

# Variable CCN formation potential of regional sulfur emissions

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**Abstract.** Aerosols are short lived so their geographical distribution and impact on climate depends on where they are emitted. Previous model studies have shown that the mass of sulfate aerosol produced per unit sulfur emission (the sulfate burden potential) and the associated direct radiative forcing vary regionally because of differences in meteorology and photochemistry. Using a global model of aerosol microphysics, we show that the total number of aerosol particles produced per unit sulfur emission (the aerosol number potential) has a different regional variation to that of sulfate mass. The aerosol number potential of N. American and Asian emissions is calculated to be a factor of 3 to 4 times greater than that of European emissions, even though Europe has a higher sulfate burden potential. Pollution from N. America and Asia tends to reach higher altitudes than European pollution so forms more new particles through nucleation. Regional differences in particle production and growth mean that sulfur emissions from N. America and E. Asia produce 50 nm diameter cloud condensation nuclei up to 70% more efficiently than Europe. For 80 nm diameter CCN, N. America and Europe produce CCN 2.5 times more efficiently than E. Asia. The impact of regional sulfur emissions on particle concentrations is also much more widely spread than the impact on sulfate mass, due to efficient particle production in the free troposphere during long range transport. These results imply that regional sulfur emissions will have different climate forcing potentials through changes in cloud drop number.

## 1 Introduction

Aerosols are important for the Earth's radiation budget, acting against the warming of greenhouse gases by directly scattering solar radiation and by increasing cloud albedo (Intergovernmental Panel on Climate Change, 2007). Most greenhouse gases, including CO<sub>2</sub> and CH<sub>4</sub>, have a sufficient atmospheric lifetime to become well mixed throughout the atmosphere. The climate forcing potential (forcing per unit emission) of greenhouse gas emissions is therefore insensitive to the location of the source, aiding the formulation of international climate policies such as the Kyoto Protocol (Berntsen et al., 2005; Rypdal et al., 2005; Shine et al., 2005; Unger et al., 2008). In contrast, aerosols have an atmospheric lifetime of days to weeks, resulting in a patchy distribution driven by the location of emissions, regional differences in transport and removal processes, and, in the case of secondary aerosol components like sulfate, by variable chemical and photochemical factors.

Model studies (Rasch et al., 2000; Koch et al., 2007) have found that the potential of anthropogenic SO<sub>2</sub> emissions to generate sulfate mass varies by a factor of 2 between E. Asia, N. America and Europe because of regional differences in these meteorological and chemical processes. Although there are inter-model differences (Rasch et al. (2000) identified E. Asia as the most efficient source, while Koch et al. (2007) found N. America to be most efficient) these studies suggest that the climate forcing potential of SO<sub>2</sub> depends on where the gas is emitted. In the Koch et al. (2007) study the aerosol direct forcing potential of the regional emissions was found to be very similar to the sulfate burden potential. Unger et al. (2008) extended the analyses of Koch et al. (2007) using future (2030) emissions and reported radiative forcing potentials with a similar regional dependence to their earlier study. Such regional variation in the forcing potential is important to quantify if climate policies are to be developed effectively.



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These previous studies have simulated regional contributions to sulfate mass but have not considered variations in the production efficiency of climate-relevant particles specifically. The impact of sulfur emissions on clouds, and therefore the aerosol indirect effect, is controlled primarily by the number of cloud condensation nuclei (CCN) produced. At low to moderate cloud supersaturations of 0.3% particles as small as 50 nm dry diameter can act as CCN. In the case of secondary aerosol produced from SO<sub>2</sub> oxidation, the concentration of such particles in the atmosphere is influenced strongly by non-linear, size-dependent microphysical processes such as nucleation, coagulation and deposition. Here, we use a global model that includes these processes and resolves the size and number of all particles to show that the regional production efficiency of CCN is very different to that of sulfate mass.

## 2 Model description

The Global Model of Aerosol Processes (GLOMAP; Spracklen et al., 2005a, b; Manktelow et al., 2007) is an extension to the TOMCAT offline 3-D global chemical transport model (Chipperfield, 2006). GLOMAP includes the processes of aerosol nucleation, condensation, hygroscopic growth, coagulation, wet and dry deposition, and cloud processing. Here we use GLOMAP-bin, which represents the particles using a two-moment sectional scheme with 20 particle size bins spanning dry diameters from about 3 nm to 25  $\mu\text{m}$ . In the runs shown here, the aerosol composition is described with 4 internally mixed components: sulfate (SO<sub>4</sub>), sea salt, black carbon (BC) and organic carbon (OC).

We use a horizontal resolution of 5.6° × 5.6° with 31 hybrid  $\sigma$ -p levels extending from the surface to 10 hPa. Large scale atmospheric transport and meteorology is specified from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses at 6-hourly intervals. The model includes the following emissions: anthropogenic SO<sub>2</sub> (Cofala et al., 2005), volcanic SO<sub>2</sub> (Halmer et al., 2002), oceanic dimethyl sulfide (DMS) (Kettle and Andreae., 2000; Nightingale et al., 2000), sea spray (Gong, 2003), primary OC/BC from biofuel and fossil fuel (Bond et al., 2004) as well as biomass burning SO<sub>2</sub> and BC/OC (Van der Werf et al., 2003). Concentrations of the oxidants OH, NO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, HO<sub>2</sub> and O<sub>3</sub> are interpolated temporally using 6-hourly monthly mean 3-D concentrations from TOMCAT runs with a comprehensive tropospheric chemistry scheme. In-cloud oxidation of SO<sub>2</sub> is assumed to occur only in low clouds, which are specified from monthly mean International Satellite Cloud Climatology Project (ISCCP) data. The depletion and recovery of oxidants following cloud chemistry is accounted for.

We define three emission regions corresponding approximately to N. America (15–75° N, 50–165.0° W), W. Europe (35–75° N, 20° W–40° E) and E. Asia (20–50° N, 100–160° E). The results have been derived by comparing mod-

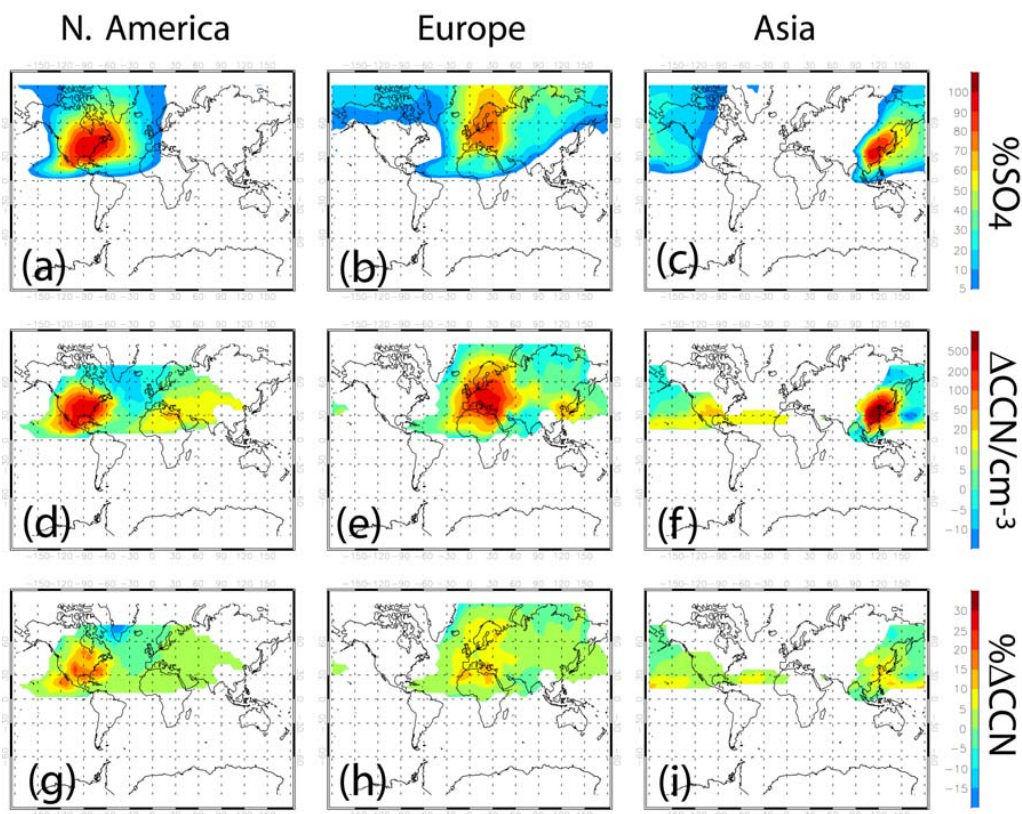
eled aerosol fields with and without anthropogenic SO<sub>2</sub> emissions from each region. Results are an annual mean over 2000, following a 2 month model spin-up over November and December 1999.

## 3 Results

### 3.1 Sulfate aerosol distribution

Figure 1 shows the contribution of regional SO<sub>2</sub> emissions to surface level SO<sub>4</sub> and CCN. In Fig. 1 CCN are defined as the number of particles larger than 50 nm dry diameter, equivalent to cloud drop activation at a cloud supersaturation of 0.3%. The impact on CCN is shown as an absolute change (Fig. 1d–f) and as a percentage of total CCN (including carbonaceous, sea-salt and SO<sub>4</sub> aerosol from all regions and sources; Fig. 1g–i). Regional contributions to sulfate mass peak over the source region and gradually decrease away from the source. The situation is more complex for CCN. For N. American and Asian emissions, CCN are depleted over a large area immediately downwind of the source, but are then enhanced over more remote locations. For example, N. American emissions cause a decrease in CCN of up to 10 cm<sup>-3</sup> across the N. Atlantic, but produce an additional 20 cm<sup>-3</sup> CCN across Central Asia and N. Africa. Likewise, Asian emissions reduce CCN by up to 15 cm<sup>-3</sup> across the N. Pacific, but contribute 5–50 cm<sup>-3</sup> CCN across W. USA and the subtropical Atlantic.

These spatial variations in surface CCN can be understood by considering the vertical transport and production of aerosol from each region. Figure 2 shows the vertical profile of regional contributions to SO<sub>4</sub> mass, total particle number (condensation nuclei, CN) and CCN, averaged over the Northern Hemisphere. Regional contributions to SO<sub>4</sub> mass peak in the lower troposphere over the source regions and diminish rapidly with distance horizontally and vertically. In contrast, contributions of regional sulfur emissions to CN peak in the free troposphere (FT) and upper troposphere (UT). The cause of the high particle concentrations in the FT and UT is the increasing nucleation rate with altitude, which is well recognized from observations (Clarke and Kapustin, 2002; Schröder et al., 2002; Hermann et al., 2008) and models (Adams and Seinfeld, 2002; Lucas and Prinn, 2003; Spracklen et al., 2005a, b; Stier et al., 2005). In our model the observed increase in particle concentration with altitude is well captured by assuming binary homogeneous nucleation of sulfuric acid-water particles (Spracklen et al., 2005a). Other studies have suggested that ion-induced nucleation may be partly or wholly the cause (Lee et al., 2003; Curtius, 2006; Yu, 2006). In either case, it is well established that particle formation rates increase with altitude. The newly formed particles from regional sources are transported eastwards before descending into the lower troposphere far from the initial source region. During transport the particles



**Fig. 1.** Simulated contribution of N. America (left column), W. Europe (middle column) and E. Asia (right column) anthropogenic  $\text{SO}_2$  sources to surface  $\text{SO}_4$  mass (a–c) and CCN concentrations (d–f). The fractional change in surface CCN (panels g–i) is calculated relative to all other sources of CCN (including BC, OC, sea spray and other sulfate sources). The fractional contribution to CCN is shown only where the source region contributes to more than  $20 \text{ ng } (\text{SO}_4)\text{m}^{-3}$ . Results are an annual mean for 2000.

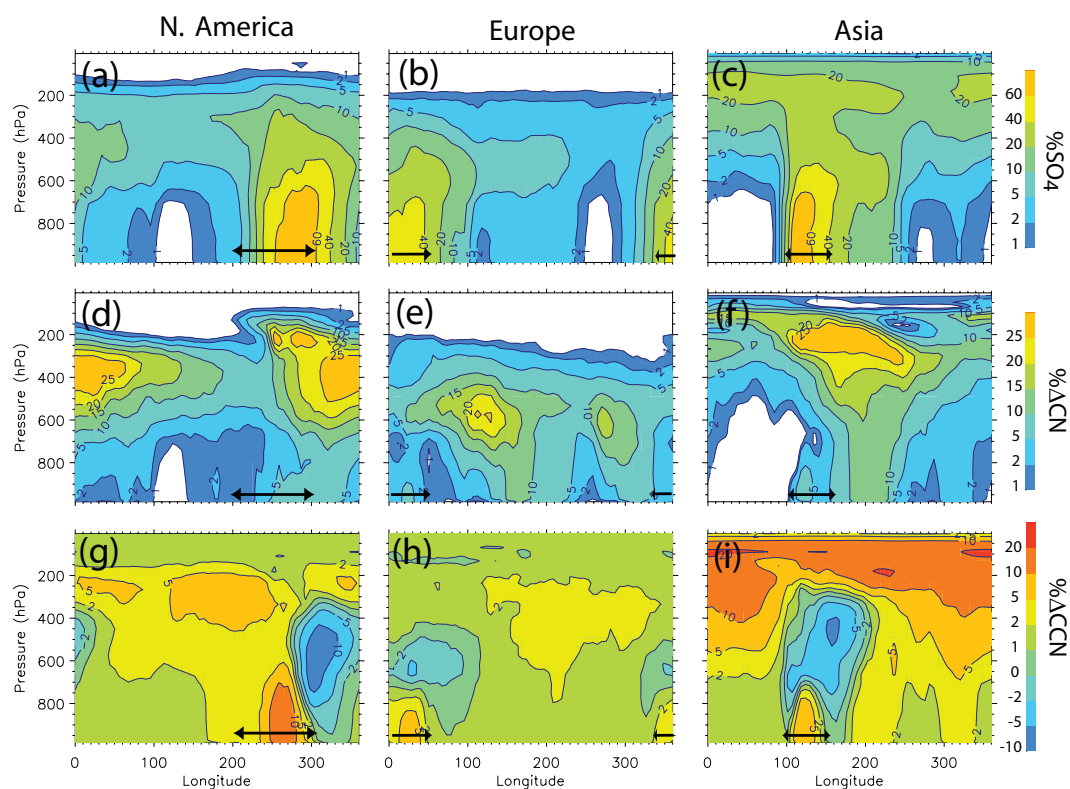
grow by coagulation and condensation of  $\text{H}_2\text{SO}_4$ . The balance between CN production and growth and the competition for available vapor controls the change in CCN shown in Figs. 1 and 2. Figure 2g–i shows that decreases in CCN occur below regions of the FT and UT where source contributions to CN are greatest. The additional particles compete with pre-existing aerosol for  $\text{H}_2\text{SO}_4$  vapor, so that fewer particles grow to CCN sizes through condensational growth. At locations more remote from the source, CN changes are smaller, and there is sufficient  $\text{H}_2\text{SO}_4$  to grow both new and pre-existing CN to CCN sizes. It is important to realize that the additional CCN are not composed entirely of  $\text{SO}_4$  derived from the regional emissions. Rather, new particles are nucleated from small amounts of the emitted sulfur and these particles then act as sites for uptake of any  $\text{SO}_4$  wherever the particles are transported. The  $\text{SO}_4$  may be derived from anthropogenic, oceanic or volcanic sources.

There are large differences in the vertical profile of CN and CCN produced from each region. Most notable is the much larger production of particles from Asian and N. American emissions compared to Europe. Vertical transport is more favorable over E. Asia and N. America than over Europe due

to the more frequent formation of warm conveyor belts and convective systems (Stohl, 2001; Stohl et al., 2002; Eckhard et al., 2004). Consequently, E. Asian and N. American emissions are lofted to higher altitudes, where low temperatures accelerate nucleation, and greatly enhance particle number at 200 hPa compared to much slower nucleation and a much weaker enhancement at 600 hPa for European emissions.

### 3.2 Regional aerosol budget

The sulfate aerosol mass and number budget for each region is shown in Table 1. The fraction of  $\text{SO}_2$  converted into  $\text{SO}_4$  (sulfate production efficiency) lies in the range 0.38–0.51 and, consistent with previous studies, is lowest for W. Europe (Chin et al., 2000; Rasch et al., 2000; Koch et al., 2007; Manktelow et al., 2007) where  $\text{SO}_2$  deposition is favored by the slow venting of the boundary layer and where oxidants are more limited than at lower latitudes. The contribution of each region to total (anthropogenic + natural) global  $\text{SO}_4$  ( $\text{SO}_{4\text{glob}}$ ) can be expressed as a fraction of the contribution to total global sulfur emissions, giving a sulfate burden potential (Rasch et al., 2000):



**Fig. 2.** Simulated meridional-height cross-section of the fractional contribution of anthropogenic sulfur sources in N. America (left column), W. Europe (middle column) and E. Asia (right column) to total Northern Hemisphere  $\text{SO}_4$  mass (a–c), CN (d–f) and CCN (g–i) concentrations. The black horizontal bar denotes the geographical extent of each source region. Results are an annual mean for 2000.

**Table 1.** Regional  $\text{SO}_4$ , CN and CCN budgets. <sup>a</sup>  $\text{SO}_4$  production efficiency = fraction of  $\text{SO}_2$  oxidised to  $\text{SO}_4$ ; <sup>b</sup> defined in Eq. (1); <sup>c</sup> Defined in Eq. (2) (values are weighted by grid box mass). <sup>d</sup> Defined in Eq. (3) (values are weighted by grid box mass). Plus and minus symbols represent the change in the number potential under nuc-max and nuc-min scenarios, respectively. <sup>e</sup> Export fraction = fraction of  $\text{SO}_4$  and CCN that exist outside each source region.

	N. America	W. Europe	E. Asia
$\text{SO}_4$ production efficiency <sup>a</sup>	0.51	0.39	0.44
$\text{SO}_4$ lifetime (days)	4.8	6.4	3.7
$\text{SO}_4$ burden potential <sup>b</sup>	0.89	0.93	0.59
Aerosol number (CN) potential <sup>c</sup>	$0.33 \pm_{0.03}^{0.02}$	$0.11 \pm_{0.01}^{0.01}$	$0.41 \pm_{0.08}^{0.08}$
CCN potential <sup>d</sup>			
$d > 50$ nm	$0.1 \pm_{0.0}^{0.02}$	$0.06 \pm_{0.0}^{0.01}$	$0.08 \pm_{0.01}^{0.0}$
$d > 80$ nm	0.15	0.14	0.06
$d > 100$ nm	0.22	0.21	0.08
$\text{SO}_4$ export <sup>e</sup>	0.32	0.61	0.35
CCN export <sup>e</sup>	0.46	0.64	0.79

$$\text{Sulfate burden potential} = \left[ \left( \sum_i \text{SO}_4(i)_{\text{reg}} \right) / \text{SO}_4_{\text{glob}} \right] / \left( \text{EmisSO}_2_{\text{reg}} / \text{EmisSO}_2_{\text{glob}} \right) \quad (1)$$

where  $i$  is the grid box index and reg implies  $\text{SO}_4$  originating from regional anthropogenic  $\text{SO}_2$ . In our model for the year 2000 European  $\text{SO}_4$  has the longest lifetime (due to slow wet deposition), giving Europe a sulfate burden potential 57% and 4% larger than E. Asia and N. America, respectively. In contrast, Rasch et al. (2000) found that Asia had the largest sulfate burden potential, while Koch et al. (2007) found N. America to be the most efficient source. These inter-model differences may be largely attributable to differences in the setup of each model experiment. Our anthropogenic  $\text{SO}_2$  emissions are derived from the AEROCOM 2000 inventory (Cofala et al., 2005), while Rasch et al. (2000) used the earlier GEIA 1B 1985 emissions (Benkovitz et al., 1996) and Koch et al. (2007) used EDGAR 3.2 1995 (Olivier and Berdowski, 2001). There are considerable differences in the magnitude of  $\text{SO}_2$  emission over Europe, N. America and Asia between each inventory, which will have a significant influence on the behavior of sulfur emitted from each region (Manktelow et al., 2007). Furthermore, each study uses a different set of coordinates to define Europe, N. America and

Asia. For example, Rasch et al. (2000) include S. E. Asia, India and China in their definition of Asia, while we include only China.

Directly equivalent to the sulfate burden potential, we can also calculate a total aerosol number potential and a CCN potential:

$$\text{aerosol number potential} = \left[ \left( \sum_i \text{CN}(i)_{\text{reg}} \right) / \text{CN}_{\text{glob}} \right] / \left( \text{EmisSO}_2_{\text{reg}} / \text{EmisSO}_2_{\text{glob}} \right), \quad (2)$$

where CN stands for all condensation nuclei (diameter > 3 nm) produced from the regional sulfur emissions.

$$\text{CCN potential} = \left[ \left( \sum_i \text{CCN}(i)_{\text{reg}} \right) / \text{CCN}_{\text{glob}} \right] / \left( \text{EmisSO}_2_{\text{reg}} / \text{EmisSO}_2_{\text{glob}} \right) \quad (3)$$

The aerosol number and CCN potentials in Table 1 differ greatly from the regional sulfate burden potentials. The aerosol number potential of E. Asia and N. America exceed by a factor of 4 and 3 respectively, the aerosol number potential of W. Europe. Such large differences exist because particle formation and loss are predominately controlled by non-linear microphysical processes (nucleation and coagulation) and do not simply scale with the sulfate mass. Although Europe has the highest sulfate burden potential it has the lowest aerosol number potential because of the much lower production of new particles in the FT.

Regional CCN potentials are determined by how efficiently new particles grow to CCN sizes as well as how they influence the growth of pre-existing particles through competition for H<sub>2</sub>SO<sub>4</sub> vapor. Regional differences in the CCN potential depend on the particle size at which CCN are counted. Counting particles larger than 50 nm dry diameter, N. America has the largest CCN potential, which exceeds by 67% and 25% respectively, the CCN potential of W. Europe and E. Asia. At 80 nm N. America and Europe have the highest CCN potentials, more than a factor 2 higher than E. Asia, while at 100 nm they are a factor 2.75 higher than for E. Asia. This change in CCN potential with particle size (or equivalently, the assumed supersaturation) is due to the competing effects of particle formation and growth. E. Asian sulfate produces high CN concentrations, which prevents the new particles from reaching the largest CCN sizes.

The CCN potential is the contribution of each region to CCN expressed as a fraction of the contribution to sulfur emissions. It can also be expressed as a fraction of the sulfate burden from each region, which takes account of the different sulfate burden potentials of each region – i.e., a relative measure of how much regional atmospheric sulfate exists at CCN sizes. Europe has the lowest CCN potential at 50 nm but the highest sulfate burden potential. On this basis, we find that Asian sulfate is twice as efficient as European sulfate at producing 50 nm CCN and N American sulfate is 1.7 times as efficient.

Table 1 also compares the SO<sub>4</sub> and CCN export fractions (fractions lying outside each region). CCN export fractions lie in the range 46–79% and exceed those of SO<sub>4</sub> mass (32–61%). For Asian emissions, CCN are exported 2.3 times as effectively as SO<sub>4</sub>. These differences reflect the fact that a large fraction of CCN are produced in the FT and UT where aerosol transport is effective, whereas SO<sub>4</sub> mainly resides in the lower troposphere where zonal and meridional transport is slower. Another factor is that CCN have a longer production timescale than SO<sub>4</sub> when generated through the nucleation and growth/coagulation mechanism.

### 3.3 Sensitivity to nucleation rate

The number of CN and CCN produced by each region will be sensitive to rates of nucleation in the FT. We use the binary H<sub>2</sub>SO<sub>4</sub> homogeneous nucleation scheme of Kulmala (1998), but it should be recognized that binary homogeneous nucleation rates are uncertain even under laboratory conditions (Vehkamäki et al., 2002). To examine how uncertainties in nucleation influence regional aerosol number and CCN potentials, we have performed additional simulations in which the nucleation rate was increased (nuc-max) and reduced (nuc-min) by a factor of 10 from the baseline model run. There is around a factor of 2–3 more CN produced by each region between nuc-min and nuc-max, but less than a 20% increase in regional CCN. Table 1 shows that the aerosol number (CCN) potential for each region changes by at most 9% (20%), 9% (17%) and 20% (13%) between the 2 nucleation scenarios for N. America, W. Europe and E. Asia, respectively. N. America and E. Asia produce new particles 3–4 times as effectively as W. Europe regardless of the nucleation rate in the model, and Europe is always the least efficient region for producing CCN.

## 4 Conclusions

Results from our global aerosol microphysics model show that the production of particles from regional SO<sub>2</sub> emissions differs greatly from the production of SO<sub>4</sub> mass. Particle formation is controlled strongly by nucleation in the free and upper troposphere. Because nucleation rates increase with altitude, the height to which emissions are transported becomes an important factor in the number of particles produced per unit SO<sub>2</sub> emission. The growth of these particles through coagulation and uptake of H<sub>2</sub>SO<sub>4</sub> governs the efficiency with which CCN are produced. In contrast, the production and removal of SO<sub>4</sub> mass is controlled largely by cloud processes throughout the lower troposphere. Because CCN and SO<sub>4</sub> burden potentials are controlled by different aerosol processes, they do not show the same regional variation.

W. Europe has the largest SO<sub>4</sub> burden potential in our model in 2000 but the lowest aerosol number (CN) and CCN potential at 0.3% supersaturation (>50 nm diameter particles). One kilogram of SO<sub>2</sub> emitted from N. America and E. Asia produces 3–4 times as many new particles as one kilogram of SO<sub>2</sub> emitted from W. Europe, despite producing less SO<sub>4</sub>. Regional differences in particle production and growth mean that N. America and E. Asia produce 50 nm diameter CCN up to 70% more efficiently than W. Europe. In other models (e.g., Rasch et al., 2000; Koch et al., 2007) where Europe had the lowest burden potential, the contrast in CCN production could be even more marked than we find here. However, at larger sizes of 80 and 100 nm Europe and N. America have CCN potentials up to 2.75 times that of E. Asia.

The nucleation rate in the free and upper troposphere is uncertain. Nevertheless, although a change in the rate by a factor of 10 has a strong effect on the total number of particles in the atmosphere, it has only a minor effect on the relative number produced by each region. Other factors in the model may be more important. For example, Trivitanurak et al. (2008) compared three models of aerosol microphysics, including GLOMAP. They found large differences in the production of particles in the free troposphere and up to 30% differences in lower atmospheric CCN due to structural and transport differences in the models. Beyond the straightforward sensitivity tests that we have performed here, a more detailed comparison of similar models would be useful to better define regional variations in CCN production. Changes in cloud drop number and indirect forcing should also be calculated based on changes in particle number and size distribution.

One consequence of our results is that long term trends in SO<sub>4</sub> aerosol forcing will not track either the emissions of SO<sub>2</sub> or the SO<sub>4</sub> burden. We have previously shown that the different oxidant limitations on SO<sub>4</sub> production in Europe, N. America and Asia can strongly affect the long term changes in the SO<sub>4</sub> burden as emissions change (Manktelow et al., 2007). The regionally varying production of CCN quantified here will determine how effectively the SO<sub>4</sub> can influence climate.

This study also highlights the importance of microphysical processes in determining the impact of aerosol on climate and suggests that aerosol mass models may not correctly diagnose regional aerosol indirect forcing due to secondary aerosol. We have focused on one factor – the regionally variable production of sulfate particles in the free troposphere – that can influence the regional forcing potential of emissions, but there are likely to be others. One example is boundary layer particle formation events, which may contribute an additional 3–20% to CCN concentrations (Spracklen et al., 2008) and will further complicate the distribution of CCN from regional emissions. As yet our understanding of regional variations in such nucleation events does not permit us to include the process here. Another regionally varying

factor is the availability of condensing secondary organic material which will influence the production of CCN-sized particles from nuclei. With these and other microphysical processes we need to be aware of potential regional variations and the impact on forcings per unit emission.

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