH_4^+. Third, each month of the year in the Swedish record was analyzed for correlations between precipitation amount and concentrations of SO_4^{2-} or NO_3^-. As is common for such analysis (e.g., Lindberg, 1982), both the dependent and independent variables were log-transformed to meet the assumptions of regression analysis. There was no evidence of curvilinearity in any of these regressions. This analysis of individual months is independent of the seasonal patterns in concentrations (Fig. 2) and precipitation amount (Fig. 4b), and resulted in weak and highly variable correlations, with the amount of explained variance for different months ranging from 0 to 27%.

Monthly emissions of SO_2 and NO_x also show distinct seasonal variations in Europe, but not in the northeastern US (Rodhe and Granat, 1984; Knudson, 1986; OECD, 1977; EMEP/MSCW, 1987). European emissions of SO_2 and NO_x vary about 2.0-fold and 1.5-fold, respectively, with maximum values in late winter and minimum values in late summer (OECD, 1977; EMEP/MSCW, 1987). To evaluate how these differences in emission patterns between the regions may affect seasonal ion concentrations, we normalized the seasonal variations in SO_4^{2-} and NO_3^- concentrations at both HBEF and Sweden by dividing them by the average emission amounts for each month.

These normalizations to emission did not affect the seasonal variations in SO_4^{2-} and NO_3^- concentrations at HBEF appreciably, but transformed the Swedish variations to appear more similar to the ones at HBEF (Fig. 5). A strong seasonal variation, similar to the one at HBEF, remained in the Swedish SO_4^{2-} concentrations after normalization to SO_2 emissions (Fig. 5a).

The strong similarity between HBEF and Sweden after normalization to emissions suggests that SO_4^{2-} concentrations in both regions are affected similarly during the year by seasonal changes in one or more additional factors such as atmospheric transport, chemical transformations and deposition. Of these factors, we find it unlikely that systematic changes in atmospheric transport during the year would be the major factor producing the similar summer peak in both regions (Fig. 5a). Indeed, it should be emphasized

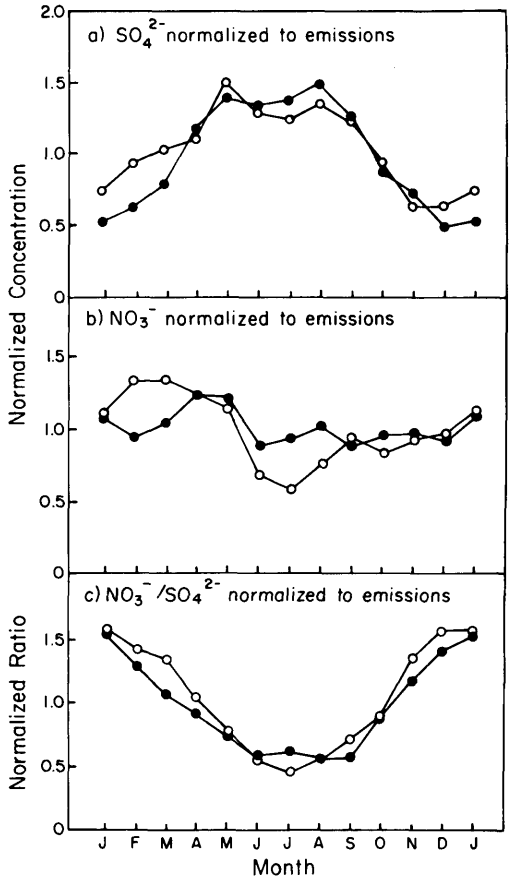

Fig. 5. Seasonal variations in concentrations and ratios at HBEF (●) and Sweden (○) normalized to seasonal variations in amounts of SO_2 and NO_x emissions. (a) Concentrations of SO_4^{2-} normalized to SO2 emissions; (b) Concentrations of NO_3^- normalized to NO_x emissions; (c) Ratio of NO_3^-/SO_4^{2-} normalized to both SO_2 and NO_x emissions.

that our stations are located on different continents and thus are influenced by different wind/transport patterns and emission areas. Rather, the seasonal variations in SO_4^{2-} that remain after normalization to SO_2 emissions (Fig. 5a) are consistent with higher rates of oxidation of SO_2 to SO_4^{2-} in the summer in both regions (Altschuller, 1979).

Normalization for emissions tended to reduce, but not eliminate, the seasonal variation in NO_3^- concentrations in Sweden (Fig. 5b). In marked

contrast to SO_4^{2-}, there are no summer maxima, either at HBEF or Sweden, in seasonal variations of NO_3^- after normalization to emissions (Fig. 5b). This distinct difference in seasonal behavior between NO_3^- and SO_4^{2-} can also be seen from the strong seasonal variations in the NO_3^-/SO_4^{2-} concentration ratio for both Sweden and HBEF. The lack of a summer maximum for NO_3^- when normalized for emissions in both regions may be explained by: (1) A more rapid deposition of HNO_3/NO_3^- during summer months between the source areas and the monitoring sites (Johansson and Granat, 1986), and/or (2) The oxidation of NO_x to HNO_3/NO_3^- is so rapid that, even in winter, most of the NO_x emitted is transformed chemically before reaching our monitoring sites (Rodhe et al., 1981). However, this latter mechanism is dependent on the assumption that NO_3^- deposition at our stations is due mainly to long-range transport. A clear answer must await a detailed analysis possibly including explicit long-range modeling.

The above normalizations suggest that the differences observed between Sweden and HBEF in seasonal variations of SO_4^{2-} concentrations (Fig. 2a), and to a large extent NO_3^- concentrations (Fig. 2b), can be explained by differences between the two regions in seasonal variations of SO_2 and NO_x emissions. The effect of such variations in emissions on concentrations of SO_4^{2-} and NO_3^- over the annual cycle appears to be more pronounced in Sweden than at HBEF because of the stronger seasonality of European emissions.

It is interesting that, in contrast to SO_4^{2-} and NO_3^- concentrations, the NO_3^-/SO_4^{2-} concentrations ratio appears to be relatively unaffected by the differences in seasonal emission patterns between Europe and the northeastern US. Despite the different emission patterns in the two regions, the seasonal variations in the ratio NO_3^-/SO_4^{2-} are surprisingly similar (Fig. 3a). This similarity possibly is due to the fact that emissions of SO_2 and NO_x vary closely together during the annual cycle in Europe (EMEP/MSCW, 1987). Thus, any change in NO_3^- in the numerator of the ratio due to a seasonal change in NO_x emissions is likely to be offset in the denominator by a similar change in SO_4^{2-} due to SO_2 emissions. That the ratio NO_3^-/SO_4^{2-} is relatively independent of seasonal variations in emissions is further suggested by the fact that normalizing the observed seasonal variations in NO_3^-/SO_4^{2-} from HBEF and Sweden to the monthly emissions of SO_2 and NO_x in each region does not affect the variations in the ratio appreciably (cf. Fig. 3a and 5c). The variations in the ratio NO_3^-/SO_4^{2-} therefore appear to reflect the relative behavior of SO_4^{2-} and NO_3^- due to factors other than emission (i.e., transport, chemical transformations and deposition). Thus, the strong similarity in seasonality of the concentration ratio NO_3^-/SO_4^{2-} between HBEF and Sweden (Fig. 3a) may be explained as follows: (1) A lack of influence of seasonal changes in emissions on the NO_3^-/SO_4^{2-} ratio, and (2) A similar influence in Sweden and HBEF of seasonal changes in transformation and deposition processes on SO_4^{2-} and NO_3^-, resulting in summer maxima of SO_4^{2-} relative to NO_3^- in both regions.

The lack of seasonality in the NH_4^+/SO_4^{2-} ratio at both HBEF and Sweden (Fig. 3c) suggests a seasonal coupling between NH_4^+ and SO_4^{2-} in both regions. Such seasonal coupling also is evidenced by a highly significant ($r^2 = 0.76$; $p < 0.0001$) correlation between monthly average concentrations of NH_4^+ and SO_4^{2-} from both sites (Fig. 6), with a slope not different from 1.0 ($p > 0.15$; t-test).

The seasonal variation of NH_4^+ concentrations in Sweden (Fig. 2c) does not follow the general seasonal variation that would be expected for NH_3 emissions. Swedish NH_4^+ concentrations are highest during winter and early spring but remain low during summer (Fig. 2c), while emissions of NH_3 tend to be high during summer and low during winter (Allen et al., 1988; ApSimon et al., 1987; Lenhard and Gravenhorst, 1980). The early spring peak may be a result of fertilizer application during the spring (Buishand et al., 1988). Nevertheless, the close coupling between NH_4^+ and SO_4^{2-} in Swedish precipitation does not appear to be due entirely to similar seasonal variations in emissions of NH_3 and SO_2.

Ammonia has a short residence time in the atmosphere due to dry deposition and reaction with acid aerosol (Asman and Janssen, 1987). However, when NH_3 reacts with acidic sulfate aerosol the residence time is increased considerably with respect to dry deposition and the resulting NH_4^+ aerosol will be subject to long-

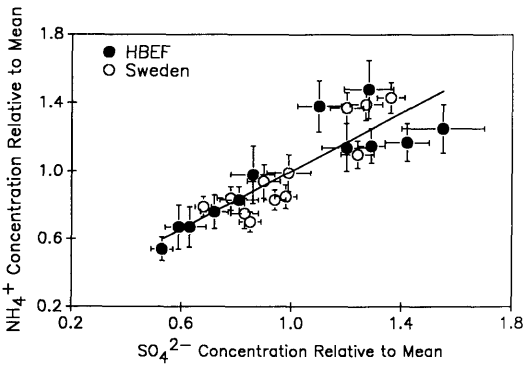

Fig. 6. Relationship between monthly average concentrations of NH_4^+ and SO_4^{2-} in bulk precipitation at HBEF (●) and Sweden (○). Concentrations are expressed relative to the average concentration of each year. Error bars represent standard errors. Line indicates linear regression ($r^2 = 0.76$; $p < 0.0001$).

range transport (Allen et al., 1988). We therefore suggest that the observed seasonal variations in NH_4^+ concentrations in Sweden may, to a large extent, be due to a chemical coupling between NH_4^+ and SO_4^{2-}, with acidic SO_4^{2-} aerosol acting as a vehicle for long-range transport of NH_3 (as NH_4^+). Seasonal variations in NH_4^+ concentrations at sites distant from major sources of NH_3 emissions thus may be influenced strongly by the supply of SO_4^{2-} aerosol, and by seasonal variations in emissions and oxidation of SO_2.

The strong seasonal similarity in the NH_4^+/SO_4^{2-} ratios between Sweden and HBEF (Fig. 3c), and the close correlation between NH_4^+ and SO_4^{2-} in both regions (Fig. 6) provides strong suggestion that the two ions are coupled in long-distance transport. Nevertheless, because the Swedish and HBEF sites are distant from major emission areas of NH_3, H_2SO_4 in precipitation is neutralized only partially by NH_4^+ (Table 1). Complete neutralization of H_2SO_4 by NH_4^+ can occur locally in areas with high emission density of NH_3 (e.g., the Netherlands) (Schuurkes et al., 1988).

5. Conclusions

Concentrations of SO_4^{2-}, NO_3^- and NH_4^+ show distinctly different seasonal variations between central Scandinavia and the northeastern US.

Seasonal variations in the concentration ratios NO_3^-/SO_4^{2-}, NH_4^+/NO_3^- and NH_4^+/SO_4^{2-} show strong and unexpected similarities between central Scandinavia and the northeastern US.

Seasonal variations in NO_3^- and SO_4^{2-} are markedly different, with highest concentrations of SO_4^{2-} relative to NO_3^- during summer.

A preliminary analysis suggests that the similar seasonal variations in concentration ratios are due to similarities between the two regions in chemical transformation and removal processes affecting SO_4^{2-} and NO_3^- in the atmosphere, and to a coupling between NH_4^+ and SO_4^{2-} aerosol in long-range transport.

Seasonal variations of individual ion concentrations (SO_4^{2-}, NO_3^- and NH_4^+) appear to be confounded strongly by variations in emissions of SO_2 and NO_x, while ion ratios appear to be less sensitive to such variations.

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