

Modelling intercontinental transport of atmospheric sulphur in the northern hemisphere

By L. TARRASÓN^{*1} and T. IVERSEN², ¹*Norwegian Meteorological Institute, PO Box 43 Blindern, N-0313 Oslo, Norway;* ²*Department of Geophysics, University of Oslo, PO Box 1022 Blindern, N-0315 Oslo, Norway*

(Manuscript received 20 September 1995; in final form 18 June 1998)

ABSTRACT

Intercontinental exchange of sulphur in major parts of the northern hemisphere has been studied with a 3-dimensional Eulerian transport model that resolves regional scale variability. Model results for 1988 have been evaluated against daily observations of sulphur dioxide and particulate sulphate in Europe and North America and show that the model reproduces the episodic character of oxidised sulphur in air. Yearly averages agree with the observations within a factor of 2, at over 75% of the sites. Monthly budgets for intercontinental exchange of sulphur are presented and related to large scale atmospheric flow patterns. Intercontinental transport of sulphur is related to mid-latitude cyclone tracks, and few events determine a considerable part of the yearly intercontinental exchange. European anthropogenic sulphur dominates the averaged air concentrations and depositions over the simulation area. The contribution of European sulphur over the Sea of Japan is calculated to be $50\text{--}75 \text{ mg(S) m}^{-2} \text{ yr}^{-1}$ or 5–10% of the total deposition calculated for that area. Over the West Siberian Planes, the European contribution is estimated to be $150\text{--}200 \text{ mg(S) m}^{-2} \text{ yr}^{-1}$ that is, 40–50% of the yearly calculated deposition. The relative contributions of intercontinental transport from anthropogenic sources in Asia and North America and biogenic sources in the North Atlantic Ocean to the European deposition levels are similar and range from 2 to 4%. In certain areas and seasons, however, these relative contributions can be much larger.

1. Introduction

Tropospheric sulphur is important for the chemistry of precipitation and atmospheric aerosols. It contributes significantly to regional acidification problems and sulphate aerosols influence clear air and cloud reflectivity thus affecting the global radiation balance and climate. Estimates on the climatic forcing of airborne sulphate indicate a net global cooling comparable in magnitude to the global warming caused by the anthropogenic greenhouse gases (Charlson et al., 1991; 1992; Wigley and Raper, 1992; Kiehl and Briegleb, 1993). Since sulphur is involved both in regional

and global scale problems, reliable estimates of the sulphur distribution covering both scales are needed.

The spatial and temporal scales of oxidised sulphur depend on the atmospheric residence time of sulphur dioxide and particulate sulphate. Average residence times have been estimated to be of the order of 1–2 days for sulphur dioxide and 3–4 days for particulate sulphate (OECD, 1979; Rodhe and Grandell, 1981; Seinfeld, 1986; Langner and Rodhe, 1991). In extreme cases, sulphate air concentrations have been reported to vary up to a factor of 5–10 over 24 hours (Pedersen et al., 1990; Hussain and Dutkiewicz, 1990). Similar variations occur over distances of about 1000 km. As opposed to long-lived species, such

* Corresponding author.

as carbon dioxide or methane, it is necessary to resolve atmospheric transport of sulphur with finer time and space resolutions than 12 hours and 300 km in order to properly reproduce its observed variability in the atmosphere.

Regional transport models have been widely used to simulate atmospheric transport of sulphur by coupling meteorological and chemical processes (Eliassen, 1978; Pudykiewicz et al., 1985; Carmichael et al., 1986; Chang et al., 1987; Berge, 1990; Iversen, 1993). Such models use spatial mesh width ranging from 50 to 150 km, and meteorological data input every 6-hours or less. They have shown considerable success in reproducing observed acid deposition patterns and trends inside the calculation domain. Three-dimensional models have also been used to calculate the global atmospheric distribution of sulphur (Langner and Rodhe, 1991; Erickson et al., 1991; Balkanski et al., 1993). These models have used coarse spatial resolutions, with mesh width ranging from 330 to 1100 km, and their meteorological fields either have been defined from climatological averages or have been calculated by coarse-resolution general circulation models. The use of this type of meteorological data may lead to inadequate descriptions of the transient eddies and their influence on the atmospheric transport of sulphur (Eliassen, 1978; Eliassen and Saltbones, 1983; Tarrasón and Iversen, 1992). With such choice of meteorological input data, results from dispersion models can only be compared with long term averages of observations (Galloway et al., 1993) and not with time-specific observations. This seriously hampers a full validation of these global models.

Global or hemispheric dispersion models that can resolve synoptic scale eddies and thus the regional variations of sulphur, have been reported in recent years. These models either use time-resolved meteorological analyses (Iversen, 1989; Tarrasón and Iversen, 1992; Benkovitz et al., 1994) or they are coupled with a weather prediction model in prognostic mode (Dastoor and Pudykiewicz, 1996; Pudykiewicz and Dastoor, 1995). In this study, we present a full year (1988) simulation of the tropospheric distribution of sulphur over major parts of the northern hemisphere, in an effort to quantify the relative importance of intercontinental contributions to sulphur depositions. Model calculations are compared with daily observations of sulphur dioxide and particulate

sulphate. A significant fraction of the anthropogenic sulphur emission is transported out of continental boundaries, thus affecting the background levels over major parts of the northern hemisphere. In particular, we are concerned with allocating the origins of European background levels to the separate contributions of anthropogenic sulphur from Asia and North America, and oceanic sulphur from the North Atlantic Ocean. Finally, budgets for intercontinental exchange of sulphur in 1988 are presented, and they are related to meteorological flow patterns in order to explain the occurrence of intercontinental transport despite the relatively short atmospheric residence time of sulphur.

2. Description of the model

The model employed is a revised version of the Eulerian time-resolved model developed by Iversen (1989) and further elaborated in Tarrasón and Iversen (1992). The sulphur cycle is explicitly described in terms of sulphur dioxide (SO_2) and particulate sulphate (SO_4^{2-}), both considered as passive species. The present version uses twice as fine spatial and temporal resolution as before and an improved treatment of wet and dry deposition. The model still uses potential temperature as vertical coordinate and resolves the troposphere of the northern hemisphere in 11 levels (10 isentropic levels and the surface boundary level). The horizontal resolution is $\sim 150 \times 150 \text{ km}^2$. The integration timestep is 1800 s and meteorological fields are introduced every 6th hour.

The horizontal simulation domain extends from 90°N to south of 20°N in the longitude sector between 60°E and 120°W , but it is limited to 35°N between 180°E and 100°E . The integration domain includes major parts of the North Atlantic Ocean and is thus well suited for calculating different contributions to the background sulphur levels over Europe. However, conclusions on transport of eastern Asian sulphur will be weak due to the chosen lateral boundaries.

Isentropic coordinate surfaces are nearly physically adaptive for synoptic scale flows. Their use diminishes numerical inaccuracies associated with vertical and horizontal advection. Since the height of isentropic surfaces varies considerably with latitude and season, the set of isentropic coordin-

ate surfaces is re-selected each month. The lowermost boundary condition is applied at the top of the surface boundary layer which is given by its potential temperature, $\theta_s(x, y, t)$. The 10 isentropic surfaces are defined so that at any place and time during one simulated month, there exist at least two coordinate surfaces above $\theta_s(x, y, t)$. The selection of the reference set of isentropic surfaces has been modified with respect to former versions of the model in order to secure an average number of 6–7 layers over mid-latitudes. The quasi-material motion of isentropic surfaces represents their strength as coordinate surfaces but also gives rise to numerical problems. In the present version, values in fictitious points below $\theta_s(x, y, t)$ are set equal to the values in lowermost isentropic level above. The mass consistency of the model is sensitive to these conditions. In addition, interpolation errors in the meteorological input fields also contribute to mass inconsistencies (Trenberth, 1991). In the present version, the model is globally mass conservative within 10% for a full year simulation. Local mass consistency is obtained by securing individual conservation of mixing ratios.

2.1. Meteorological data

Input meteorological data are 6-hourly analyses from the European Centre for Medium Range Weather Forecast (ECMWF). Analyses of the 3-dimensional wind fields, relative humidity and geopotential height are given in a $2^\circ \times 2^\circ$ latitude/longitude grid at 00 UT, 06 UT, 12 UT and 18 UT, at eight standard pressure levels: 100 hPa, 200 hPa, 250 hPa, 300 hPa, 500 hPa, 700 hPa, 850 hPa and 1000 hPa. In addition, analyses of surface temperature and surface albedo are used.

A separate meteorological module provides the necessary meteorological input for dispersion calculations in isentropic coordinates. This is a diagnostic model that derives diabatic heating, turbulent exchange coefficients and precipitation fields on the basis of ECMWF analyses. Diabatic heating is the vertical motion in isentropic coordinates and consist of three processes: radiation, latent heat release, and turbulent conduction of sensible heat, all parameterised as in Iversen (1989). Surface layer turbulent drag coefficients and the height of the mixing layer are determined from the Louis (1979) functions and the static

stability. Precipitation fields are derived by separating between convective and stratiform precipitation. The meteorological module provides also the vertical distribution of precipitating cloud layers. The resulting precipitation fields have been verified against observations over Europe. The timing and geographical distribution of precipitation events correlate well with observations, as illustrated in Fig. 1. Still, the model tends to underestimate precipitation amounts but the underestimation is not larger than a factor of 2. The importance of this underestimation for the calculation of atmospheric dispersion of sulphur has been studied with sensitivity tests and is reported in Subsection 3.1.

2.2. Emissions

Sulphur emissions considered in the calculations are anthropogenic emissions of sulphur dioxide and sulphate from Europe, North America and northern Asia, as well as biogenic emissions of reduced sulphur from the North Atlantic Ocean. Emission totals are given in Table 1.

European values are the 1988 official emissions compiled for the Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, hereafter called EMEP (Sandnes and Styve, 1992). Over North America, the 1985 National Acid Precipitation Assessment Program (NAPAP) inventory is used (Saeger et al., 1989). Since Alaska is not included in the NAPAP inventory, estimates from Semb (1985) are adopted. Asian anthropogenic emissions are based on Kato and Akimoto's (1992) inventory and point sources in the Asian part of Russia are added (Pacyna, 1992 pers. comm.). Sulphur emissions provided by the

Table 1. *Sulphur emission totals for 1988; units: $10^9 \text{ g (S) yr}^{-1}$*

European sources (EMEP area)	21 500	42%
North American sources	12 500	24%
North Asian sources*	16 000	31%
North Atlantic Ocean (biogenic sources)	1 600	3%
Total sources	51 600	100%

*Refers to the part of northern Asia inside the simulation domain.

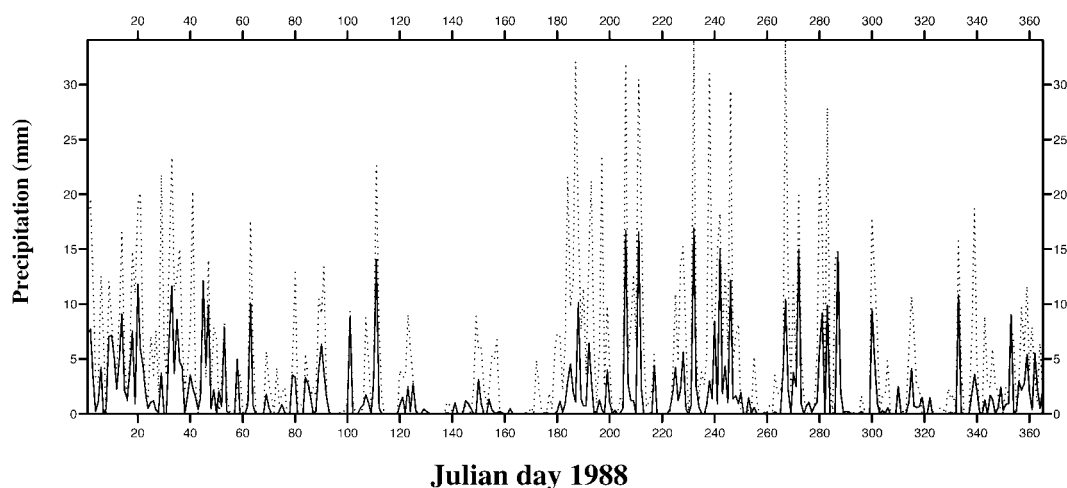


Fig. 1. Time series of modelled (solid line) and observed (dotted line) precipitation amounts over Birkenes (Norway) in 1988. Units: mm.

NAPAP inventory explicitly distinguish between sulphur dioxide and sulphate. For all other anthropogenic emissions of sulphur dioxide, it is prescribed that a fraction of the emissions ($\beta=0.05$) is directly released as particulate sulphate (OECD, 1979; Eliassen and Saltbones, 1983).

European emissions are assumed to follow a sinusoidal variation with maximum values in January and minimum in July (Semb, 1978; Sandnes and Styve, 1992). The main reason is a seasonally varying demand for domestic heating. For southern Europe, however, the actual seasonal variation is probably much smaller than considered in the model (cf. results from the GENEMIS project at the University of Stuttgart, Germany, see e.g. Barrett and Berge, 1996). The seasonal variation of North American anthropogenic sources is much less pronounced, with only a slight decrease in the emissions during summer (Saeger et al., 1989). As no information was available on the seasonal variation of Asian sources, they have been assumed constant over the year.

Natural sources of sulphur are only partially considered in this study. So far, only biogenic production of dimethyl sulphide (DMS) from the North Atlantic Ocean is included. DMS is considered to be the main source of gaseous sulphur from the ocean (Andreae, 1986; Turner and Liss, 1985). The spatial distribution of DMS fluxes over the North Atlantic Ocean and their monthly variation are taken from Tarrasón et al. (1995).

Terrestrial emissions from plants and soils, and emissions from biomass burning are not believed to contribute with more than 2% to the total sulphur emissions in the northern hemisphere (Andreae, 1990; Bates et al., 1992) and have been neglected in the simulations. The sulphur content in wind blown dust seems to be more important in the trade wind region, with limited influence over Europe (Li et al., 1996; Tegen et al., 1996). Marine and volcanic sources represent each about 8% of the total sulphur emissions in the northern hemisphere. The bulk of volcanic emissions in the northern hemisphere is situated over eastern Asia, the Aleutian Islands and Alaska, and so we can expect the influence of volcanic sources over Europe to be considerably smaller than that of marine emissions.

2.3. Dry deposition

The flux of gases and particles from the atmosphere to different types of surfaces is modelled following a resistance analogy (Wesely and Hicks, 1977; Fowler, 1985). The process is divided in three different stages controlled by the aerodynamic resistance of the atmospheric surface layer, the sub-laminar resistance which is determined by molecular diffusion, and the surface resistance, determined by the physio-chemical affinity of the underlying surface. If V_{dc} is defined as the inverse of the sum of the surface and the

sub-laminar resistance, the effective dry deposition velocity at the top of the surface layer, V_d can be written as:

$$V_d = \frac{V_{dc}}{V_{dc} \frac{1}{C_H |v_s|} + 1}, \quad (1)$$

where C_H is the surface layer drag coefficient, and $|v_s|$ is the wind speed at top of the surface layer. Table 2 summarises the choice of surface dry deposition velocities. For sulphur dioxide, V_{dc} , is primarily controlled by the value of the surface resistance (Wesely, 1989; Erisman and Baldocchi, 1994). The model distinguishes between: land areas with vegetation, open sea, ice-and-snow-covered flat areas, and bare soils. Over open sea, ice-and-snow-covered flat areas, and bare soils V_{dc} is assumed to be constant. The largest surface deposition velocity is presumed over open sea (Whelpdale and Shaw, 1974). Over land areas covered by vegetation, V_{dc} is determined according to Wesely (1989) and Erisman (1994). Diurnal, seasonal and latitudinal variations of V_{dc} are prescribed to account both for the effect of changes in the biochemical uptake by vegetation and for differences in solar radiation and temperature. The parametrisation follows Eliassen and Saltbones (1983). For particulate sulphate, surface resistances are assumed to be negligible (Voldner et al., 1986) with the consequence that the V_{dc} for SO_4^{2-} is mainly determined by the sub-laminar resistance, as indicated in Table 2.

Dry deposition velocities, V_d , are computed every timestep by using area-weighted averages of

the deposition velocities. The resulting dry deposition velocities compare well over Europe with monthly averaged deposition velocities calculated with a more sophisticated surface resistance parametrisation model as reported in Seland et al. (1995).

2.4. Sulphur air chemistry

The atmospheric transformation of sulphur dioxide to particulate sulphate involves a gas phase oxidation by the hydroxyl radical (OH), and an heterogeneous phase oxidation in clouds by hydrogen peroxide (H_2O_2), ozone (O_3) and oxygen (O_2), catalysed by iron and manganese ions. It is generally believed that the heterogeneous oxidation of sulphur is responsible for a large fraction of the production of sulphate in the atmosphere (Lelieveld, 1990; Feichter et al. 1996; Pham et al., 1995). In the model, oxidation processes are separated in two categories. The first one, which we call sulphur air chemistry, involves gas phase oxidation and heterogeneous oxidation in non-precipitating clouds. The second process, which we call chemical scavenging, parameterises the heterogeneous oxidation of SO_2 and subsequent deposition by precipitating clouds. Both parametrisations follow a linear transformation rate according to Eliassen and Saltbones (1983).

The air transformation rate, K_{ch} , is prescribed to vary with latitude and season in crude accordance with observations and model calculations of the atmospheric distributions of oxidants. It has a maximum and constant value of $4 \cdot 10^{-6} \text{ s}^{-1}$ at

Table 2. Adopted surface deposition velocities V_{dc} for sulphur dioxide and particulate sulphate. R_c is the surface resistance and R_b is the sub-laminar resistance (see text for comments)

Surface types (SO_2)	R_c (s m^{-1})	V_{dc} (cm s^{-1})	Ref.
bare soils	1000	0.1	Garland (1977)
sea	50	2.0	Whelpdale and Shaw (1974); Voldner et al. (1986)
ice covered flat areas	1000	0.1	Dovland and Eliassen (1976); Davidson and Wu (1990)
land areas			
constant at equator	83	1.2	seasonal, latitudinal and diurnal variations parameterized as described in text
max at north pole	167	0.6	
min at north pole	250	0.4	
SO_4^{2-}	R_b (s m^{-1})	V_{dc} (cm s^{-1})	Ref.
all surfaces	1000	0.1	Voldner et al. (1986)

the equator, while it varies seasonally at the north pole between $0.2 \cdot 10^{-6} \text{ s}^{-1}$ at winter solstice and $2.4 \cdot 10^{-6} \text{ s}^{-1}$ at summer solstice. Between the north pole and the equator, K_{Ch} varies linearly with the distance to the north pole.

The chosen values for K_{Ch} implicitly infer some assumptions about oxidant levels, cloudiness, cloud water content and acidity, average residence time of air-parcels inside clouds, and time scales for replenishment of oxidants and sulphur dioxide in cloud droplets. Following Rodhe and Grandell (1981) we can express the air oxidation rate as:

$$K_{\text{Ch}} = \frac{\tau_d k_d + \tau_w k_w + \tau_d k_d (\tau_w k_w)}{\tau_d + \tau_w + \tau_d \tau_w ((1-f)k_w + f k_d)}, \quad (2)$$

where k_d and k_w are the clear air and in-cloud oxidation rates respectively, τ_d and τ_w are the average air-parcel residence time in clear and cloud air respectively, and $f = \tau_w / (\tau_d + \tau_w)$ is the unconditional probability for an air-parcel to be situated inside a cloud. Since wet scavenging of sulphur dioxide is taken care of separately, the values for τ_d and f in (3) only reflect the distribution of non-precipitating clouds. The dry oxidation rate is

$$k_d = k_{\text{OH}}[\text{OH}]. \quad (3)$$

Here $[\text{OH}]$ is the concentration of OH-molecules in air and k_{OH} is the gas phase reaction rate. The in-cloud oxidation rate is defined as:

$$k_w = V_w H^* \{k_{\text{Mn}}[\text{Mn(II)}] + k_{\text{Fe}}[\text{Fe(III)}] + k_{\text{O}_2}[\text{O}_2(\text{aq})] + k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2(\text{aq})]\} \quad (4)$$

Here is V_w the volume mixing ratio of cloud water in cloud air, H^* is the dimensionless Henry law constant for SO_2 in air and the totally dissolved S(IV) in cloud droplets. $[\text{Mn(II)}]$, $[\text{Fe(III)}]$, $[\text{O}_2(\text{aq})]$ and $[\text{H}_2\text{O}_2(\text{aq})]$ are concentrations of the manganese ion, ferri ion, ozone and hydrogen peroxide dissolved in cloud water. The coefficients k_{Mn} , k_{Fe} , k_{O_2} and $k_{\text{H}_2\text{O}_2}$ are reaction rates for the production of sulphate in cloud droplets which transforms into airborne particulate sulphate as the droplets evaporate. The different reaction rates involve different species of S(IV) in water and depend heavily on the pH of the droplets. Reaction rates and their dependence with temperature can be found in Seinfeld (1986) and Warneck (1988). Estimates of oxidant concentrations are taken from global photochemical model-calculations by Bernsten and Isaksen (1997) and Jaffe et al. (1997).

In the rural and background atmosphere influenced by anthropogenic pollutants on regional to global scales, OH varies from virtually zero in darkness up to $10^7 \text{ molecules cm}^{-3}$ under very favourable conditions (Poppe et al., 1995). O_3 varies typically between 20 and 60 ppb (Pedersen, 1992; Simpson, 1993; Bernsten and Isaksen, 1997). Model-calculations of H_2O_2 yields values typically between 1 ppt and 1 ppb. Typical background atmospheric values of manganese and iron in anthropogenic aerosols causes aqueous concentrations of $1-5 \cdot 10^{-8} \text{ mol/l}$ for Mn(II) and $1-5 \cdot 10^{-7} \text{ mol/l}$ for Fe(III) (Warneck, 1988).

By using typical values for the coefficients and concentrations one arrives at in-cloud oxidation rates on the order of 10^{-4} – 10^{-2} s^{-1} for most cases. This fast oxidation is mainly caused by the H_2O_2 reaction which means that SO_2 and H_2O_2 are efficiently consumed in cloud air. Newly formed clouds are efficient "oxidation chambers" while old clouds need continuous replenishment of SO_2 and H_2O_2 . Assuming a time constant of one hour for the replenishment, and stepping the in-cloud reaction with 10 seconds timestep-length for depleting SO_2 , H_2O_2 and O_3 during the reaction, yields an effective 1800s oxidation rate. This is the timestep in the model, and the resulting in-cloud oxidation rate is the one used for k_w in eq. (4). The effective reaction rate can be up to a factor 100 smaller than the momentary oxidation rate in a new cloud, although normally it varies by a factor of 10. The replenishment time-scale of one hour is probably about a factor 3 too long for cumulus clouds and a factor 2–4 too small for stratus clouds (Lelieveld, 1990), so one hour has been chosen as an average. Table 3 summarises estimates of k_d , k_w and K_{Ch} , based on assumptions on oxidant concentration levels, liquid water contents in clouds, and cloudiness parameters, for different summer and winter conditions. All estimates in Table 3 assume $[\text{Mn(II)}] = 3 \cdot 10^{-8} \text{ mol/l}$ and $[\text{Fe(III)}] = 3 \cdot 10^{-7} \text{ mol/l}$ and $\text{pH} = 4$. These metal-ion concentrations ensure a maximum chemical lifetime for SO_2 of about 100 h. The table to a large extent supports the oxidation rates used in the model.

For oceanic sulphur, emissions are considered in terms of DMS fluxes to the atmosphere, but the atmospheric oxidation of DMS by OH is not explicitly considered in the model. Field experiments and laboratory studies indicate that the

Table 3. Estimates of air oxidation rates of sulphur dioxide to airborne sulphate, K_{Ch} , and chemical scavenging ratios, Λ , under different conditions

	V_w (10^{-2})	τ_d (h)	f (%)	OH (10^5 mol cm^{-3})	O ₃ (ppb)	H ₂ O ₂ (ppt)	k_d (10^{-6} s^{-1})	k_w (10^{-6} s^{-1})	K_{Ch} (10^{-6} s^{-1})	Λ (10^5)
Summer										
mid-lat. continent	3	24	0.05	15	40	300	1.6	47	3.6	3.1
mid-lat. ocean	3	18	0.1	9	30	200	1.0	65	5.7	2.7
arctic	1	24	0.15	3	25	100	0.33	14	2.1	1.9
Winter										
mid-lat. continent	2	18	0.1	5	25	30	0.55	7.4	1.2	1.5
mid-lat. ocean	2	12	0.1	3	25	70	0.33	31	3.0	2.0
arctic	1	36	0.1	0.0	25	10	0.0	2.4	0.24	0.7

Values of different parameters, rates and oxidant mixing ratios used to derive K_{Ch} are also given in the table. Note that oxidant mixing ratios are supposed to represent average conditions, thus [OH] includes averages over daylight and night (see text for comments).

dominant products of these oxidation are methane sulphonic acid ($\text{CH}_3\text{SO}_3\text{H}$ or MSA) and sulphur dioxide which is subsequently oxidised to sulphate (Andreae, 1986; Plane, 1989; Yin et al., 1990a,b). The estimated lifetime of DMS in air is considered to vary between 12 h and 30 h depending on the concentrations of OH (Plane, 1989; Hynes et al., 1986). Based on these estimates the model assumes a rapid oxidation of DMS in air, so that most DMS enters long range transport already as sulphur dioxide. Given the observed ranges of NO_x over Europe, the fraction of DMS sulphur which turns to SO_2 is considered to be 0.66 in accordance with laboratory studies by Yin et al. (1990b). The further oxidation of oceanic sulphur dioxide to particulate sulphate is treated in the same way as for anthropogenic sulphur dioxide.

2.5. Wet removal

The different microphysical processes involved in wet removal are parameterised using a common formulation based on experimentally determined scavenging ratios. The model distinguishes three different removal processes: nucleation (or in-cloud) scavenging, precipitation (or sub-cloud) scavenging and chemical transformation inside clouds, with subsequent rain-out.

For sulphate, the model distinguishes between in-cloud or nucleation scavenging and sub-cloud or precipitation scavenging. In-cloud or nucleation scavenging refers to the incorporation of aerosol in cloud water by their activation as cloud con-

densation nuclei (CCN) and by impaction of non-activated particles by cloud droplets. Measurements of nucleation scavenging for aerosol in the range 0.1 to 1.0 μm , primarily sulphate, yield an average value of 0.7 ± 0.2 (Hobbs, 1993 and references therein). This is the value that is used in the model for nucleation scavenging efficiency, although it is probably an underestimation. Precipitation or sub-cloud scavenging is the removal of aerosol that occurs below precipitating clouds as the aerosol is encountered by precipitation hydrometers. In accordance with field studies carried out by Radke et al. (1980), the precipitation scavenging efficiency for sulphate is considered to be 0.5 ± 0.2 .

For sulphur dioxide, chemical scavenging is applied. This involves the heterogeneous oxidation of SO_2 in precipitating clouds and its subsequent rain-out. In the model, analogous formulas to those used for the air oxidation rate K_{Ch} are applied and a similar seasonal and latitudinal variation is prescribed. The chemical scavenging ratio of SO_2 is determined by:

$$\Lambda = H^* + \frac{K_{\text{Ch,p}} H_p \rho_w}{V_w v_p}, \quad (5)$$

where v_p is downward speed of rain droplets and $K_{\text{Ch,p}}$ is the oxidation rate in precipitating clouds. v_p is set to 1 m s^{-1} except in the arctic and over winter continents where it is assumed to be 0.5 m s^{-1} . $K_{\text{Ch,p}}$ is calculated according to (2) with the only difference that now the values for τ_d and f reflect the distribution of precipitating clouds.

Values of the scavenging ratio at the equator and the north pole used in the model are given in Table 4, while typical values of Λ are listed in the last column of Table 3.

2.6. Initial and boundary conditions

At inflow, lateral boundary concentrations are set to zero. This choice of boundary conditions may hamper our results over north-eastern Asia because sulphur emissions in Japanese and Chinese regions south of 35°N are not included in the simulations. The top of the model's domain corresponds roughly to the tropopause, except in subtropical areas, and it is defined by a sufficiently high value of the vertical coordinate, well above the uppermost θ -layer defined in each monthly simulation. Inflow concentrations at the top of the model's domain are also set to zero.

For January 1988 initial conditions are determined by integrating the model for December 1987, starting with zero concentrations. In this way, we secure that the initial conditions for the simulation period are consistent with the previous meteorological conditions.

2.7. Computer use

The FORTRAN 77 codes of the model have been optimised for use both with SUN SPARC and CRAY computers. Production runs were carried out on a CRAY Y-MP/464, and required approximately 0.03 min. of CPU time for each simulation hour. A full month simulation on CRAY Y-MP/464 used 25 min. CPU time.

3. Results

A full year simulation for 1988 has been carried out and results have been compared with observa-

tions and with budgets from other model studies. Source allocation estimates are based on separate runs with emission data from each of the four different source groups.

3.1. Comparison with observations

Over Europe, model calculations have been compared with observations from the EMEP program. In 1988, the EMEP network had 87 operative stations reporting air and precipitation data, with largest density over western Europe. Approximately 80% of these stations reported daily data in 1988 for more than 75% of the time (Pedersen et al., 1990). The stations in the EMEP network are expected to comply with the sampling and analysis guidelines elaborated by its Chemical Co-ordination Centre which is also responsible for reporting regular intercomparison results (Hanssen and Skjermoen, 1994).

Over North America, surface measurements from the Eulerian Model Evaluation Field Study (EMEFS) were used although in this case only daily data for the second half of 1988 were available. Surface monitoring in EMEFS includes five different networks. Each network has separate sampling protocols and analysis laboratories. Stations are primarily distributed along the east coast of North America, and are specially concentrated around the industrial Great Lakes region. Approximately 70% of EMEFS stations reported daily air data for more than 25% of the days for the second half year of 1988, and only 10% of these covered daily data for more than 75% of the period.

Fig. 2 shows the European and North American scatter plots for modelled and observed concentrations of sulphur dioxide and particulate sulphate averaged over 1988. Both over Europe and over North America, about 75% of the modelled sul-

Table 4. Adopted wet scavenging ratios Λ , depending on the type of process

Process type	Λ	Refs.
nucleation scavenging (in-cloud)	$0.7 \cdot 10^6$	Radke (1983); Leaitch et al. (1983); Hegg et al. (1983)
precipitation scavenging (sub-cloud)	$0.5 \cdot 10^6$	Radke et al. (1980)
chemical scavenging		
constant at equator	$0.5 \cdot 10^6$	Seasonal and latitudinal variations parameterized as described in text.
max at north pole	$0.15 \cdot 10^6$	
min at north pole	$0.1 \cdot 10^6$	

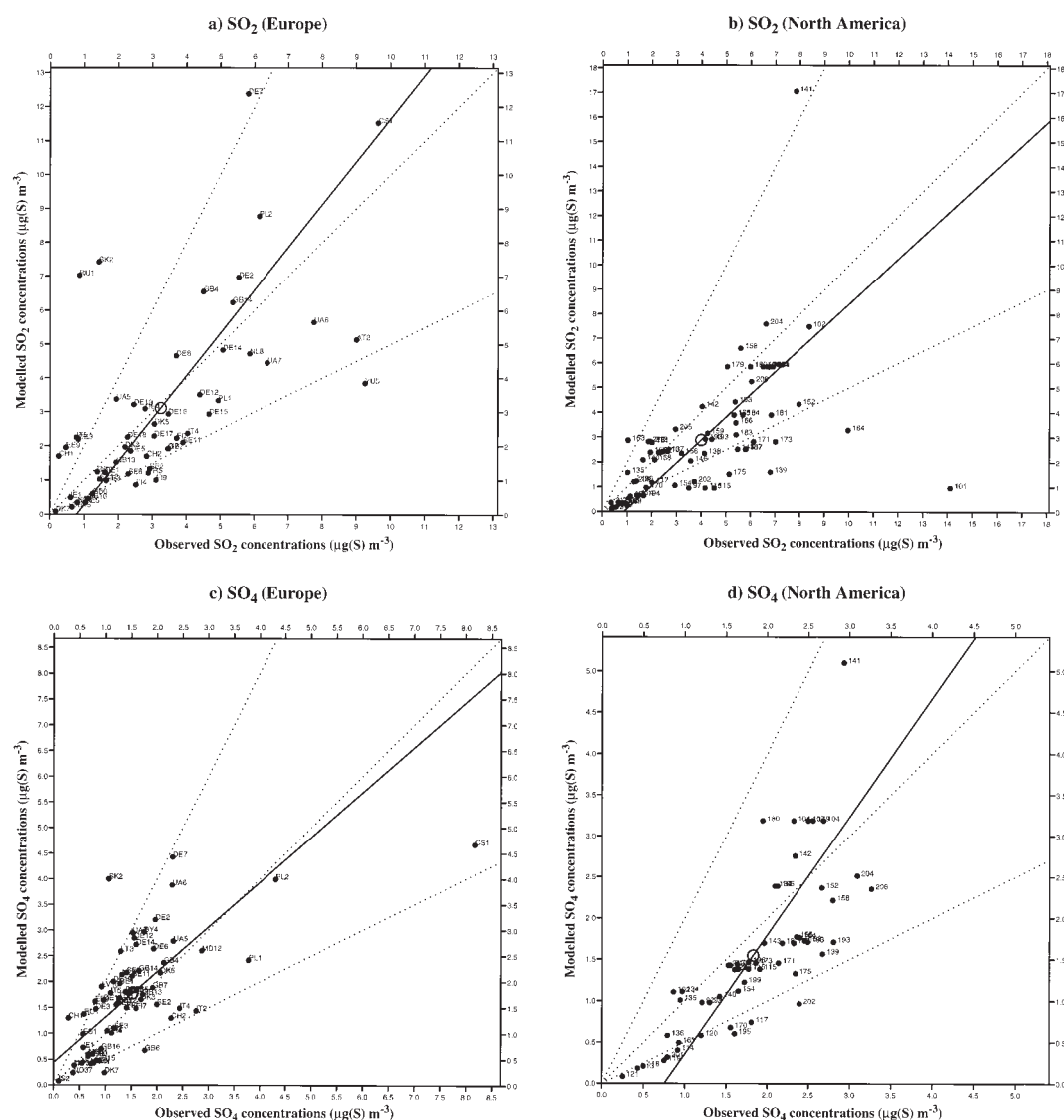


Fig. 2. Scatter plot for modelled and observed yearly averaged air concentrations of: (a) sulphur dioxide in the European network, (b) sulphur dioxide in the North American networks, (c) particulate sulphate in the European network, (d) particulate sulphate in the North American networks. The dashed lines indicate agreement or disagreement by a factor of 2. The full line represents an optimal linear regression. The circle denotes the mean values. Units: $\mu\text{g}(\text{S}) \text{m}^{-3}$.

phur dioxide is within a factor of 2 or closer to observations. For particulate sulphate, scatter plots of yearly averages show better agreement, with 90% of the European stations and 80% of the North American stations within a factor of two or closer to observations. Yearly correlations

between observed and modelled surface air concentrations over Europe are 0.62 for SO_2 and 0.64 for SO_4^{2-} . Over North America, yearly correlations are 0.57 for SO_2 and 0.76 for SO_4^{2-} when stations with 25% temporal coverage are considered. If the comparison is restricted to stations

with data reported over 75% of the days in the second half of 1988, the correlations increase to 0.74 and 0.95 respectively. The higher correlation of the model with the North American stations is probably a consequence of the fact that the North American stations cover a homogeneous region close to large sources, while the European network includes also remote and coastal areas.

In remote European stations, the model tends to underestimate both sulphur dioxide and particulate sulphate air concentrations. In general, the model tends to underestimate low air concentrations and overestimate high air concentrations, which related to seasonal variations implies that the model overestimates SO_2 and SO_4^{2-} in air during winter and underestimates during summer. This behaviour may be related to the parametrisation of wet scavenging rather than to the general underestimation of precipitation amounts. A sensitivity test carried out to quantify the implications of a systematic underestimation of the precipitation amounts in the model, concluded that a doubling in the precipitation amounts would lead to under 20% decrease of the surface air concentrations over source regions and up to 40% in remote areas. Comparison with precipitation data over Europe shows that in 65% of the cases wet deposition estimates are within a factor of two or closer to the observed values. The reason for this is that wet scavenging is so efficient in the model that most of the sulphur is removed from the air already with the underestimated precipitation amounts. Therefore, the parametrisation of wet removal used in the model yields reasonable wet

deposition results despite the underestimation of precipitation amounts.

3.2. Averaged sinks, yields and turn-over times

Tables 5, 6 contain an overview of yearly averaged atmospheric burdens, sink rates and turn-over times of sulphur dioxide and particulate sulphate. Sulphate yields are defined as the fraction of SO_2 oxidised to sulphate in the atmosphere, that is, the ratio between the chemical sink rate to the sum of all sink rates of sulphur dioxide. Turn-over times are defined as the ratio of the atmospheric burden to the sum of all sink rates. We have estimated the averaged 1988 values of these quantities on a monthly basis from our 6-hourly model integration. All these quantities depend strongly on the physical and chemical conditions that determine sulphur dispersion in the atmosphere and we can expect them to be highly variable depending on the areas and the time of the year considered for their averaging.

Table ranges for the present estimate correspond to maximum and minimum monthly turn-over times calculated for 1988 and different source types. In the case of data from Langner and Rodhe (1991), values on the right column correspond to a slow in-cloud oxidation rate while the left column gives the standard case. Ranges in the data by Benkovitz et al. (1994) are standard deviations from daily values calculated for a period of two months in the early autumn of 1986.

For sulphur dioxide, we calculate a yearly averaged turn-over time of 1.6 days ranging from 0.8

Table 5. Yearly averaged atmospheric burdens, sink rates and turn-over times for sulphur dioxide; $\text{SO}_{2\%}$ of emissions are given in bold numbers (see text for comments)

	Europe	North America	Asia	North Atlantic Ocean	All sources	Northern hemisphere (Langner and Rodhe, 1991)
burden (Tg S)	0.09	0.04	0.05	0.002	0.19	0.23–0.35
dry deposition (Tg S a^{-1})	9.2 (43%)	5.0 (40%)	6.2 (39%)	0.5 (31%)	20.9 (41%)	26.3–30.4
wet deposition (Tg S a^{-1})	5.2 (24%)	2.8 (22%)	3.2 (20%)	0.2 (13%)	11.4 (22%)	11.0–17.8
chemistry (Tg S a^{-1})	5.5 (26%)	2.9 (23%)	3.5 (22%)	0.2 (13%)	12.1 (23%)	48.6–25.8
turnover time (days)	1.7	1.4	1.5	0.9	1.6	1.1–1.7
	2.0–1.5	0.8–1.9	1.2–2.0	0.9–1.4	1.5–1.7	
turnover time (days)						
Benkovitz et al. (1994)	3.0 ± 0.3	2.7 ± 0.3	—	2.1 ± 0.2	2.8 ± 0.2	1.1–1.7

Table 6. Yearly averaged atmospheric burdens, sink rates and turn-over times for particulate sulphate, SO_4^{2-} (see text for comments)

	Europe	North America	Asia	North atlantic ocean	All sources	Northern hemisphere (Langner and Rodhe, 1991)
sulphate yield (%)	28%	27%	27%	21%	27%	
Benkovitz et al. (1994)	47%	60%	—	72%	53%	48%–34%
burden (Tg S)	0.08	0.04	0.04	0.003	0.16	0.55–0.39
dry deposition ($Tg\ S\ a^{-1}$)	0.97	0.43	0.7	0.041	2.11	6.4–4.5
wet deposition ($Tg\ S\ a^{-1}$)	5.57	2.59	3.07	0.146	11.35	33.5–24.5
turnover time (days)	4.5	4.7	3.8	6.1	4.3	
	3.2–7.2	2.1–7.2	2.6–6.0	3.1–6.9	3.1–6.2	4.4–4.9
turnover time (days)						
Benkovitz et al. (1994)	5.0 ± 1.4	4.4 ± 1.1	—	8.6 ± 1.3	4.7 ± 1.1	4.4–4.9

to 2.0 days depending on the type of sources and the month of the year. This estimate corresponds well to the slow in-cloud oxidation rate values from Langner and Rodhe. Differences in the atmospheric burden are partly caused by the fact that our model domain does not include the whole northern hemisphere. For SO_2 , dry deposition accounts for 41% of all sink rates in our model calculations, which is comparable with the 46% calculated by Benkovitz et al. and the 31–41% estimated by Langner and Rodhe. Wet deposition accounts for 22% in our model, in agreement with the 15–25% in Langner and Rodhe calculations. This value contrasts with the 0.6% estimate by Benkovitz et al., which is probably a too low estimate, as these authors also recognise, and the reason why the estimated turn-over times of SO_2 in Benkovitz et al. are somewhat larger than in the other estimates. Our chemistry sink rate in Table 6 corresponds both to gas phase OH oxidation and liquid phase oxidation of SO_2 in non-precipitating clouds. In our calculations, 23% of the total sink rate represents the fraction of sulphur dioxide oxidised into particulate sulphate that remains still in the air, without being scavenged by precipitation. The sum of this chemistry sink rate and the sink rate of chemical scavenging in precipitating clouds represents 53% of the total SO_2 sink which agrees with the 52% calculated by Benkovitz et al. and is within the 37%–57% ranges calculated by Langner and Rodhe. The sum of all three atmospheric sinks of sulphur dioxide does not balance the total emissions of sulphur because a part of the total sulphur emis-

sions was considered to be emitted directly as particulate sulphate, and there is also transport of sulphur out of the model boundaries, as detailed below.

Variations in the turn-over times of sulphur dioxide due to different source types are in agreement with previous estimates of Benkovitz et al. Both models agree in concluding that biogenic sulphur dioxide from the north Atlantic Ocean have a shorter turn-over time than anthropogenic SO_2 . This is due mainly to enhanced dry deposition over the ocean. Also in both models, the turn-over time for biogenic particulate sulphate is larger than for anthropogenic sulphate since biogenic emissions take place mainly during spring and summer when precipitation rates over the oceans are low.

For particulate sulphate, we estimate a turn-over time of 4.3 days, varying from 2.1 to 7.2 depending on the source region and the monthly average. These values, as well as the calculated sink rates for SO_4^{2-} are very similar in the three model estimates. According to our estimates, 84% of particulate sulphate in the atmosphere is removed by wet deposition and 16% by dry deposition. The same values were evaluated by Langner and Rodhe whilst Benkovitz et al. calculated 22% for dry and 78% for wet deposition of sulphate. However, the atmospheric burden of particulate sulphate in the present calculation is considerably smaller than in the other estimates, caused by the generally lower oxidation sink rates we have used for sulphur dioxide. In general, we can conclude that our model estimates correspond

better with the slow in-cloud oxidation rate case in Langner and Rodhe.

Comparison with ground level observations in remote areas also show the tendency of our model to underestimate sulphate in these areas. Free tropospheric measurements of sulphate are actually needed for a proper evaluation of the sulphate burden, but these are sparse at the moment. The comparison with ground level observations and other model estimates suggests that the estimates of intercontinental transport of sulphur presented in the next section may be regarded as conservative estimates.

3.3. Intercontinental transport

3.3.1. Geographical distribution and seasonal variations. Maps of yearly sulphur deposition allocated to each source group are given in Fig. 3 which shows that a significant fraction of anthropogenic sulphur emission is transported away from the continents.

The deposition of European sulphur well over the North Pacific Ocean and reaching the coasts of Alaska and British Columbia occurs mainly during winter when strong westerly winds and relatively low precipitation over Siberia favour ultra long transport. During winter 1988, maximum depositions of European sulphur over the North Pacific Ocean occurred in the Sea of Japan reaching values of $25\text{--}30 \text{ mg (S) m}^{-2} \text{ season}^{-1}$. This is roughly somewhat less than half of the calculated European yearly deposition over that area. For most of the year, European sulphur deposition extends to the Ural mountains and the West Siberian Plains with yearly values of $150\text{--}200 \text{ mg (S) m}^{-2}$. The minimum extension of European sulphur out of its continental boundaries occurs during the summer, when European sulphur emissions are smaller and scavenging by convective precipitation over the source area is efficient.

In contrast, North American sulphur experiences the longest trans-Atlantic transport during summer 1988, with an accumulated sulphur deposition of $\sim 10 \text{ mg (S) m}^{-2}$ along the west coast of Europe that is about half of the yearly North American contribution. The variations in trans-Atlantic transport are primarily due to meteorology. The synoptic conditions that favour the trans-Atlantic transport of North American sul-

phur over the stable atmosphere of the summer Atlantic are further discussed in Section 4 and contrast significantly with the transport conditions experienced by biogenic marine sulphur in middle latitudes.

Spring and summer are the seasons with largest biogenic DMS emissions and maximum deposition values of $\sim 12 \text{ mg (S) m}^{-2} \text{ month}^{-1}$ are reached during these seasons. Deposition of oceanic sulphur has a limited extension in adjacent coastal areas where the yearly deposition is calculated to be $10\text{--}15 \text{ mg (S) m}^{-2} \text{ yr}^{-1}$. This suggests that biogenic sulphur is effectively removed in the model by dry and wet deposition shortly after it has been emitted. The instantaneous oxidation of biogenic DMS to sulphur dioxide in the model may overestimate the removal of biogenic sulphur over the ocean because dry deposition of SO_2 over sea is very effective. However, it is during the summer, when biogenic emissions are largest that the chemical lifetime of DMS is shortest, and the strong static stability of marine air during summer may cause biogenic marine sulphur to stay close to the ocean surface, where dry deposition is efficient and horizontal advection relatively small.

The dispersion of Asian sources is not fully modelled because the model domain does not include Asian latitudes south of 35°N , implying that a large fraction of Asian pollution is advected out of the model domain. Thus, no conclusions are drawn for the influence of Asian sulphur over the North Pacific Ocean and North America. The influence of north Asian sulphur over north-eastern Europe is largest during spring and autumn with an averaged deposition of $5\text{--}10 \text{ mg (S) m}^{-2} \text{ season}^{-1}$. Yearly accumulated deposition of north Asian origin over these same areas is calculated to be $10\text{--}20 \text{ mg (S) m}^{-2} \text{ yr}^{-1}$ and is primarily related to the influence of two single source areas, namely, Norilsk and Kuybyshev.

3.3.2. Sulphur budgets for 1988. Table 7 compares the total mass of sulphur deposited outside each source region (exported deposition) with the total mass of sulphur deposited inside the source region (indigenous deposition), and the transport out of the model's simulation domain. For all source regions, indigenous deposition dominates over exported deposition. In general, wet deposition is the process dominating exported deposition, while dry deposition dominates the indigenous depos-

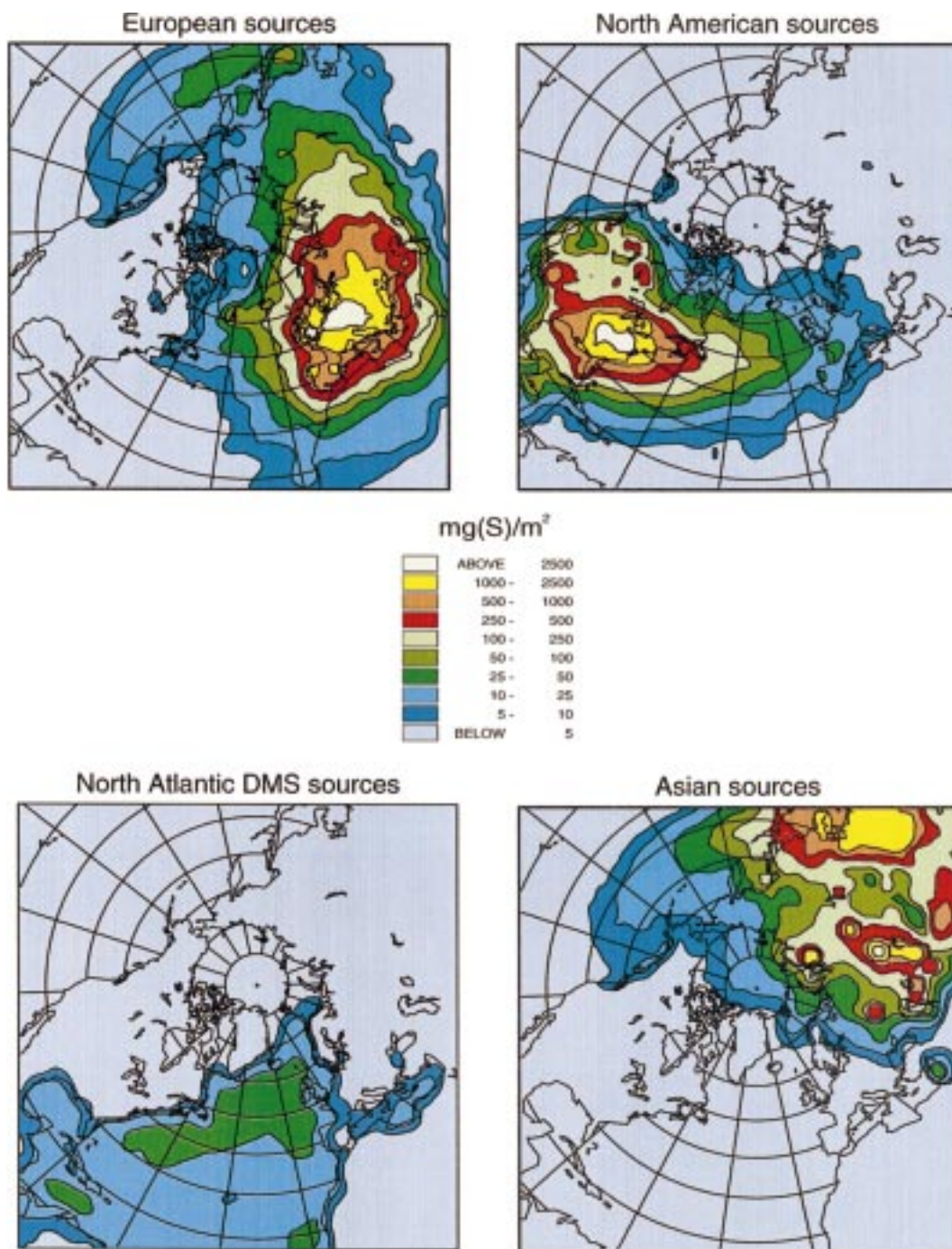


Fig. 3. Yearly accumulated deposition of sulphur from European, North American, North Atlantic Ocean biogenic sources and Asian sources. Simulation year is 1988. Units: $\text{mg(S)} \text{ m}^{-2} \text{ yr}^{-1}$.

Table 7. Fate of emissions from different modelled sources as deposition over source region (indigenous), deposition out of source regions (exported) and transport out of model's simulation domain; units: $10^9 \text{ g (S) yr}^{-1}$

	Indigenous	Exported	Out of model's boundaries
Europe	16 700	4300	500
N. America	8200	2700	1600
N. Atlantic	700	200	100
N. Asia*	9100	4100	2800

*Refers to the part of northern Asia inside the simulation domain.

ition. This is because particulate sulphate is the dominant sulphur compound in remote regions, with wet scavenging as the most efficient removal process. 20% of the European sulphur emissions were deposited outside the European boundaries in 1988. The percentage of exported deposition is 22% for North American sources and 26% for Asian sources inside the simulation domain. The smallest exported fraction is calculated for biogenic North Atlantic sources with 19%. The fraction of emissions transported out of the model domain are 17% for north Asian sources, 13% for North American sources, 6% for biogenic North Atlantic sources and 2% for European sources.

Significant fractions of the European exported sulphur are deposited over the North Atlantic Ocean (35%) and Asia (25%). Deposition over African and Arctic regions and large areas over the North Pacific Ocean adds up to $\sim 40\%$ the European export, making the European contribution over these areas relatively important. Exported North American sulphur is primarily deposited over the North Atlantic Ocean (63%) and only 10% of the total North American export actually reaches the west coast of Europe. Other areas receiving North American deposition are Central America, the North Pacific Ocean and Canadian sub-Arctic regions. Biogenic sulphur from the North Atlantic Ocean is transported primarily over the west coasts of Europe (83%) and North America (15%) although central America, the Caribbean Islands and northern Africa receive also a part of the biogenic export.

Fig. 4 shows the monthly variations of the inter-

continental sulphur deposition over each source area. Over Europe, the intercontinental contributions from Asian, North American and biogenic North Atlantic sulphur over Europe are similar. The largest contribution comes from Asian sources, $350 \text{ Gg(S) yr}^{-1}$ with maximum during spring and autumn. The contribution from North American sulphur dominates during summer and adds up to a yearly mass flux of $230 \text{ Gg(S) yr}^{-1}$ which is $\sim 2\%$ of the North American yearly emissions. North Atlantic biogenic sources contribute with $160 \text{ Gg(S) yr}^{-1}$, with largest deposition calculated during spring and early summer and a pronounced monthly variation. In 1988, the accumulated depositions from the 3–4 largest contributing months represented more than half of the yearly deposition from each individual intercontinental source.

The periods of larger trans-Atlantic transport may change from year to year, according to meteorological variability. Previous estimates for 1983 by Tarrasón and Iversen (1992) showed larger transport from North-America to Europe during January 1983, while in 1988 the largest deposition of North American sulphur over Europe occurs in August.

The contribution of European sulphur over North America is roughly an order of magnitude smaller than the North American contribution over Europe. It should be mentioned, however, that the budget of intercontinental sulphur transport to North America depicted in Fig. 4b is not complete. The influence of Asian sulphur is most certainly underestimated, and important contributions from natural oceanic and volcanic sources over the North Pacific Ocean are not included.

Over the North Atlantic Ocean, anthropogenic sulphur from North America and Europe dominate the yearly deposition while the contribution of biogenic oceanic sulphur represents only 20%. The monthly cycle of North American export to the North Atlantic Ocean shows an even distribution over the year while the European export is determined by the seasonal variations prescribed to European sulphur emissions.

Over Asia, the export of European sulphur has a pronounced seasonal variation, with a significant maximum in April. This seasonal variation is related to particular meteorological conditions and will be discussed in Section 4.

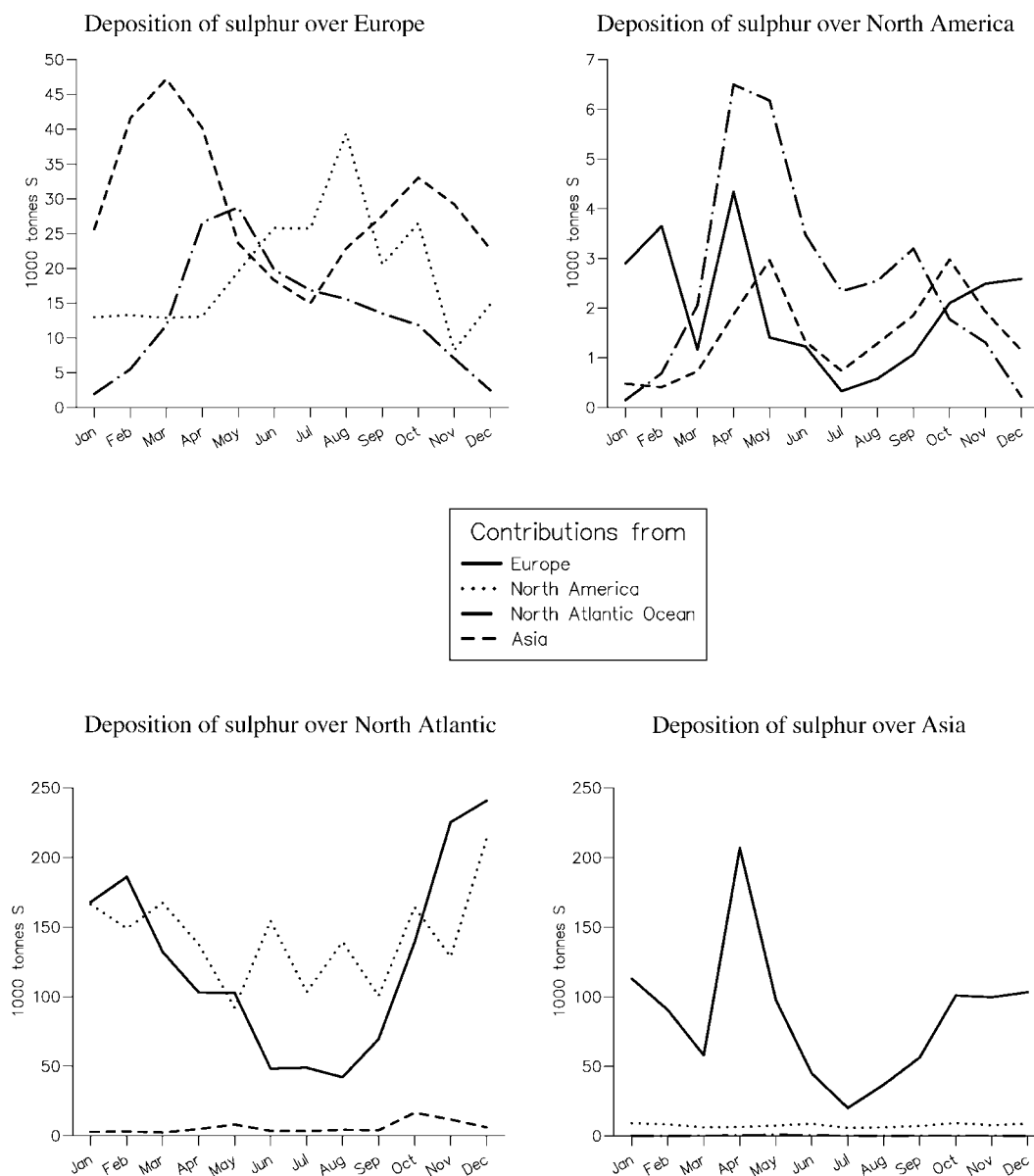


Fig. 4. 1988 monthly budgets for the import of sulphur deposition from intercontinental sources in the four selected source areas. Units: 10^9 g(S).

3.3.3. Relative importance of intercontinental transport. The relative importance of the intercontinental deposition received by each source region is given in Table 8. Although the intercontinental contribution to sulphur deposition over Europe represents only $\sim 4\%$ of the total yearly depos-

ition, the relative contribution of each intercontinental source over particular areas can be higher. For example, the Asian contribution to yearly deposition over northern parts of Scandinavia and Eurasia exceeds 3% of the total deposition over those areas. North Atlantic biogenic sources affect

Table 8. % contribution of different sources to the total yearly deposition of sulphur over the 4 studied regions

Total deposition over	by European sources	by N. American sources	by N. Atlantic sources	by Asian sources*
Europe	95.8%	1.3%	0.9%	2.0%
N. America	0.3%	99.1%	0.4%	0.2%
N. Atlantic Ocean	37.0%	42.0%	19.0%	2.0%
N. Asia*	10.1%	0.9%	0.0%	89.0%

*Refers to the part of northern Asia inside the simulation domain.

mostly the west coast of Europe, where their relative contribution to the yearly total deposition is $\sim 2\%$. Annually, the relative contribution of North American sources along the west coast of Europe is 3% of the total deposition. During summer months when European indigenous deposition is at its minimum, the North American contribution been calculated to 20% of the total deposition in countries like Ireland and Norway (Tarrasón et al., 1995). Over the North Atlantic Ocean, the dominant anthropogenic contribution to sulphur deposition switches from North American to European sources around longitude 25°W . The relative importance of the biogenic contribution increases towards the equator, since biogenic emissions increase towards lower latitudes and the meridional component of trans-Atlantic transport displaces the North American export towards the northwest.

The European contribution over Asia, which in average was calculated to be 10%, is more significant over Siberia where it represents over 40–50% of the yearly total deposition. This is due to the preferred pathways of European export over Asia and also to the fact that sources over Siberia are all point sources. Over the central north Pacific Ocean, the relative contribution of European sulphur is probably overestimated because the present simulation does neither include oceanic or volcanic sources over the area nor describe transport from Asian sources south of 35°N . Also over the seas of Japan and Okhotsk the relative influence of European sources is likely to be smaller than the given 5–10% of the total calculated deposition.

Over the Arctic, European sources dominate the sulphur air column above 1000 m while Asian sources situated inside the Arctic circle dominate surface air concentrations and dry deposition. For

particulate sulphate, the European percentage contribution above 1000 m is larger than for sulphur dioxide, indicating that a significant fraction of the particulate sulphate in the Arctic is transported from mid-latitudes.

4. Discussion

This discussion focuses on the links between large-scale atmospheric flows and intercontinental transport of sulphur. Following Blackmon (1976), filters have been applied in order to isolate meteorological phenomena with different frequencies. The following results are derived by applying a band-pass filter, discerning situations with a persistence of between 2.5 and 6 days, to the six-hourly analyses of 500hPa geopotential height. RMS maps of the filtered data have been constructed for each month in 1988. Multi-annual analyses have indicated that regions of maximum band-pass RMS are usually connected with migrating cyclones and anticyclones (storm tracks) with maximum regions confined to latitudes between 30°N and 60°N (Blackmon, 1976; Wallace and Blackmon, 1983). These activity regions are centred in the north-eastern Pacific Ocean, near the Aleutians, and over the north Atlantic Ocean, south of Iceland. A third weaker maximum is found over north central Asia, extended over the Siberian Plains. These activity regions are related to baroclinic waves embedded in the westerly flow and are connected to areas of pronounced frontogenetic flows. Their intensity is a measure of atmospheric baroclinity and their position, down-flow from large pollution source areas, make them potentially important for intercontinental transport of contaminants.

It is shown in Fig. 4 that the export of North

American sulphur across the North Atlantic Ocean experiences relative maxima during June, July, August and October 1988. The amount of North American sulphur deposited over the west coast of Europe during these four months accounts for over 50% of the total yearly deposition. Comparison of the monthly deposition maps with the band-pass filtered RMS charts indicates a relation to the position of areas with frontogenetic activity over the North Atlantic Ocean. When the centre of maximum RMS is situated south of Greenland and extending towards the west coast of Europe, the confluent frontogenetic flow enhances the transport of North American pollution over the North Atlantic Ocean and its release by precipitation along the European west coast. The vertical motions associated with frontal passages transport North American sulphur upwards and along the baroclinic waveguides over the North Atlantic Ocean. The eventual sulphur removal is determined by the release of precipitation corresponding to the cyclone development as it matures over western Europe. This was the situation during the above mentioned months in 1988 (Fig. 5a). In contrast, when the centre of maximum RMS is situated over Newfoundland and Labrador, North American sulphur mostly from the Great Lakes region is efficiently scavenged shortly after leaving North America by the precipitation associated with synoptic scale cyclones already developed in that area. This was the case in November 1988 as indicated in Fig. 5b.

Similarly, there is a relation between frontogenetic activity over Eurasia and the deposition of European sulphur east of the Urals. The Eurasian baroclinic waveguide is climatically much weaker than the centres situated in the north Atlantic and the north Pacific Oceans, and it is not regularly present. In 1988, the Eurasian synoptic variability region was pronounced in April, October and November, and it was during these months that the modelled European deposition over the Urals surpasses $25 \text{ mg (S) m}^{-2} \text{ month}^{-1}$. The most extreme case in April 1988 (Fig. 4d). The extent of the transport of European sulphur over Siberia is clearly linked to a zone of high baroclinic activity as illustrated in Fig. 6.

It can be speculated that variations in the distribution of areas with maximum baroclinicity will be responsible for inter-annual variations in the extent of intercontinental transport over the

northern hemisphere. For the case of North American sulphur, previous simulations with the meteorological conditions of 1983 (Tarrasón and Iversen, 1992) which indicated larger trans-Atlantic transport of sulphur during winter months are probably not representative for different years. Climatological studies (Wallace and Blackmon, 1983) show that baroclinic wave activity is usually more intense during the winter season but the position of the cyclone tracks seems then to limit the extension of intercontinental transport. In this sense, the situation encountered during 1988 may be more in line with the expected climatological behaviour. However, considering that there is significant inter-decade variance (the NAO-index), conclusions remain weak until climatologies for longer periods are established.

5. Conclusions

We have quantified the extent of intercontinental transport of sulphur over major parts of the northern hemisphere with the help of a time-resolved 3-dimensional model that is able to reproduce regional scale variations of sulphur.

Model results for 1988 have been evaluated against daily observations of particulate sulphate and sulphur dioxide compiled over more than 200 stations distributed over North America and Europe. The comparison has shown that the model manages to reproduce the episodic character of sulphur in air observed at ground level. Particulate sulphate in surface air over source regions tends to be overestimated, while the sulphur content in remote air is underestimated by the model. Comparison of column burdens and sink rates has shown that the present model calculates a slower conversion rate for the oxidation of sulphur dioxide to particulate sulphate than other model estimates. Consequently, the present values on intercontinental transport of sulphur should be considered as conservative estimates, even though free tropospheric measurements are needed to confirm this.

European sources dominate the averaged air concentrations and depositions both over mid-latitudes and over Arctic areas. The maximum extension of European sulphur occurs during winter, when European emissions are largest and strong westerlies over northern Asia favour the

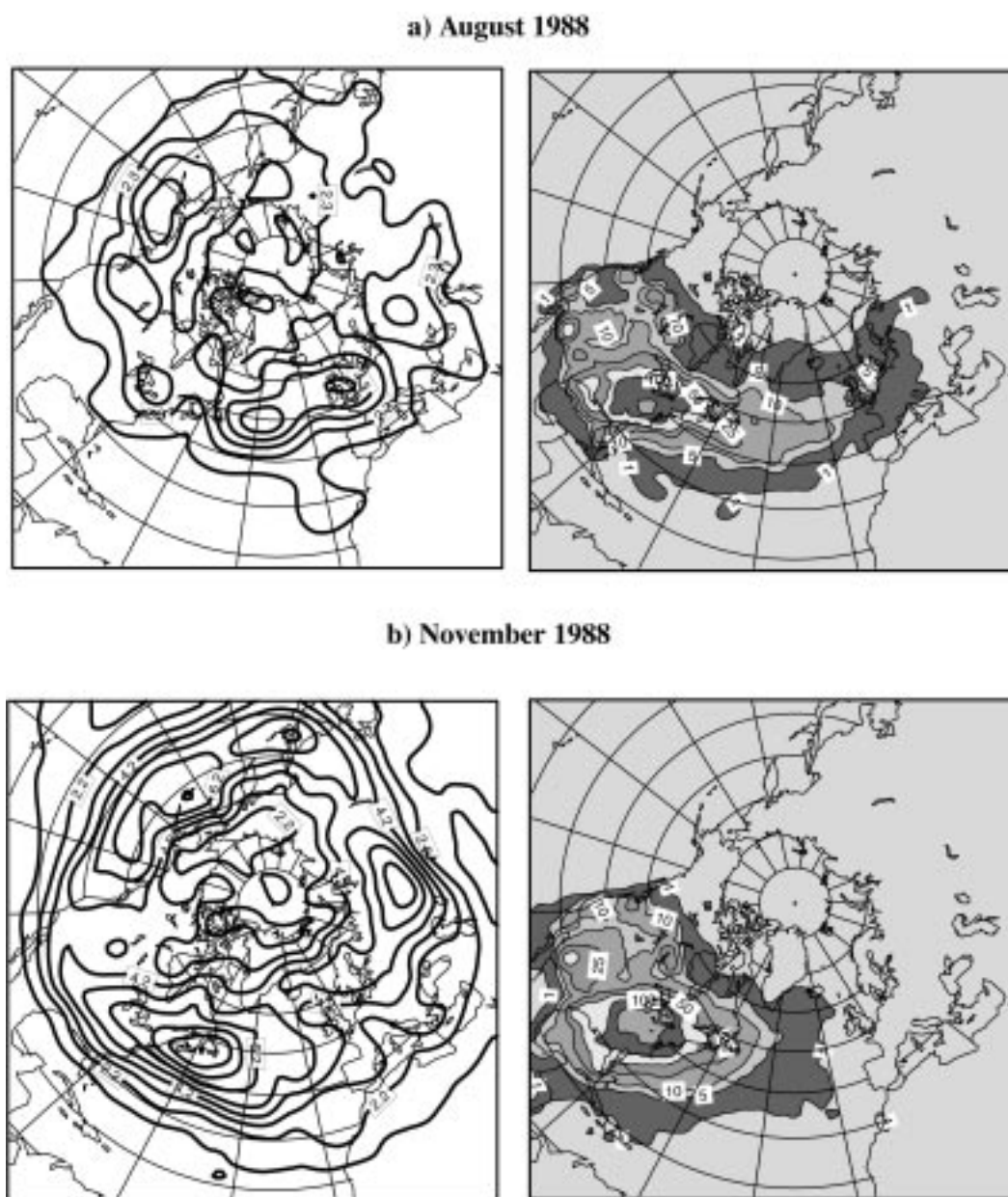


Fig. 5. Comparison between the position of baroclinic waveguides, or storm tracks, over the North Atlantic Ocean and the extent of the North American sulphur deposition. Filtered variances of the 500 hPa geopotential height and total S deposition from North American sources are given for (a) August 1988 and (b) November 1988. Units: $\text{mg(S) m}^{-2} \text{ month}^{-1}$ for depositions; m, for rms of geopotential height.

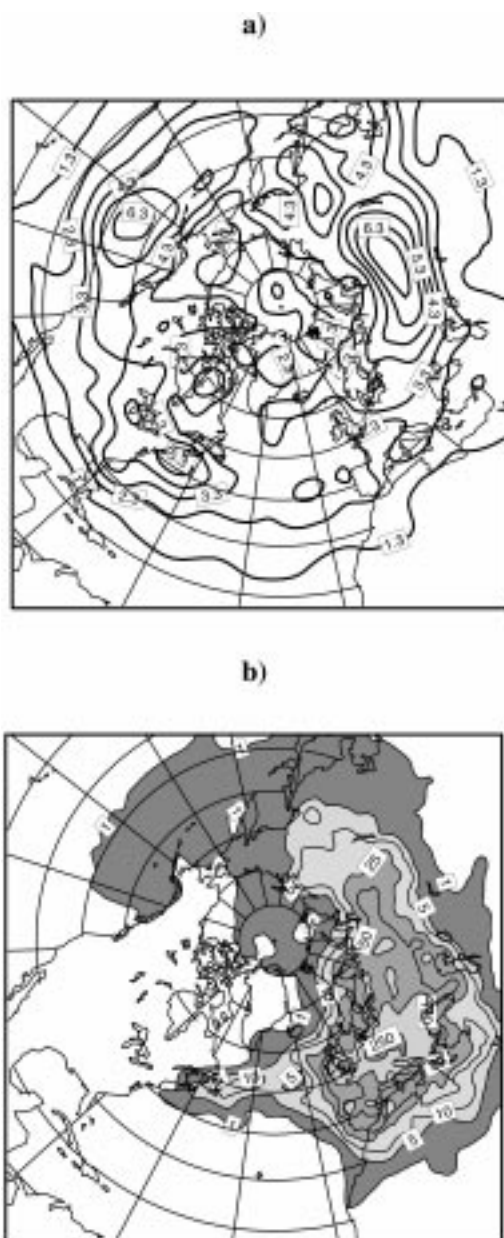


Fig. 6. Comparison between (a) the position of band-pass filtered rms maxima over the Eurasia and (b) the extent of the European sulphur deposited over the area. Values for April 1988. Units: $\text{mg (S) m}^{-2} \text{ month}^{-1}$ for deposition; m, for rms of geopotential height.

transport of European pollution well into the North Pacific Ocean. It is the largest single contribution of an intercontinental source to the deposition levels over another continent and it is mostly due to the transport of European sulphur over Siberia. The relative influence of European sulphur over Siberia is 40–50% of the yearly deposition of sulphur in that region.

All three intercontinental contributions over Europe are similar in amount and add up to 4% of the total deposition in Europe. Asian sources affect European pollution levels on Eurasia and northern Scandinavia with maximum deposition during spring and autumn. The contributions of biogenic sulphur from the North Atlantic Ocean and anthropogenic sources from North America over Europe are more important along the west coast of Europe where they result in a yearly accumulated deposition of $10\text{--}15 \text{ mg (S) m}^{-2} \text{ yr}^{-1}$ for biogenic sources and $20\text{--}25 \text{ mg (S) m}^{-2} \text{ yr}^{-1}$ for North American sulphur. This represents respectively 2% and 3% of the yearly accumulated total deposition along the west coast of Europe.

The influence of biogenic sulphur is largest during summer and late spring, when biogenic production of sulphur over the ocean is at its maximum and deposition from European sources reaches its minimum. During the summer the biogenic contribution over countries along the west coast of Europe, can be comparable to contributions from other European countries. Similar conclusions are drawn for the influence of North American sulphur along the west coast of Europe.

The yearly flux of North American sulphur over the west coast of Europe in 1988 is calculated to be $\sim 230 \text{ Gg(S) yr}^{-1}$ in agreement with previous estimates (Whelpdale et al., 1988; Tarrasón and Iversen, 1992). This contribution is then one order of magnitude larger than the contribution of European sulphur over North America and represents 2% of the total North American emissions. Approximately 10% of the total sulphur fraction exported out of North American boundaries is estimated to reach Europe, and about 60% is expected to be deposited over the North Atlantic Ocean.

The transport of North American sulphur over the North Atlantic Ocean are related to the position of baroclinic waves embedded in the large scale westerly flow. Variations in the position and strength of these baroclinic waveguides can

explain inter-annual variations in the timing of the largest contribution of trans-Atlantic transport towards Europe.

Over the North Atlantic Ocean, the dominant contribution to sulphur deposition shifts from North American anthropogenic sources to European sources around longitude 25°W. Over the Arctic, Asian sources dominate the averaged dry deposition and surface air concentrations while European sources determine to a large extent wet deposition amounts and sulphur air concentrations above 1000 m.

These results quantify the importance of the anthropogenic component in background sulphur depositions over the northern hemisphere and show that the contribution of intercontinental transport is comparable to contributions from individual areas or countries inside the continents. It is seen that synoptic scale phenomena determine the extent of intercontinental transport of sulphur. This supports the use of a model capable of resolving individual cyclones and anticyclones in

order to accurately describe the dispersion and distribution of sulphur in the northern hemisphere.

6. Acknowledgements

The authors are indebted to Prof. A. Eliassen for his decisive participation in the discussions. Thanks are also due to Dr. R. Dennis and Dr. C. Benkovitz for providing gridded emission data for North America and northern Asia. The EMEFS data utilised in this study was collected and prepared under the co-sponsorship of the United States Environmental Protection Agency, the Atmospheric Environment Service, Canada, the Ontario Ministry of Environment, the Electric Power Research Institute and the Florida Electric Power Co-ordinating Group. The calculations have used meteorological data from the European Centre for Medium Range Weather Forecast and were made possible by access to CRAY Y-MP4D/464 at the Norwegian Technical University (SINTEF), Trondheim, Norway.

REFERENCES

- Andreae, M. O. 1986. The ocean as a source of atmospheric sulphur compounds. In: *The role of air sea exchange in geochemical cycling*, edited by P. Buat-Ménard, pp. 331–362. Reidel, Dordrecht.
- Andreae, M. O. 1990. Ocean–atmosphere interactions in the global biogeochemical sulphur cycle. *Mar. Chem.* **30**, 1–29.
- Balkanski, Y. J., Jacob, D. J., Gardner, G. M., Graustein, W. C. and Turekian, K. K. 1993. Transport and residence times of tropospheric aerosols inferred from a global three-dimensional simulation of ²¹⁰Pb. *J. Geophys. Res.* **98**, 20573–20586.
- Barrett, K. and Berge, E. 1996. *Transboundary air pollution in Europe. Part 1: estimated dispersion of acidifying agents and of near surface ozone*. EMEP/MSC-W Report 1/96, The Norwegian Meteorological Institute, Oslo, Norway.
- Bates, T. S., Lamb, B. K., Guenther, A., Dignon, J. and Stoiber, R. E. 1992. Sulphur emissions to the atmosphere from natural sources. *J. Atmos. Chem.* **14**, 315–337.
- Benkovitz, C. M., Berkovitz, C. M., Easter, R. C., Nemessure, S., Wagener, R. and Schwartz, S. E. 1994. Sulphate over the North Atlantic and adjacent continental regions: Evaluation for October and November 1986 using a three-dimensional model driven by observation-derived meteorology. *J. Geophys. Res.* **99**, 20725–20756.
- Berge, E. 1990. A regional numerical sulphur dispersion model using a meteorological model with explicit treatment of clouds. *Tellus* **42B**, 389–407.
- Berntsen, T. K. and Isaksen, I. S. A. 1997. A global three-dimensional chemical transport model for the troposphere, 1. Model description and CO and ozone results. *J. Geophys. Res.* **102**, no. D17, 21,239–21,281.
- Blackmon, M. L. 1976. A climatological spectral study of the 500 mb geopotential height of the northern hemisphere. *J. Atmos. Sci.* **33**, 1607–1623.
- Carmichael, G. R., Peters, L. K. and Kitada, T. 1986. A second-generation model for regional scale transport/chemistry/deposition. *Atmos. Environ.* **20**, 173–188.
- Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R. and Walcek, C. J. 1987. A three-dimensional eulerian acid deposition model: Physical concepts and formulation. *J. Geophys. Res.* **92**, 2930–2938.
- Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B. and Warren, S. G. 1991. Perturbation of the northern hemisphere radiative balance by backscattering of aerosols. *Tellus* **43AB**, 152–163.
- Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, Jr., Hansen, J. E. and Hoffman, D. J. 1992. Climate forcing by anthropogenic aerosols. *Science* **255**, 423–430.
- Dastoor, A. P. and Pudykiewicz, J. 1996. A numerical global meteorological sulphur transport model and its application to Arctic air pollution. *Atmos. Environ.* **30**, 1501–1522.

- Davidson, C. I. and Wu, Y. L. 1989. Dry deposition of particles and vapors. In: *Acidic precipitation*, vol. 3, eds. Lindberg, S. E., Page, A. L. and Norton, S. A. Springer-Verlag, Berlin, pp. 103–209.
- Dovland, H. and Eliassen, A. 1976. Dry deposition on a snow surface. *Atmos. Environ.*, **10**, 783–785.
- Eliassen, A. 1978. The OECD Study of long range transport of air pollutants: long range transport modelling. *Atmos. Environ.* **12**, 479–487.
- Eliassen, A. and Saltbones, J. 1983. Modelling of long-range transport of sulphur over Europe: a two year model run and some experiments. *Atmos. Environ.* **17**, 1457–1473.
- Erickson, III D. J., Walton, S. J., Ghan, S. J. and Penner, J. E. 1991. Three-dimensional modelling of the global atmospheric sulphur cycle: a first step. *Atmos. Environ.* **25A**, 2513–2520.
- Erismann, J. W. and Baldocchi, D. 1994. Modelling dry deposition of SO₂. *Tellus* **46B**, 159–171.
- Erismann, J. W. 1994. Evaluation of a surface resistance parametrisation of sulphur dioxide. *Atmos. Environ.* **28**, 2583–2594.
- Feichter, J., Kjellström, E., Rodhe, H., Dentener, F., Lelieveld, J. and Roelofs, G.-J. 1996. Simulation of the tropospheric sulphur cycle in a global climate model. *Atmos. Environ.* **30**, 1693–1708.
- Fowler, D. 1985. Dry deposition of SO₂ onto plant canopies. In: *Sulphur dioxide and vegetation*, eds. Winner, W. E., Mooney, H. A. and Goldstein, R. A. Stanford University Press, California, pp. 75–95.
- Galloway, J. N., Prospero, J. M., Rodhe, H., Artz, R. S., Atherton, C. S., Balkanski, Y. J., Bingemer, H. G., Brost, R. A., Bürgermeister, S., Carmichael, G. R., Chang, J. S., Charlson, R. J., Cober, S., Ellis, Jr. W. G., Fisher, C. J., Hales, J. M., Hastie, D. R., Iversen, T., Jacob, D. J., John, K., Johnson, J. E., Kasibhatla, P. S., Langner, J., Lelieveld, J., Levy, II H., Lipschultz, F., Merrill, J. T., Michaels, A. F., Miller, J. M., Moody, J. L., Penner, J. E., Pinto, J., Pszenny, A. A. P., Spiro, P. A., Tarrasón, L., Turner, S. M. and Whelpdale, D. M. 1993. Sulfur and nitrogen cycling in the north atlantic ocean's atmosphere: synthesis of field and modelling results. *NOAA Tech. Memorandum, ERL ARL-204*.
- Garland, J. A. 1977. The dry deposition of sulphur dioxide to land and water surfaces. *Proc. R. Soc. Lond.* **A354**, 245–268.
- Hanssen, J. E. and Skjellmoen, J. E. 1994. *The 13th inter-comparison of analytical methods within EMEP*. EMEP/CCC Report 1/94, Kjeller, Norway.
- Hegg, D. A., Rutledge, S. A. and Hobbs, P. V. 1986. A numerical model for sulphur and nitrogen scavenging in cold-frontal rainbands (2) Discussions of chemical fields. *J. Geophys. Res.* **91**, 14403–14416.
- Hobbs, P. V. 1993. *Aerosol–cloud–climate interactions*, ed. Peter, V. Hobbs. International geophysics, vol. 54, Academic Press, Inc., San Diego, California, p. 233.
- Hussain, L. and Dutkiewicz, V. A. 1990. A long-term (1975–1988) study of atmospheric SO₄²⁻: regional contributions and concentration trends. *Atmos. Environ.* **24A**, 1175–1187.
- Hynes, A. J., Wine, P. H. and Semmes, D. H. 1986. Kinetics and mechanism of OH reactions with organic sulphides. *J. Phys. Chem.* **90**, 4148–4156.
- Iversen, T. 1989. Numerical modelling of the long range atmospheric transport of sulphur dioxide and particulate sulphate to the Arctic. *Atmos. Environ.* **23**, 2571–2595.
- Iversen, T. 1993. Modelled and measured transboundary acidifying pollution in Europe: verification and trends. *Atmos. Environ.* **27**, 889–920.
- Jaffe, D. A., Berntsen, T. K. and Isaksen, I. S. A. 1997. A global three-dimensional chemical transport model, 2, Nitrogen oxides and non methane hydrocarbon results. *J. Geophys. Res.* **102**, no. D17, 21,281–21,296.
- Kato, N. and Akimoto, H. 1992. Anthropogenic emissions of SO₂ and NO_x in Asia: emission inventories. *Atmos. Environ.* **26A**, 2997–3017.
- Kiehl, J. T. and Briegleb, B. P. 1993. The relative roles of sulphate aerosols and greenhouse gases in climate forcing. *Science* **260**, 311–314.
- Langner, J. and Rodhe, H. 1991. A global three-dimensional model of the tropospheric sulphur cycle. *J. Atmos. Chem.* **13**, 225–263.
- Leaitch, W. R., Strapp, J. W., Wiebe, H. A. and Isaac, G. A. 1983. Measurements of scavenging and transformation of aerosol inside cumulus. In: *Precipitation scavenging, dry deposition and resuspension*, vol. 1, eds. H. R. Pruppacher, R. G. Semonin and W. G. N. Slinn. Elsevier, New York, pp. 53–70.
- Lelieveld, J. 1990. *The role of clouds in tropospheric photochemistry*. Ph.D. thesis, University of Utrecht, The Netherlands.
- Li, X., Maring, H., Savoie, D., Voss, K. and Prospero, J. M. 1996. Dominance of mineral dust in aerosol light-scattering in the North Atlantic trade winds. *Nature* **380**, 416–419.
- Louis, J. F. 1979. A parametric model of vertical eddy fluxes in the atmosphere. *Boundary Layer Meteor.* **17**, 187–202.
- OECD 1979. *The OECD programme on long-range transport of air pollutants. Measurements and findings*, 2nd edition. OECD, Paris, France.
- Pedersen, U. 1992. *Ozone data report 1988*. EMEP/CCC Report 1/92. The Norwegian Institute of Air Research, Kjeller, Norway.
- Pedersen, U., Schaugh, J., Skjellmoen, J. E. and Hanssen, J. E. 1990. *Data report 1988, Part 2: Monthly and seasonal summaries*. EMEP/CCC Report 5/90, Kjeller, Norway.
- Pham, M., Müller, J.-F., Brasseur, G. P., Granier, C. and Mégie, G. 1995. A three-dimensional study of the tropospheric sulphur cycle. *J. Geophys. Res.* **100**, 26061–26092.
- Plane, J. M. C. 1989. Gas-phase atmospheric oxidation of biogenic sulphur compounds: a review. In: *Biogenic sulphur in the environment*, edited by Saltzman, E. S.

- and Cooper, W. J., pp. 404–423. American Chemical Society, Washington, D.C.
- Poppe, D., Zimmermann, J. and Dorn, H. P. 1995. Field data and model calculations for the hydroxyl radical. *J. Atmos. Sci.* **52**, 3402–3407.
- Pudykiewicz, J. A., Benoit, R. and Staniforth, A. 1985. Preliminary results from a LRTAP model based on an existing meteorological forecast model. *Atmos. Ocean*, **23**, 267–303.
- Pudykiewicz, J. A. and Dastoor, A. P. 1995. On numerical simulation of the global distribution of sulphate aerosol produced by a large volcanic eruption. *J. Climate*, **8**, 464–473.
- Radke, L. F., Hobbs, P. V. and Eltgroth, M. W. 1980. Scavenging of aerosol particles by precipitation. *J. Appl. Met.* **19**, 715–722.
- Radke, L. F. 1983. Preliminary measurements of the size distribution of cloud interstitial aerosol. In: *Precipitation scavenging, dry deposition and resuspension*, vol. 1, eds. H. R. Pruppacher, R. G. Semonin and W. G. N. Slinn. Elsevier, New York, pp. 71–78.
- Rodhe, H. and Grandell, J. 1981. Estimates of characteristic times for precipitation scavenging. *J. Atmos. Sci.* **38**, 370–386.
- Sandnes, H. and Styve, H. 1990. *Calculated budgets for airborne acidifying components in Europe, 1985, 1987, 1988, 1989, 1990 and 1991*. EMEP/MSC-W Report 1/92. The Norwegian Meteorological Institute, Oslo, Norway.
- Saeger, M., Langstaff, J., Walters, R., Modica, L., Zimmermann, D., Fratt, D., Dulleba, D., Ryan, R., Demmy, J., Tax, W., Sprangue, D., Mudgett, D. and Werner, A. S. 1989. The 1985 NAPAP emissions inventory (version 2): development of the annual data and modeler's tape. *Report no. EPA-600/7-80-012a*. US Environmental Protection.
- Seinfeld, J. H. 1986. *Atmospheric chemistry and physics of air pollution*. Wiley Interscience, John Wiley & Sons, Inc.
- Seland, Ø., van Pul, A., Sorteberg, A. and Tuovinen, J. P. 1995. *Implementation of a resistance dry deposition module and a variable local correction factor in the Lagrangian EMEP model*. EMEP/MSC-W Report 3/95. The Norwegian Meteorological Institute, Oslo, Norway.
- Semb, A. 1978. Sulphur emissions in Europe. *Atmos. Environ.* **12**, 455–460.
- Semb, A. 1985. *Circumpolar SO₂ emission survey*. NILU Report OR:69/85, Reference 0–8516, Norwegian Institute for Air Research, Kjeller, Norway.
- Simpson, D. 1993. Photochemical model calculations over Europe for two extended periods: 1985 and 1989. Model results and comparison with observations. *Atmos. Environ.* **27A**, 921–943.
- Smolarkiewicz, P. K. 1983. A simple positive definite advection scheme with small implicit diffusion. *Mon. Wea. Rev.* **111**, 467–486.
- Tarrasón, L. and Iversen, T. 1992. The influence of North American anthropogenic sulphur emissions over western Europe. *Tellus* **44B**, 114–132.
- Tarrasón, L., Turner, S. M. and Floisand, I. 1995. An estimation of seasonal DMS fluxes over the North Atlantic Ocean and their contribution to European pollution levels. *J. Geophys. Res.* **100**, 11623–11639.
- Tegen, I., Lacis, A. A. and Fung, I. 1996. The influence on climate forcing of mineral aerosols from disturbed soils. *Nature* **380**, 419–422.
- Trenberth, K. E. 1991. Climate diagnostics from global analyses: conservation of mass in ECMWF analyses. *J. Clim.* **4**, 707–722.
- Turner, S. M. and Liss, P. S. 1985. Measurement of various sulphur gases in a coastal marine environment. *J. Atmos. Chem.* **2**, 223–232.
- Voldner, E. C., Barrie, L. A. and Sirois, A. 1986. A literature survey of dry deposition of oxides of sulphur and nitrogen with emphasis on long-range transport modelling in North America. *Atmos. Environ.* **20**, 2101–2123.
- Wallace, J. M. and Blackmon, M. 1983. Observations of low frequency atmospheric variability. In: *Large-scale dynamical processes in the atmosphere*, eds. B. J. Hoskins and R. P. Pearce. Academic Press, pp. 55–94.
- Wallace, J. M., Gyo-Ho Lim and Blackmon, M. 1988. Relationship between cyclone tracks, anticyclone tracks and baroclinic waveguides. *J. Atmos. Sci.* **45**, 439–462.
- Warneck, P. 1988. *Chemistry of the natural atmosphere*. International Geophysics Series, vol. 41, Academic Press, Inc.
- Wesely, M. L. and Hicks, B. B. 1977. Some factors that affect the deposition rates of sulphur dioxide and similar gasses on vegetation. *J. Air. Poll. Contr. Ass.* **27**, 1110–1116.
- Wesely, M. L. 1989. Parametrisation of surface resistances to gaseous dry deposition in regional-scale models. *Atmos. Environ.* **23**, 1293–1304.
- Whelpdale, D. M. and Shaw, R. W. 1974. Sulphur dioxide removal by turbulent transfer over grass, snow, and water surfaces. *Tellus* **26**, 196–204.
- Whelpdale, D. M., Eliassen, A., Galloway, J. N., Dovland, H. and Miller, J. M. 1988. The transatlantic transport of sulphur. *Tellus* **40B**, 1–15.
- Wigley, T. M. L. and Raper, S. C. B. 1992. Implications for climate and sea level of revised IPCC emission scenarios. *Nature* **357**, 293–300.
- Yin, F., Grosjean, D. and Seinfeld, J. H. 1990a. Photooxidation of dimethyl sulphide and dimethyl disulphide (I). Mechanism development. *J. Atmos. Chem.* **11**, 309–364.
- Yin, F., Grosjean, D. and Seinfeld, J. H. 1990b. Photooxidation of dimethyl sulphide and dimethyl disulphide (II). Mechanism evaluation. *J. Atmos. Chem.* **11**, 365–399.