

Formation of sulfuric and nitric acid in the atmosphere during long-range transport

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ABSTRACT

A simple photochemical model has been used to simulate the formation of sulfuric and nitric acid during long-range transport through the atmosphere. Comparisons have been made with observations of sulfate and nitrate in precipitation at various distances from the source areas in northern Europe.

Both observations and model calculations indicate that HNO_3 is formed at a faster rate than H_2SO_4 and that the long-range transport of HNO_3 is thus somewhat less pronounced than that of H_2SO_4 . Mainly because of the common dependence of the oxidation of SO_2 and NO_x on the concentration of the OH radical, the concentration of NO_x has a significant influence on the rate of formation of H_2SO_4 : A higher emission of NO_x tends to reduce the levels of OH and H_2O_2 close to the source area thereby delaying and decreasing the transformation of SO_2 to H_2SO_4 .

Because of the interactions of the chemical species, the dependence of the concentrations on emission rates is not linear. Our model suggests that the concentrations of H_2SO_4 at travel distances up to a few tens of hours should have increased significantly less over the last 20 years than the rates of emission of SO_2 . This also seems to be brought out by observations of sulfate in precipitation.

1. Introduction

During the last few years there has been a growing realization that emission of SO_2 is not the only important cause of acid precipitation but that nitrogen oxides also play a very significant role. For example, Söderlund (1977) estimated that the relative contribution of nitrate and sulfate to the overall acidification in the northern parts of West Europe in the early seventies was about 1:3. The same author also noted the very rapid increase of the nitrate concentration in precipitation during the last 20 years. Precipitation data from the U.S. (Likens et al., 1977) indicate that the relative importance of nitrogen oxides for the formation of acid in precipitation is even higher in the north-eastern U.S. than in Europe.

Thus, it would seem a natural step to try to include nitrogen oxides and nitric acid explicitly in long-range transport models. The nitrogen oxide radicals NO and NO_2 are photochemically very active and contribute in important ways to the determination of the concentrations of the hydroxyl (OH) radical and of hydrogen peroxide (H_2O_2). Both these species are involved in the oxidation of SO_2 in the atmosphere. The conversion of SO_2 to H_2SO_4 is, therefore, indirectly influenced by emissions of NO_x in the atmosphere.

The aim of the present paper is to formulate a simple chemical model describing the basic photochemical transformation of sulfur and nitrogen oxides to the corresponding acid. We combine this chemical model with a very simple model for transport and deposition over time scales of a few days. Observations of nitrate and sulfate in precipitation are used for a qualitative comparison with the results of the model calculations.

¹ Contribution No. 402.

2. Model description

We consider a box of air with a horizontal dimension of several hundred km and extending from the earth's surface up through the mixed layer (of the order of 1 km). The air inside the box is assumed to be well mixed. The initial concentrations of the various chemical compounds in the box are specified and thought of as representing average conditions prevailing in the air within an industrialized area. The initial mixing is assumed to occur rapidly enough for the initial concentrations to be roughly proportional to the emission rates of the various compounds.

As the box is carried by the wind away from the source area, the concentrations inside will change due to chemical transformations, removal processes and mixing with the surrounding air. The mixing is described as a constant rate of exchange of mass with the surrounding air the concentrations in which are specified and kept constant.

The chemical reactions considered are given in Table 1. The philosophy behind this choice of reactions has been first to consider the most important reactions describing the transformation of SO_2 and NO_x to H_2SO_4 and HNO_3 (R17, R18, and R19) and then to include those reactions which by and large determine the concentration of the

oxidizing agents (OH and H_2O_2). The present choice of reactions is by no means unique. For example, a more complete treatment should take into account other hydrocarbons than those two considered here (CH_4 and C_2H_4). C_2H_4 has been taken to represent the whole class of reactive hydrocarbons.

The following compounds are integrated explicitly in time (using an implicit Crank-Nicolson scheme): SO_2 , H_2SO_4 , $\text{NO}_x \equiv \text{NO} + \text{NO}_2$, HNO_3 , CO , H_2O_2 , C_2H_4 , CH_2O and O_3 . The distribution of NO_x between NO and NO_2 is assumed to be instantaneous. HO_2 and OH are also assumed to be in equilibrium with the other compounds. H_2O and CH_4 are kept constant in each run. Most of the reaction rates have been taken from Hampson and Garvin (1978). The photodissociation probabilities represent 24-h averages for conditions at the appropriate seasons of the year and are calculated for ground level conditions adopting a two-stream radiative model (Isaksen et al., 1978).

Reaction R19 represents the liquid phase transformation of SO_2 occurring in cloud droplets and in precipitating drops. The rate of this reaction includes not only the chemical reactions taking place in the liquid phase but also the rates of exchanges of the reacting species between the droplets and the surrounding air and the frequency of occurrence of clouds and precipitation. In view of the influence of all these factors the numerical value of this rate coefficient is very uncertain indeed. Field measurements (Georgii, 1970; Hales and Dana, 1979) and laboratory experiments (Penkett et al., 1979) do, however, indicate that liquid phase oxidation of SO_2 is of importance in the atmosphere. We have here simply chosen a value of k_{19} which makes the liquid phase transformation of SO_2 comparable in magnitude to the gas phase transformation for typical summertime OH concentrations.

Several of the reactions are incomplete in that they do not specify the intermediate stages and all "third molecules" involved. It has been assumed that the initial steps determine the overall rates. The model does not explicitly distinguish between the various phases. Thus, for example, " HNO_3 " represents the sum of the HNO_3 occurring in gas phase, in liquid phase and as particulate matter.

Constant removal rates are specified for each compound. Table 2 gives the values which have been used. The distribution between removal by

Table 1. Chemical reactions considered in the model. Reaction rates are given in units of $\text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ and dissociation rates in s^{-1} . Numbers in parentheses represent powers of ten

R1	$\text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(^1\text{D})$	$j_1 = 4.1(-6)$
R2	$\text{O}(^1\text{D}) + \text{M} \rightarrow \text{O} + \text{M}$	$k_2 = 5(-11)$
R3	$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH}$	$k_3 = 2.3(-10)$
R4	$\text{CO} + \text{OH} \rightarrow \text{HO}_2 + \text{CO}_2$	$k_4 = 3(-13)$
R5	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{HO}_2$	$k_5 = 5(-15)$
R6	$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{HO}_2 + 2\text{CH}_2\text{O}$	$k_6 = 9(-12)$
R7	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CO} + \text{HO}_2$	$k_7 = 1.2(-11)$
R8	$\text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + 2\text{HO}_2$	$j_8 = 1.1(-5)$
R9	$\text{CH}_2\text{O} + h\nu \rightarrow \text{CO} + \text{H}_2$	$j_9 = 2.6(-5)$
R10	$2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_{10} = 2.5(-12)$
R11	$\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_{11} = 5.1(-11)$
R12	$\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$k_{12} = 6.9(-13)$
R13	$\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$	$j_{13} = 3.3(-6)$
R14	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	$j_{14} = 4(-3)$
R15	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$k_{15} = 1.4(-14)$
R16	$\text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2$	$k_{16} = 8(-12)$
R17	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$k_{17} = 8(-12)$
R18	$\text{SO}_2 + \text{OH} \rightarrow \text{H}_2\text{SO}_4$	$k_{18} = 6(-13)$
R19	$\text{SO}_2 + \text{H}_2\text{O}_2 + \text{CLOUD} \rightarrow \text{H}_2\text{SO}_4$	$k_{19} = 6(-16)$

Table 2. Assumed rates of removal by precipitation and by dry deposition. Unit: 10^{-6} s^{-1}

Compound	Removal by precipitation	Dry deposition	Total removal
SO ₂	1	5	6
H ₂ SO ₄	3	1	4
NO _x	0	3	3
HNO ₃	3	5	8
O ₃	0	3	3
H ₂ O ₂	3	5	8
CH ₂ O	1	3	4

precipitation and by dry deposition is somewhat arbitrary since it is only the sum which enters the calculations. We do not suggest that the removal rates are known with any great accuracy. However, since we are aiming mainly at a qualitative description, moderate changes in these numbers will not significantly affect our results.

Fig. 1 shows the result of a run for summertime conditions in northern Europe. The initial value of SO₂ (2.2×10^{11} molecules/cm³ or 8.8 ppbv) corresponds roughly to the average of the surface air SO₂ concentrations observed over north western Europe during the mid seventies (OECD, 1977). The initial value of NO_x (1.5×10^{11} molecules/cm³ or 6 ppbv) was chosen so that the NO_x/SO₂ ratio was equal to the ratio of the emissions of these two compounds within the west European countries participating in the OECD project on long-range transport of air pollutants (OECD, 1977). The initial value of C₂H₄ was chosen as 12.5×10^{10}

molecules/cm³ (5 ppbv) making the initial C₂H₄/NO_x ratio equal to 0.8.

The initial values of H₂SO₄ and HNO₃ were estimated as a background level of 0.5×10^{10} molecules/cm³ plus 10% of the initial concentration of the primary pollutant (SO₂ and NO_x). The 10% figure is taken to include the effect of an oxidation—not specified as to the exact mechanism—occurring during the first several hours after the emission. It is for this reason that the percentage is higher than the corresponding number often used to specify the rate of emission of H₂SO₄ (see e.g. OECD, 1977). If we use significantly lower values of the initial H₂SO₄ concentration, our model tends to produce unrealistically low values of H₂SO₄ relative to HNO₃ during the first 20–30 h travel time. A similar indication of a fairly rapid oxidation of SO₂ occurring during the first hours after the emission is the study by Prahm et al. (1980). From a systematic comparison between observed daily values of SO₂ and SO₄⁻ and applying the dispersion model used in the OECD project (OECD, 1977) these authors suggested an initial oxidation of about 12% followed by a much smaller rate. We wish to point out that different assumptions about the initial levels of H₂SO₄ and HNO₃ will have no effect on the concentrations of the other compounds. Hence, the qualitative picture is not critically dependent upon the choice of these parameters. The emphasis in our discussion will be on the fate of the remaining 90% as it is transported over travel times of a few days.

The formation of HNO₃ proceeds rapidly during the first several hours through reaction R17. The maximum rate of formation, about 0.14 ppbv h⁻¹, occurs after 10–15 h. The maximum rate of removal of NO₂ by the same reaction, 8.4% h⁻¹, occurs after about 25 h when the concentration of OH reaches its peak. The maximum concentration of OH occurs at a NO_x concentration of about 1 ppbv. Higher concentrations of NO_x, occurring during the first 20 h, tend to suppress the OH concentration through reaction R17.

H₂SO₄ is formed more gradually through reactions R18 and R19. It takes about 60 h before the concentration of H₂SO₄ exceeds that of HNO₃. After 100 h the H₂SO₄/HNO₃ ratio is about 2.3. The peak H₂SO₄ concentration occurs about 15 h later than the peak HNO₃ concentration. The rate of transformation of SO₂ through reaction R18

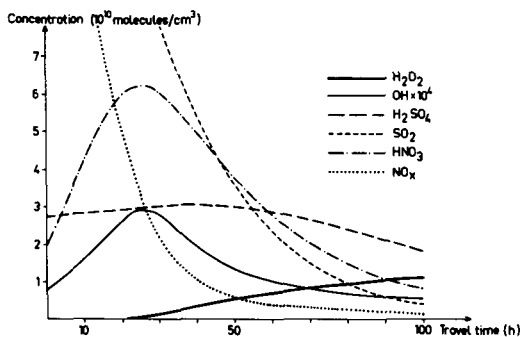


Fig. 1. Concentration of key species as a function of time in the reference run (cf. text).

decreases from about $0.6\% \text{ h}^{-1}$ at 25 h to $0.1\% \text{ h}^{-1}$ at 100 h. The corresponding values for reaction R19 are 0.1 and $2.4\% \text{ h}^{-1}$, respectively.

The concentration of C_2H_4 (not shown in Fig. 1) decreases from its initial value (12.5×10^{10}) to 2.4×10^{10} after 25 h and 0.28×10^{10} after 100 h. CO decreases much more slowly from 6.3×10^{12} initially to 5.3×10^{10} after 100 h. The concentration of O_3 , initially set at 1.0×10^{12} (40 ppbv), reaches a peak of 1.3×10^{12} after about 35 h. Thereafter it decreases slowly reaching 0.86×10^{12} after 100 h.

In the following section we proceed to investigate the consequences for the formation of HNO_3 and H_2SO_4 of differences in, among other things, initial concentrations of NO_x and C_2H_4 . The run shown in Fig. 1 has been used as a reference case.

3. Results of model runs

3.1. Variations of initial concentrations of CO, O₃ and CH₂O

In order to study the sensitivity of the model to changes in the initial concentrations of compounds other than NO_x and C_2H_4 , we have run the model with such changes—up and down in concentrations—applied to one compound at a time.

An increase of the initial concentration of CO by 30% reduces the concentration of OH by a few percent (cf. reaction R4). On the other hand, the concentration of HO_2 and of H_2O_2 increases slightly and the effect on the rate of formation of HNO_3 and H_2SO_4 is not very significant.

If the initial concentration of O_3 is increased by the same proportion (30%), there is only a very small change in the concentration of OH whereas that of H_2O_2 increases by about 15%. This implies a corresponding increase in the rate of formation of H_2SO_4 through reaction R19.

The initial concentration of CH_2O —set at 1 ppbv in the reference run—has a moderate but significant influence on the concentration of OH and H_2O_2 and thereby on the rate of formation of HNO_3 and H_2SO_4 during the first 20 h. More CH_2O leads to more OH and H_2O_2 and a more rapid build up of HNO_3 and H_2SO_4 . After 50 h the effect of varying the initial concentration of CH_2O is small.

It follows from this analysis that our model is not too sensitive to assumptions about the initial

concentrations of CO, O_3 and CH_2O and that therefore the conclusions drawn in the following sections are not unduly affected by these assumptions.

3.2. Variations in rates of emission of NO_x and hydrocarbons

The effect of changes in rate of emission of NO_x on the concentration of OH and H_2O_2 and thereby on the rate of formation of H_2SO_4 has been studied by running the model with different initial conditions of NO_x and C_2H_4 . The main results may be summarized as follows.

- (i) As long as the ratio between the initial concentrations of NO_x and C_2H_4 remains constant, changes within a factor of two of the absolute concentration values have only a moderate influence on the rate of formation of H_2SO_4 . A doubling of the rates of emission of NO_x and C_2H_4 leads to a certain delay in the formation of the peak in the OH concentration. This leads to a delay (from 40 to 50 h) and a lowering (from 3.1 to 2.6×10^{10} molecules per cm^3) of the maximum concentration of H_2SO_4 .
- (ii) If the initial concentration of NO_x is doubled compared to the reference case (Fig. 1), but that of C_2H_4 kept constant, OH levels are very significantly reduced during the first 40 h travel time. As a result, the formation of H_2SO_4 proceeds at a slower rate and no maximum value of the concentration of H_2SO_4 is produced. This, in turn, implies that a large fraction of SO_2 is removed by deposition and the total number of SO_2 molecules transformed to H_2SO_4 is reduced by about 45%. The effect on the rate of formation of H_2SO_4 of changes in the initial concentration of NO_x is illustrated in Fig. 2. It is seen that a fourfold increase in NO_x emission affects not only the concentration of HNO_3 but also very significantly the concentration of H_2SO_4 . The influence on the concentration of SO_2 is less pronounced mainly because this is determined to a large degree by the dry and wet removal processes.
- (iii) The main effect of increasing the initial concentration of C_2H_4 is the formation of a pronounced peak in the OH concentration during the first few hours' travel time. This

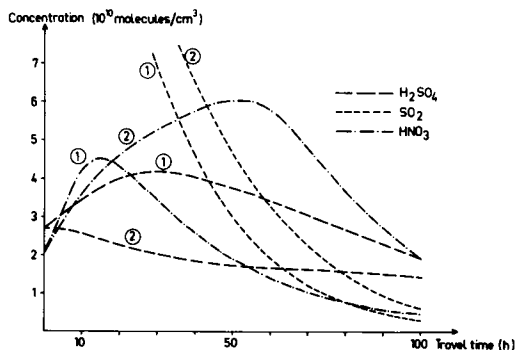


Fig. 2. Concentration of SO_2 , H_2SO_4 and HNO_3 as a function of time for two different values of the concentration of NO_x : 7.7×10^{10} (1) and 31×10^{10} (2). The initial concentration of C_2H_4 is equal to that in the reference run (12.5×10^{10}).

leads to a rapid build up of acid—particularly HNO_3 —through reaction R17. This effect is demonstrated in Fig. 3 which shows the concentrations of H_2SO_4 and HNO_3 for initial ratios of $\text{C}_2\text{H}_4/\text{NO}_x = 0.4$ and 1.6. The peak OH concentrations in these two cases are 2.5×10^6 and 4.1×10^6 , respectively, and they occur after 40 and about 15 h, respectively. One might ask whether the low rate of formation of acid during the first several hours in the case with the low C_2H_4 concentration would be compensated by a higher rate of formation further out so that, in fact, a lowering of the $\text{C}_2\text{H}_4/\text{NO}_x$ ratio would simply push the acid further away from the source region. Fig. 3 shows that for HNO_3 there is

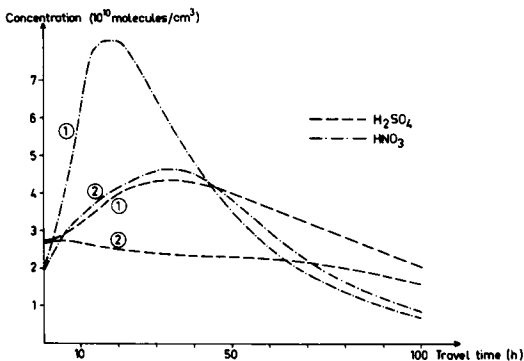


Fig. 3. Concentration of H_2SO_4 and HNO_3 as a function of time for two different values of the initial concentration of C_2H_4 : 25×10^{10} (1) and 6.2×10^{10} (2). The initial concentration of NO_x is equal to that in the reference run (15.5×10^{10}).

actually a tendency for such a compensating effect: the two curves for HNO_3 cross over after about 50 h. However, for SO_2 no such effect is evident. The reason for this is simply that a major part of the SO_2 is removed by dry and wet deposition so that little SO_2 is left to form H_2SO_4 further away.

3.3. Simulation of long-term trends

In order to simulate the conditions relevant to the formation of acid precipitation in northern Europe over the latest several years, we have run the model with different initial concentrations of NO_x and SO_2 , estimated from emission data. Emission trends of SO_2 for northwestern Europe have been published by Semb (1978) and of NO_x for the same region by OECD (1977). Assuming a direct proportionality between these emissions and the initial concentrations applicable to our model, it is a straightforward matter to estimate concentrations representative for earlier years. As indicated above the initial concentration for H_2SO_4 and HNO_3 were assumed to consist of a background component—constant in time—and a man-made component proportional to the initial concentrations of SO_2 and NO_x respectively. The initial concentration of C_2H_4 has been assumed to be equal to 0.8 times that of NO_x . The initial conditions for the other compounds were kept constant in all runs.

In Table 3 we have tabulated the concentrations of NO_x , HNO_3 , SO_2 and H_2SO_4 for three different travel times: 10, 30 and 90 h. The initial concentrations (proportional to the emission rates) are also given in the same table.

It is interesting to note that because of the chemical interactions between the various species in the model, the trends in the concentrations in many cases are significantly different from the trends in emission rates. For example, for short travel times (10 h) the increase in the NO_x concentration over the years is much larger than the increase in the NO_x emission rate, whereas the concentration of HNO_3 and H_2SO_4 show a much smaller increase than what would have been expected from the figures on emissions of the primary pollutants. In spite of a nearly 70% increase in the rate of emission—and initial concentration—of SO_2 the concentration of H_2SO_4 increases by only 20–30% after travel times between 10 and 30 h.

Table 3. Model estimates of the long-term changes in the summer time concentrations in the air of NO_x , HNO_3 , SO_2 and H_2SO_4 at different travel times. Unit: 10^{10} molecules/ cm^3

Compound	Travel time (h)	1955	1975	Increase	(%)
NO_x	0	6.3	15.5	9.2	(146)
HNO_3	0	1.1	2.0	0.9	(82)
SO_2	0	13.0	21.8	8.8	(68)
H_2SO_4	0	1.8	2.7	0.9	(50)
NO_x	10	3.06	9.96	6.90	(225)
HNO_3	10	2.82	4.19	1.37	(49)
SO_2	10	9.12	15.8	6.7	(73)
H_2SO_4	10	2.17	2.80	0.63	(29)
NO_x	30	0.75	2.18	1.43	(191)
HNO_3	30	2.56	6.05	3.49	(136)
SO_2	30	4.23	7.88	3.65	(86)
H_2SO_4	30	2.48	3.01	0.53	(21)
NO_x	90	0.12	0.16	0.04	(33)
HNO_3	90	0.48	1.08	0.60	(125)
SO_2	90	0.30	0.59	0.29	(97)
H_2SO_4	90	1.50	2.09	0.59	(39)

This modest increase in the concentration of H_2SO_4 is due mainly to the assumed increase in the rate of emission of H_2SO_4 . In fact, if the rate of emission of H_2SO_4 had been kept constant over the years the concentration of H_2SO_4 after 10 and 20 h would have decreased slightly despite the large increase in the rate of emission of SO_2 . The main reasons for this behavior of the model is that the increase in the rate of emission of NO_x very significantly reduces the concentration of the OH radicals for short travel times through reaction R17. This, in turn, decreases and delays the formation of H_2SO_4 through reaction R18.

For longer travel times (90 h) the most notable result seems to be that HNO_3 shows a relatively large increase whereas the concentration of NO_x increases much less than the increase in its rate of emission.

It should be pointed out that more pronounced effects along similar lines would have been obtained if the initial $\text{NO}_x/\text{C}_2\text{H}_4$ ratio also had been allowed to vary over the years. However, in view of the sparsity of relevant data we have not seen it fit to complicate further the trend simulation in the model by introducing assumptions about such changes.

4. Comparison with observations

A comparison of the results with observational data is made difficult by the lack of systematic measurements outside urban areas of NO_x and HNO_3 , in particular. It is only for NO_3^- in precipitation that there exist data with a fair areal coverage over northern Europe and extending back several years. These measurements are made on a monthly basis and form part of the European Air Chemistry Network (EACN; cf. Granat, 1978). The measurement stations are generally located outside urban areas and at least several km away from other large sources. Consequently, the data from this network are believed to be representative for the regional chemical climate of the area. The EACN network also provides data on SO_4^{2-} in precipitation.

Fig. 4 shows the location of those stations in the EACN network which we have used for the comparison. In order to avoid some of the variabilities inherent in this kind of data, we have grouped the stations together, as indicated in the figure. The groups of stations were chosen to represent different distances from the major source regions. Stations in group 1 are all inside or close to the major emission area in central U.K. and along a band from the Benelux countries across the Ruhr area in West Germany and further eastwards (Semb, 1978). Group 2 corresponds essentially to Denmark with moderate emissions but close to (and on the leeward side of) the major source area. Groups 3, 4 and 5 mainly in Sweden represent an increasing distance from the source area in the direction of the prevailing wind.

Table 4 shows a summary of observed values of nitrate and sulfate (sea salt sulfate has been deducted) in precipitation for the various groups of stations. Each value represents the median of the individual values for each station in the group which in turn is a median value of all monthly values—for the particular season—within the indicated 5-year period. A positive trend over the years is evident for both sulfate and nitrate for all groups of stations. Generally, the nitrate values have increased at a faster rate than the sulfate values. For station groups 1 and 2 the absolute values of nitrate have become comparable to those of sulfate. Further out sulfate is seen to dominate over nitrate.

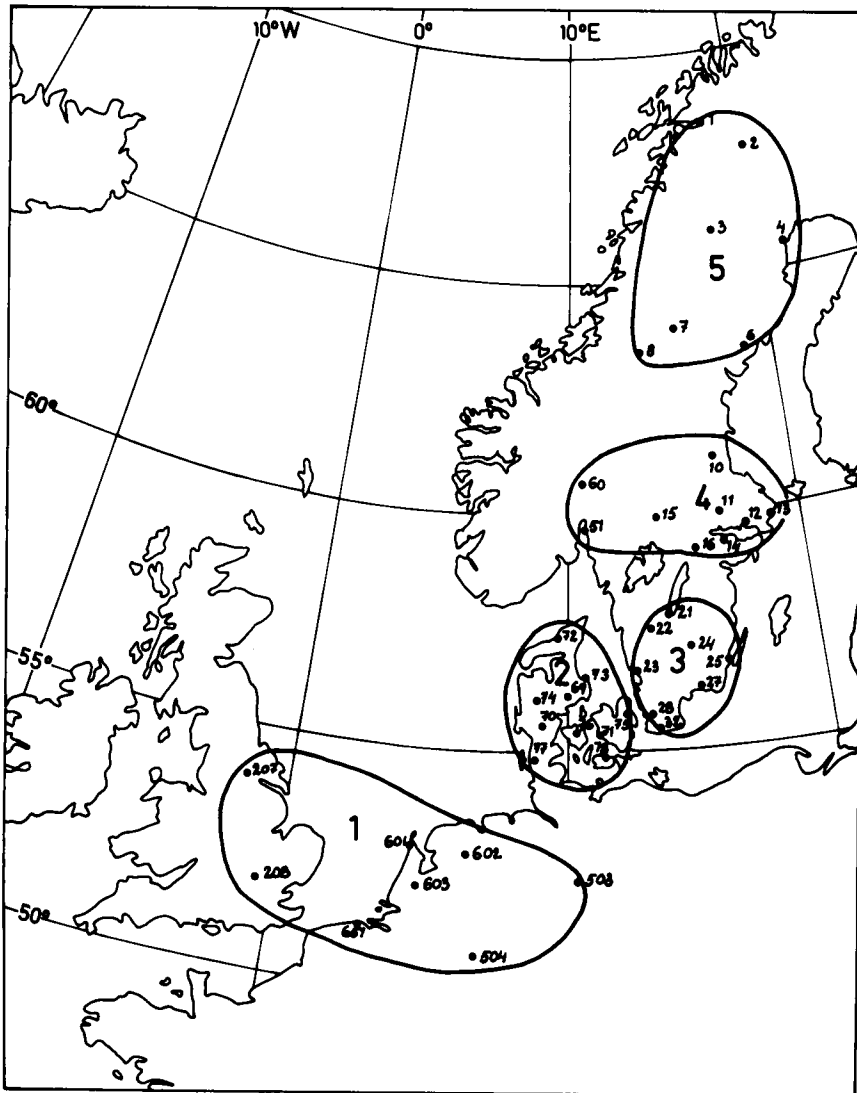


Fig. 4. Precipitation chemistry stations used in the data analysis shown in Table 4.

By and large the absolute values of the sulfate and nitrate concentrations decrease with increasing distance from the continent. The rate of decrease of the concentration values from the source area (group 1) and up to Northern Scandinavia (group 5) is much more rapid for nitrate than for sulfate. Thus the ratio between group 1 and group 5 is 8.5 for nitrate and only 2.2 for sulfate in the 1970–74 period.

The relative increase over the years of sulfate seems to be smaller near the source areas (groups 1

and 2) than further away (groups 3, 4 and 5). This agrees well with the model estimates of H_2SO_4 in the air.

The relative increase in the concentration of nitrate in precipitation exhibits a less systematic variation between the various groups of stations.

In view of the uncertainties involved in the model as well as in the observations it is probably wise to refrain from a more detailed quantitative comparison between the model estimates and the observations.

Table 4. Observed monthly concentration values (medians) of SO_4^- and NO_3^- ($\mu\text{mole/l}$). Summer season

Group of stations	1955-59	1970-74	Increase	(%)
SO_4^-				
1	62.5	90.6	28.1	(45)
2	50.0	56.3	6.3	(13)
3	28.1	50.0	21.9	(78)
4	25.0	40.6	15.6	(63)
5	15.6	40.6	25.0	(160)
NO_3^-				
1	35.0	60.7	25.7	(73)
2	22.9	51.4	28.5	(125)
3	13.6	25.0	11.4	(84)
4	7.1	21.4	14.3	(200)
5	4.3	7.1	2.8	(67)

5. Concluding remarks

We have formulated a rather crude photochemical model to simulate the formation of sulfuric and nitric acid during long-range transport through the atmosphere. Initial and boundary conditions were chosen as roughly representative of the situation in northwestern Europe. Comparisons with observations of sulfate and nitrate in precipitation in that area have lead us to the following tentative conclusions.

1. Because of the relatively rapid reaction of NO_2 with OH, the formation of HNO_3 in our model takes place significantly faster than the formation of H_2SO_4 . Provided that the scavenging by precipitation of these two compounds are not grossly different, one would expect the nitrate in precipitation to be of a more local origin than the sulfate. This is borne out by observations. From Table 4 it is seen that the average value for the ratio SO_4^-/NO_3^- (on a molecular basis) during summer season in the period 1970-74 is about 1 for station groups 1 and 2, about 2 for groups 3 and 4 and more than 5 for group 5. Thus, sulfate is transported over greater distances than nitrate. Qualitatively, this conclusion agrees with the finding of Pack (1978) who studied the characteristic length-scale for the spatial correlation of monthly values of the concentrations of nitrate and sulfate in pre-

cipitation in the U.S.A. He found a significantly shorter value for nitrate than for sulfate. One consequence of this finding is that sulfate of man-made origin is much more likely to contribute to the arctic aerosol than nitrate.

2. The model suggests that, other things being equal, an increase in the emission rate of hydrocarbons will enhance the rate of production of sulfuric and nitric acid. This effect is particularly pronounced during the first few tens of hours. This seems to indicate that as far as detrimental effects caused by the concentration of acid in air and in precipitation are concerned a reduction of the regional hydrocarbon emissions is desirable. If one considers the total deposition of acid compounds including the dry deposition of NO_x and SO_2 , the effect of changes in hydrocarbon emissions is probably less significant. However, one might expect that a lowering of the HC emission would imply a somewhat longer average residence time for ($NO_x + HNO_3$) and for ($SO_2 + H_2SO_4$).
3. Changes in the emission of NO_x may similarly affect the formation of not only nitric acid but also of sulfuric acid through its effect on the concentration of oxidants. If NO_x emissions are increased (and C_2H_4 emissions kept constant) more OH is used up initially in the formation of HNO_3 so that the rate of formation of H_2SO_4 is decreased. The main consequence is that less H_2SO_4 is formed in the atmosphere and that relatively more SO_2 is removed by deposition: a doubling of the NO_x emission rate compared to the reference case decreases the total amount of H_2SO_4 formed by about 45%. At the same time, there is a tendency for the peak H_2SO_4 concentration to occur later than in the reference case.

In the real atmosphere an increase in the NO_x emission rate will also have a reducing effect on the rate of formation of H_2SO_4 through a lowering of the pH of cloud water leading to a decrease in the uptake of SO_2 .

4. When dealing with a coupled chemical system like the one we have studied one may not assume a proportional dependence of concentrations on emission rates. This is exemplified in our model simulations of the long-term trends in concentration of nitric and sulfuric acid which show that close to the emission areas the increase of the concentration of acid in the air is

significantly less than the increase in the emission rates of NO_x and SO_2 , respectively.

This effect may be a contributing factor to the observation (Granat, 1978) that the deposition of sulfate by precipitation over northern Europe during the last 20 years has not increased at the same rate as the emission of SO_2 (cf. Rodhe, 1980).

We suggest that attempts should be made to include the concentration of oxidizing species like OH , H_2O_2 and O_3 explicitly in models that simulate the long-range transport of sulfur and nitrogen compounds. Most present models simply assume constant transformation rates with no feedback mechanisms. As is evident from the above discussion, such simplified models are, for example, unable to properly model long-term trends in concentration values. It would also be interesting to investigate whether a more detailed description of the chemical reactions would improve the correlation between simulated and observed short-term concentration values of sulfur compounds (cf. OECD, 1977).

Much as we believe that photochemical reactions are important for the formation of HNO_3 and H_2SO_4 —as is implied in the present study—we

want to emphasize a significant limitation of the model. If the model is applied to winter conditions in northern Europe, where the intensity of solar radiation is much lower than it is in summer, the formation of HNO_3 and H_2SO_4 is not large enough to account for the observed concentration of nitrate and sulfate in precipitation during that season. A lower rate of formation of H_2SO_4 in winter is indicated by the observations since the concentration of sulfate in precipitation is about the same in winter as in summer (Granat, 1978) whereas the rate of emission of SO_2 is about 50% higher in winter (OECD, 1977). However, if photochemical processes were the only oxidation mechanism, an even larger difference between summer and winter would have been expected.

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ОБРАЗОВАНИЕ СЕРНОЙ И АЗОТНОЙ КИСЛОТ В АТМОСФЕРЕ ВО ВРЕМЯ ПЕРЕНОСА НА ДАЛЕКИЕ РАССТОЯНИЯ

Для моделирования образования серной и азотной кислот во время переноса в атмосфере на далекие расстояния используется простая фотохимическая модель. Ее результаты сравниваются с данными наблюдений сульфатов и нитратов в осадках на различных расстояниях от областей выпуска примесей в северной Европе.

Как наблюдения, так и расчеты показывают, что HNO_3 образуется с большей скоростью, чем H_2SO_4 , и что перенос HNO_3 на дальние расстояния несколько менее выражен, чем перенос H_2SO_4 . В основном благодаря общей зависимости окисления SO_2 и NO_x от концентрации радикала OH , концентрация NO_x значительно влияет на

скорость образования H_2SO_4 : большие эмиссии NO_x имеют тенденцию уменьшать уровни OH и H_2O_2 вблизи области источника, тем самым замедляя и уменьшая трансформацию SO_2 в H_2SO_4 .

Благодаря взаимодействию химических веществ зависимость концентраций от скоростей эмиссий нелинейная. Наша модель показывает, что концентрации H_2SO_4 на расстояниях, проходимых за несколько десятков часов, увеличиваются значительно меньше за последние 20 лет, чем скорости эмиссий SO_2 . Это также кажется подтверждающимся наблюдениями сульфатов в осадках.