Weak global sensitivity of cloud condensation nuclei and the aerosol indirect effect to Criegee + SO₂ chemistry

J. R. Pierce¹,², M. J. Evans³,⁴, C. E. Scott⁵, S. D. D’Andrea²,¹, D. K. Farmer⁶, E. Swietlicki⁷, and D. V. Spracklen⁵

¹Department of Atmospheric Science, Colorado State University, Ft. Collins, CO, USA
²Department of Physics and Atmospheric Science, Dalhousie University, Halifax, NS, Canada
³National Centre for Atmospheric Science, University of York, York, UK
⁴Department of Chemistry, University of York, York, UK
⁵School of Earth and Environment, University of Leeds, Leeds, UK
⁶Department of Chemistry, Colorado State University, Ft. Collins, CO, USA
⁷Division of Nuclear Physics, Lund University, Lund, Sweden

Correspondence to: J. R. Pierce (jeffrey.robert.pierce@gmail.com)

Received: 7 December 2012 – Published in Atmos. Chem. Phys. Discuss.: 20 December 2012 Revised: 27 February 2013 – Accepted: 4 March 2013 – Published: 15 March 2013

Abstract. H₂SO₄ vapor is important for the nucleation of atmospheric aerosols and the growth of ultrafine particles to cloud condensation nuclei (CCN) sizes with important roles in the global aerosol budget and hence planetary radiative forcing. Recent studies have found that reactions of stabilized Criegee intermediates (CIs, formed from the ozonolysis of alkenes) with SO₂ may be an important source of H₂SO₄ that has been missing from atmospheric aerosol models. For the first time in a global model, we investigate the impact of this new source of H₂SO₄ in the atmosphere. We use the chemical transport model, GEOS-Chem, with the online aerosol microphysics module, TOMAS, to estimate the possible impact of CIs on present-day H₂SO₄, CCN, and the cloud-albedo aerosol indirect effect (AIE). We extend the standard GEOS-Chem chemistry with CI-forming reactions (ozonolysis of isoprene, methyl vinyl ketone, methacrolein, propene, and monoterpenes) from the Master Chemical Mechanism. Using a fast rate constant for CI+SO₂, we find that the addition of this chemistry increases the global production of H₂SO₄ by 4%. H₂SO₄ concentrations increase by over 100% in forested tropical boundary layers and by over 10–25% in forested NH boundary layers (up to 100% in July) due to CI+SO₂ chemistry, but the change is generally negligible elsewhere. The predicted changes in CCN were strongly dampened to the CI+SO₂ changes in H₂SO₄ in some regions: less than 15% in tropical forests and less than 2% in most mid-latitude locations. The global-mean CCN change was less than 1% both in the boundary layer and the free troposphere. The associated cloud-albedo AIE change was less than 0.03 W m⁻². The model global sensitivity of CCN and the AIE to CI+SO₂ chemistry is significantly (approximately one order-of-magnitude) smaller than the sensitivity of CCN and AIE to other uncertain model inputs, such as nucleation mechanisms, primary emissions, SOA (secondary organic aerosol) and deposition. Similarly, comparisons to size-distribution measurements show that uncertainties in other model parameters dominate model biases in the model-predicted size distributions. We conclude that improvement in the modeled CI+SO₂ chemistry would not likely lead to significant improvements in present-day CCN and AIE predictions.

1 Introduction

Atmospheric aerosol particles regulate climate by scattering/absorbing sunlight (aerosol direct effect on climate) (Charlson et al., 1992) and by acting as cloud condensation nuclei (CCN) and affecting cloud albedo and lifetime (aerosol indirect effects, AIEs) (Albrecht, 1989; Twomey, 1974). These aerosol/climate effects, in particular the AIEs, represent the largest uncertainties in the radiative forcing change between 1750 and 2000 as quantified by the Intergovernmental Panel on Climate Change (Forster et al., 2007).
The uncertainties in the indirect effect are due, in part, to uncertainties in the processes that shape CCN in global aerosol predictions.

CCN represent the subset of atmospheric aerosols on which cloud droplets may form. Whether or not a particle acts as a CCN in a cloud depends on the maximum supersaturation in the cloud, as well as the size and composition of the particle. Typically, particles must have dry diameters > 30–100 nm to act as CCN, with smaller particles activating if there is a strong cloud updraft and if the particle is hygroscopic (Nenes and Seinfeld, 2003; Petters and Kreidenweis, 2007). CCN are created when (1) particles of CCN size/hygroscopicity are emitted directly to the atmosphere, (2) particles are emitted at sizes too small to act as CCN but grow to CCN size through condensation of vapors (generally sulfuric acid and organics), or (3) nucleation of ~ 1 nm particles occurs (via clustering of sulfuric acid and likely organic NH3 and H2O molecules), with these particles also growing via condensation to CCN sizes (Merikanto et al., 2009; Pierce and Adams, 2009c). However, not all ultrafine (Dp < 100 nm) particles will survive to grow to CCN-sized particles as many will be lost by coagulation before reaching CCN sizes (Pierce and Adams, 2007). Thus, the balance of emissions, nucleation, condensational growth and coagulational losses must be accurately represented in models in order to predict CCN.

Sulfuric acid (H2SO4) vapor is a key component of CCN creation as it contributes to both aerosol nucleation and the growth of the ultrafine particles to CCN sizes (Kulmala et al., 2004). While H2SO4 is not the only species involved in tropospheric nucleation, nucleation rates measured in all parts of the troposphere have been shown to have at least linear dependence on H2SO4 concentrations (e.g. Sihto et al., 2006). In many locations, such as the polluted boundary layer, remote oceans and the free troposphere, H2SO4 may be a dominant species in aerosol growth (Jung et al., 2006), although organic condensation may dominate in many continental regions (Jimenez et al., 2009; Riipinen et al., 2011). Thus, uncertainties in the production of H2SO4 vapor (via gas phase oxidation of SO2) may lead to uncertainties in CCN predictions.

SO2, the precursor of H2SO4 vapor, has three dominant fates in the atmosphere: (1) it may be removed from the atmosphere through dry or wet deposition without any chemical transformation in the atmosphere, (2) it may be oxidized by H2O2 or O3 in cloud water to form condensed sulfate, or (3) it may be oxidized in the gas phase (traditionally in models this is only by OH) to form H2SO4 vapor, which will participate in aerosol nucleation or condensation as described earlier. Models generally agree that the deposition is the dominant pathway globally followed by aqueous chemistry, then gas-phase chemistry, and the gas-phase chemistry pathway has been predicted to contribute 5–18 % of the loss of SO2 (Berglen et al., 2004; Chin et al., 1996; Koch et al., 1999; Sofen et al., 2011). Thus, there are uncertainties in the production of H2SO4 vapors in models that may lead to errors in the aerosol microphysical processes associated with H2SO4.

Traditionally, the sole pathway of H2SO4 vapor production in models was via the reaction of SO2 gas with the hydroxyl radical OH (e.g. Berglen et al., 2004; Chin et al., 1996; Koch et al., 1999; Sofen et al., 2011). However, there has recently been much attention given to the reaction of SO2 with stabilized Criegee intermediates (CIs) (Boy et al., 2012; Mauldin et al., 2012; Vereecken et al., 2012; Welz et al., 2012). (Throughout this paper, we will abbreviate the stabilized Criegee intermediates as simply “CIs”. When discussing the energetic Criegee intermediate, which may either decompose or stabilize (by collision with O2 or N2), we will explicitly state that it is the energetic Criegee.) The CI+SO2 reaction has gained much attention because of the possibility of these reactions creating H2SO4. CIs are zwitterions of carbonyl oxides that are formed during ozonolysis of alkenes. Because there are many different alkenes emitted to the atmosphere, there are many different potential CIs relevant to the atmosphere. As alkenes tend to be short-lived in the atmosphere (~ hours), the CIs will be limited to alkene source regions, such as the vegetated continental boundary layer (particularly tropical, broad-leaf and boreal forests) and regions with anthropogenic VOC emissions.

The chemical loss of the CIs is dominated by reaction with water vapor. The CIs can potentially also react with other compounds such as CO, SO2, NO, NO2, but based on previous rate-constant evaluations, these routes were not considered important oxidation pathways for most atmospheric modeling studies. However, the recent study of Welz et al. (2012) showed that the reaction of a CI, H2COO, with SO2 and NO2 was significantly faster (3.9 × 10−11 and 7.0 × 10−12 cm3 s−1, respectively) than previously considered (e.g. 7.0 × 10−14 and 1 × 10−15 cm3 s−1, Jenkin et al., 1997). These reaction rates published by Welz et al. (2012) suggest that the CI could be an additional important oxidant for SO2 in regions with alkene emissions. Although significant, the study of Welz et al. (2012) left several unresolved issues. The rates were only measured for the smallest CI, H2COO, leaving the potential for different CIs to react at different rates. Additionally, the study was also done at low pressure (4 Torr), making it unclear if this rate constant is appropriate for atmospheric conditions.

Independently, Mauldin et al. (2012) found that they needed an additional oxidant of SO2 to reach closure for H2SO4 concentrations. They also found that this additional oxidant was strongly enhanced by the presence of emissions from vegetation, to which they concluded that the alkenes from the vegetation (mostly isoprene and various monoterpenes, such as α-pinene) enhanced the production of CIs and H2SO4. Mauldin et al. (2012) deduced that the reaction rate constants of SO2 with CIs from ozonolysis of α-pinene and limonene were 6 × 10−13 cm3 s−1 and 8 × 10−13 cm3 s−1, respectively, under boundary-layer atmospheric conditions.

www.atmos-chem-phys.net/13/3163/2013/
While slower than the rates found in Welz et al. (2012), these rates are still about 1 order-of-magnitude faster than previously used (e.g. 7.0 × 10^{-14} \text{cm}^3 \text{s}^{-1}, Jenkin et al., 1997). A recent study by Boy et al. (2012) used measurements and modeling of Hyytiälä, Finland, and Hohenpeissenberg, Germany, to determine the importance of CIs for SO_2 oxidation and H_2SO_4 formation at these sites. When using the rate coefficients estimated in the Mauldin et al. (2012) and Welz et al. (2012) studies, they found that the CIs could be responsible for up to 50% of SO_2 oxidation at these locations.

Theoretical calculations of the reaction of CIs with SO_2 by Vereecken et al. (2012) showed that while smaller CIs (e.g. H_2COO) produce H_2SO_4 from the reaction with SO_2, larger CIs (such as those that may be produced from typical alkenes in the atmosphere) may produce stable sulfur-bearing secondary ozonides (i.e. the SO_2 sticks to the CI). Although entirely speculative at this point, these sulfur-bearing secondary ozonides may have low volatilities and may be a possible reaction in the enhancement of biogenic SOA (secondary organic aerosol) by anthropogenic pollution (e.g. Spracklen et al., 2011b).

Thus, there are still large uncertainties regarding CI+SO_2 chemistry. The theoretical findings of Vereecken et al. (2012) conflict with the measurements of Mauldin et al. (2012), and the CI+SO_2 rate constants derived from the larger alkenes in Mauldin et al. (2012) are over 1 order-of-magnitude slower than the rate constants measured for H_2COO by Welz et al. (2012). However, while these uncertainties in CI+SO_2 chemistry persist, scoping studies of the potential importance of CI chemistry on CCN and climate can be performed to determine how critical these CI+SO_2 reactions may be.

In this paper, we attempt to provide an upper bound for the potential of CI+SO_2 → H_2SO_4 chemistry to enhance CCN concentrations and the cloud albedo AIE in a global chemical transport model with online aerosol microphysics. Our goal is to determine if the CI+SO_2 reactions may have an appreciable effect on CCN/AIE predictions and to provide recommendations for future measurements. The following section provides an overview of the model used in this study. The results and conclusions follow in Sects. 3 and 4.

2 Methods

In this paper, we use GEOS-Chem-TOMAS, a global chemical transport model with online aerosol microphysics. GEOS-Chem-TOMAS uses GEOS-Chem v8.02.02 (http://www.geos-chem.org), and has 4° × 5° horizontal resolution as well as 30 vertical layers from the surface to 0.01 hPa. Limitations due to the model resolution are discussed in the conclusions. Meteorological inputs are from the GEOS3 reanalysis (http://gmao.gsfc.nasa.gov).

GEOS-Chem was extended with the TOMAS aerosol module (Adams and Seinfeld, 2002; Lee and Adams, 2010; Lee et al., 2009; Pierce and Adams, 2006, 2009a, b, c; Pierce et al., 2007, 2009; Snow-Kropla et al., 2011; Trivitayanurak et al., 2008; Westervelt et al., 2012). This version of TOMAS simulates the aerosol size distribution using 40 size sections ranging from 1 nm to 10 µm. In TOMAS, we simulate sulfate, sea-salt, organic carbon, black carbon and dust. In our base-case simulations, secondary organic aerosol (SOA) is formed from terrestrial biogenic sources only. The biogenic SOA source is 10% of monoterpene emissions, and represents an annual flux of 18 Tg yr^{-1}. In this paper, we perform sensitivity studies where we add 100 Tg yr^{-1} of additional SOA that is correlated with CO based on the findings of Spracklen et al. (2011b). This additional SOA is used as a sensitivity case because the efficacy of nucleated particles forming CCN depends on the rate of SOA condensation (Pierce and Adams, 2009c; Spracklen et al., 2008). SOA is assumed to be non-volatile and is distributed across the aerosol size distribution proportionally to the Fuchs-corrected aerosol surface area (Pierce et al., 2011; Riipinen et al., 2011). Nucleation in these simulations is the binary scheme of Vehkamäki et al. (2002), and we use activation nucleation (Silhó et al., 2006) in the boundary layer with an A-factor of 2 × 10^{-6} s^{-1} (Spracklen et al., 2008). Nucleation, growth and CCN formation rates in this version of the model were tested against observations at 5 locations in Westervelt et al. (2012). Details on emissions in GEOS-Chem are found in Van Donkelaar et al. (2008).

We calculate the first aerosol indirect effect (AIE), or cloud albedo effect, using the offline version of the Edwards and Slingo (1996) radiative transfer model. Our method is described in detail in Spracklen et al. (2011a); the fractional change in cloud droplet number concentration (CDNC) between two simulations is used to perturb the effective radii of cloud droplets in the radiative transfer model. To determine the AIE, net radiative fluxes at the top of the atmosphere are then compared to those obtained from a control experiment with no perturbation to cloud droplet effective radii. CDNC are calculated using the aerosol size distributions predicted by the GEOS-Chem-TOMAS simulations along with a mechanistic parameterization of cloud drop formation (Nenes and Seinfeld, 2003). As a base assumption, we assume a uniform updraft velocity of 0.2 m s^{-1}, but test values between 0.1 and 0.5 m s^{-1} to examine the sensitivity of the AIE to this assumption. We employ a 1983–2008 multiannual mean cloud climatology from the International Satellite Cloud Climatology Project (ISCCP). Rap et al. (2013) found a low sensitivity to the cloud climatology used when comparing the AIE obtained using cloud fields for a single year to the AIE obtained when a multi-annual mean cloud climatology is used (Table A1, Rap et al., 2013). As we only quantify the cloud albedo AIE sensitivity to CI+SO_2 chemistry, the total AIE (when cloud lifetime effects are included) may be larger.

We updated the standard GEOS-Chem alkene-O_3 chemistry scheme following the methodology used in the Master Chemical Mechanism (MCM) (Jenkin et al., 1997) (http:
Overview of simulations

Table 1 shows an overview of the four GEOS-Chem-TOMAS simulations performed in this study. The two BASE simulations include only biogenic SOA, while the two XSOA simulations include an extra 100 Tg SOA yr$^{-1}$. This extra SOA does not contribute to additional CI formation or alter the gas-phase chemistry scheme in any way. The simulations without “CI” in their name do not include CI+SO$_2$ chemistry, and the simulations with “CI” in the name do include this chemistry. The BASE-CI and XSOA-CI simulations use the fast CI+SO$_2$ rate constant found by Welz et al. (2012), which are over 1 order-of-magnitude larger than those found by Mauldin et al. (2012) and over 2 orders-of-magnitude faster than those used in MCM. The Welz et al. (2012) rate constant is used for all CIs simulated in the model, and it allows us to provide an upper bound for the impact of CI chemistry on CCN and the aerosol indirect effect.

Each model simulation was run for 13 months (1 December 2000–1 January 2002) from a pre-spin-up restart file. The first month of the simulation was used as additional spin-up to let the different simulations tested here diverge.

3 Results

3.1 Criegee intermediate budget

Table 2 shows the sources and sinks of CIs in the BBASE-CI (and the XSOA-CI) simulations. About 62 % of the CI molecules are formed from the ozonolysis of isoprene (including CIs from the ozonolysis of isoprene products, methyl vinyl ketone (MVK) and methacrolein (MACR)). The ozonolysis of monoterpenes is responsible for about 25 % of the CIs, and the rest (13 %) is from the ozonolysis of the grid boxes where CO is emitted. This extra SOA does not contribute to additional CI formation or alter the gas-phase chemistry scheme in any way. The simulations without “CI” in their name do not include CI+SO$_2$ chemistry, and the simulations with “CI” in the name do include this chemistry. The BASE-CI and XSOA-CI simulations use the fast CI+SO$_2$ rate constant found by Welz et al. (2012), which are over 1 order-of-magnitude larger than those found by Mauldin et al. (2012) and over 2 orders-of-magnitude faster than those used in MCM. The Welz et al. (2012) rate constant is used for all CIs simulated in the model, and it allows us to provide an upper bound for the impact of CI chemistry on CCN and the aerosol indirect effect.

Each model simulation was run for 13 months (1 December 2000–1 January 2002) from a pre-spin-up restart file. The first month of the simulation was used as additional spin-up to let the different simulations tested here diverge.

3 Results

3.1 Criegee intermediate budget

Table 2 shows the sources and sinks of CIs in the BBASE-CI (and the XSOA-CI) simulations. About 62 % of the CI molecules are formed from the ozonolysis of isoprene (including CIs from the ozonolysis of isoprene products, methyl vinyl ketone (MVK) and methacrolein (MACR)). The ozonolysis of monoterpenes is responsible for about 25 % of the CIs, and the rest (13 %) is from the ozonolysis of the grid boxes where CO is emitted. This extra SOA does not contribute to additional CI formation or alter the gas-phase chemistry scheme in any way. The simulations without “CI” in their name do not include CI+SO$_2$ chemistry, and the simulations with “CI” in the name do include this chemistry. The BASE-CI and XSOA-CI simulations use the fast CI+SO$_2$ rate constant found by Welz et al. (2012), which are over 1 order-of-magnitude larger than those found by Mauldin et al. (2012) and over 2 orders-of-magnitude faster than those used in MCM. The Welz et al. (2012) rate constant is used for all CIs simulated in the model, and it allows us to provide an upper bound for the impact of CI chemistry on CCN and the aerosol indirect effect.

Each model simulation was run for 13 months (1 December 2000–1 January 2002) from a pre-spin-up restart file. The first month of the simulation was used as additional spin-up to let the different simulations tested here diverge.
source regions (forests and industrial regions), the CI production rates are orders-of-magnitude slower due to the short chemical lifetimes of CI precursors. Figure 1b shows the fraction of CI that is lost by reaction with SO$_2$ in the boundary layer. Regions with high SO$_2$ concentrations and/or low absolute humidities have the highest fractional loss of CIs by SO$_2$. In the mid-latitudes, the fraction of CI loss by SO$_2$ can be more important, and it exceeds 40% in several SO$_2$-rich regions. Additionally, the poles have large regions where CI loss by reaction with SO$_2$ exceeds 30% due to low absolute humidities. In the tropical regions, the loss of CIs is almost entirely (over 95%) by reaction with H$_2$O due to the high absolute humidity and generally low SO$_2$ concentrations. Since the tropics have the highest CI production rates (Fig. 1a), the global-mean loss of CIs by reaction with SO$_2$ is low, 2.9% (Table 2).

3.2 Effect of CIs on SO$_2$-loss pathways

Figure 2 shows the global relative contributions to the various SO$_2$-loss pathways as predicted by GEOS-Chem for the BASE and BASE-CI cases (XSOA and XSOA-CI, respectively, gave identical results). Just over 60% of SO$_2$ is removed through deposition without any chemical loss in the atmosphere, and about two-thirds of this deposition is dry deposition. About 26% of the SO$_2$ is removed through aqueous chemistry, and this aqueous removal is dominated by chemistry with H$_2$O$_2$. The balance of the SO$_2$ loss (13–14%) is via gas-phase chemistry, which in the BASE simulation is entirely through oxidation with OH. Figure 2 shows that when Criegee chemistry is turned on in the BASE-CI case, the CIs contribute 0.4% globally to the loss of SO$_2$ from the atmosphere. The CIs also indirectly affect the fractional SO$_2$ loss pathways by increasing oxidant concentrations (via CI+NO$_x$ reactions) such that the OH and H$_2$O$_2$ pathways each increase by 0.1%. To compensate for the fractional 0.6% increase in the chemical loss of SO$_2$ in BASE-CI, the fractional deposition pathway is reduced by 0.6%. The decrease in the fractional contribution of deposition to SO$_2$ loss is driven by a 1.2% decrease in the lifetime and burden of SO$_2$ due to the CI+SO$_2$ chemistry. Overall, there is a net global increase...
in the fraction of SO₂ that forms H₂SO₄ vapor by 0.5% due to the addition of Criegee chemistry in GEOS-Chem, which corresponds to a 4% increase in the production of H₂SO₄ vapor in the model. However, the global H₂SO₄ burden increases only by 1.6% due to an increase in the condensation sink from an increase in nucleation in the BASE-CI case (these feedbacks will be discussed in the results section). This increase in H₂SO₄ production/concentration is not, however, homogeneous around the Earth due to CIs being located in several hot-spots in the continental boundary layer. The distribution of H₂SO₄ (and aerosols) will be explored next.

3.3 CI influence on global aerosol microphysics

Figure 3 shows the BL- and zonal-mean percent changes in the gas-phase H₂SO₄ concentrations between the BASE and BASE-CI cases (red denotes higher concentrations in the BASE-CI case) for both an annual average and the month of July (when alkene emissions from the Northern Hemispheric (NH) boreal forests are highest). The annual-mean boundary-layer plot (Fig. 3a) shows H₂SO₄ more than doubling in tropical forests due to the addition of CI+SO₂ chemistry. The large fractional change in H₂SO₄ above the tropical forests is for two reasons: (1) there is a large isoprene source in these regions resulting in a large source of alkenes for production of CI, and (2) the OH concentrations are very low in these regions (Fig. 4) due to isoprene acting as a net OH sink in the GEOS-Chem chemistry scheme, meaning that the conversion of SO₂ to H₂SO₄ is slow in these regions in the BASE simulation. The annual-average changes in H₂SO₄ in the NH boreal and broad-leaf (e.g. southeastern US) forest regions are generally 10–25% increases. The H₂SO₄-enhancement region extends from the boreal forests into the Arctic where OH concentrations are low, particularly outside of the summer. The annual-average zonal-mean plot (Fig. 3b) shows that most of the H₂SO₄ enhancement is in the boundary layer due to the short lifetime (several hours to ~1 day) of the CI precursor gases. There is some enhancement in the tropical tropopause region due to transport of CI precursors, ozone and SO₂ in deep convection.

In July (Fig. 3c, d), the H₂SO₄ enhancements in the tropics due to CI+SO₂ chemistry are nearly identical to the annual-mean plots. On the other hand, the NH forests show a much larger sensitivity of H₂SO₄ concentrations to CI chemistry due to increased isoprene and monoterpenes emissions in the

Fig. 3. Percent change in gas-phase H₂SO₄ concentration due to the addition of the CI+SO₂ chemistry (BASE-CI-BASE). The left column (a and b) is annual-mean values, and the right column (c and d) is for July. The top panels (a and c) show the boundary-layer values, and the bottom panels (b and d) show zonal-mean values.

Fig. 4. Annual-mean boundary-layer OH concentrations in the BBASE simulation.
summer. H₂SO₄ concentrations change by over 100% in the southeastern US and by over 50% in many regions of the boreal forests, which means that CI+SO₂ is responsible for about 50% and 35% of the H₂SO₄ in the BASE-CI simulation in these regions, respectively. This increase in the boreal forest regions is slightly lower than the estimates of the summertime H₂SO₄ enhancements due to CI chemistry calculated by Boy et al. (2012), where CI+SO₂ chemistry was found to explain up to 50% of the gas-phase H₂SO₄ production in Hyytiälä, Finland and Hohenpeissenberg, Germany (as opposed to ~35% in this study) even though a faster CI+SO₂ rate constant for large CIs was used here than in their work. This lower sensitivity in our model may be due to the coarse horizontal and vertical resolution of our global model compared to their local 0-D and 1-D models (that explicitly resolve the alkene-rich forest regions) used for their analysis. Nevertheless, it is possible that our estimates are not actually a sufficient upper bound for H₂SO₄ production through CI+SO₂ chemistry, and we will discuss this possibility in our conclusions. In July, the H₂SO₄ is enhanced by high percentages over Antarctica throughout the entire troposphere due to CI chemistry. This high sensitivity is due to extremely low OH and H₂SO₄ concentrations in the absence of CI chemistry. Although there is a large fractional change in Antarctica, the absolute change in this location is negligible, and CI chemistry has virtually no impact on the particle concentrations in this region (discussed next).

The H₂SO₄ differences between the XSOA and XSOA-CI cases (not shown) are nearly identical to Fig. 3. While the H₂SO₄ concentrations in XSOA are lower than BASE due to a larger condensation sink for H₂SO₄ in XSOA (and a similar difference for XSOA-CI versus BASE-CI), the fractional changes in H₂SO₄ between XSOA and XSOA-CI are similar to the fractional changes between BASE and BASE-CI. It would be useful to evaluate the model-predicted H₂SO₄ concentrations against field observations (e.g. at Hyytiälä, Finland where these observations have been performed over extended time periods (Riipinen et al., 2011) to determine if the CI+SO₂ chemistry improves modeled H₂SO₄ concentrations. However, (1) the model overpredicts H₂SO₄ by a factor of 2 at Hyytiälä even without CI+SO₂ chemistry (likely because the large model grid box also includes cities and source regions, and there are uncertainties in the condensation sink), and (2) the modeled H₂SO₄ is more sensitive to the condensation sink (80% reduction in H₂SO₄ concentrations at Hyytiälä due to the addition of the extra 100 Tg of SOA per year in the XSOA simulation) than the CI+SO₂ chemistry (25% increase in H₂SO₄ at Hyytiälä). Similarly, uncertainties in the accommodation coefficient and primary emissions would also cause uncertainties in the condensation sink. Thus, we were not able to gain any useful information about CI+SO₂ chemistry on improving H₂SO₄ concentrations in our model. On the other hand, the study of Boy et al. (2012), which simulated the local conditions explicitly with constrained condensation sinks and SO₂ concentrations, did predict that CI+SO₂ chemistry was needed for the closure of H₂SO₄ concentrations. There is no evidence from our current study to either support or refute their conclusions, so we defer to their study as the current best estimate of the role of CI+SO₂ in generating H₂SO₄.

Figures 5 and 6 show the annual-mean and July-mean, respectively, boundary-layer changes in N₃, N₁₀, N₄₀ and N₈₀ (the total number of particles larger than 3 nm, 10 nm, 40 nm and 80 nm, respectively) due to CI+SO₂ chemistry (BASE-CI – BASE). N₄₀ and N₈₀ represent a rough bound

Fig. 5. The annual-mean boundary-layer change in N₃, 10, 40 and 80 due to the addition of CI+SO₂ chemistry (BASE-CI-BASE).
for the CCN concentrations for most clouds. Similar to the enhancements in H$_2$SO$_4$ concentrations due to CI chemistry, the largest annually averaged $N$ enhancements (Fig. 5) for all size ranges are in the tropics. The enhancements are particularly large in the Amazon, where $N$ is enhanced by CI chemistry by over 25%, and CCN are enhanced by 5–15%. Outside of the tropics, the enhancements are more minor, where $N$ is nearly always less than a 15% enhancement, and CCN enhancements are generally less than 2% except for the southeast US for both $N_{40}$ and $N_{80}$ and part of Canada for $N_{40}$. There are a few regions where the addition of CI chemistry causes a decrease in $N$ and $N_{10}$. These are due to chemical feedbacks in SO$_2$ and OH concentrations due to the CI chemistry and microphysical feedbacks due to changes in aerosol surface area.

The July averages (Fig. 6) show a stronger signal in the NH forested regions due to the larger source of CI precursors (isoprene and monoterpenes) as well as more noise due to the shorter averaging period. $N_{3}$ are enhanced by over 15% in many parts of Canada and southeastern US and over 5% in northeastern Europe. In general, the enhancements in $N_{40}$ and $N_{80}$ are about a factor of 3 lower due to microphysical dampening (and do not exceed 5% in the NH outside of the southeastern US) that will be discussed shortly.

Figure 7 shows the annual- and zonal-mean change in $N_{3}$, $N_{10}$, $N_{40}$ and $N_{80}$ concentrations due to CI chemistry (BASE-CI–BASE), and unlike the similar plots for H$_2$SO$_4$ (Fig. 3b and d), the influence of the tropical CIs extend to the upper troposphere due to deep convection. The enhancements in the different size ranges show that small particles that nucleated in the tropical BL are transported to the upper troposphere by deep convection (the enhancements in H$_2$SO$_4$ in the upper troposphere were minor (Fig. 3b and d), but may have contributed to the enhancements in $N_{3}$ there also). The small particles then grow to larger sizes via condensation in the upper troposphere and during transport. Thus, the CI chemistry contributes to more than 1% enhancements in CCN concentrations throughout much of the free troposphere.

The differences in $N_{3}$, $N_{10}$, $N_{40}$ and $N_{80}$ between XSOA-CI and XSOA are very similar to the differences between BASE-CI and BASE (not shown). Although the changes in $N$ are significant between BASE and XSOA (and BASE-CI and XSOA-CI), the relative influence of CI chemistry is similar.

Figures 3 and 5–7 show that although H$_2$SO$_4$ concentrations increase by over 10% due to CI chemistry throughout the forested boundary layer (and over 100% in the tropics and over 50% in the boreal summer), the annually averaged CCN increase is generally less than 1% in the boundary layer outside of the tropics (exceptions are in some NH forests, exceeding 2% in several locations). Even in the Amazon, where the H$_2$SO$_4$ concentrations more than doubled due to CI chemistry, the CCN concentrations only increased by 5–15%. Thus, there is a strong microphysical dampening of changes in CCN to changes in H$_2$SO$_4$ in these locations. Although H$_2$SO$_4$ contributes to both nucleation and growth, the growth of particles in the forested boundary layer (where CI chemistry is important) in measurements (e.g. Riipinen et al., 2011) and in GEOS-Chem-TOMAS (Westervelt et al., 2012) is dominated by SOA. At Hyvittä, Finland, the measurements show and model predicts that SOA condensation is responsible for over 90% of the particle growth. If 90% of the condensable material in a region is SOA and the remaining 10% is H$_2$SO$_4$, a 50% increase in H$_2$SO$_4$ due to CI+SO$_2$ chemistry only represents a ~5% increase in condensible
CCN sensitivity to CI in CCN were also just under 1%. This globally averaged XSOA-CI simulations. The tropospheric-averaged changes BASE-CI simulations as well as between the XSOA and N
than the sensitivity in CCN predictions to uncertainties in

fractional changes in H$_2$SO$_4$ has only a minor influence on the growth of the particles. Nucleation, on the other hand, is linear with H$_2$SO$_4$ concentrations in the boundary layer in the model (i.e. Fig. 3a and c also show the relative change in nucleation rates due to CI chemistry), and a 50% increase in H$_2$SO$_4$ due to CI+SO$_2$ chemistry represents a 50% increase in nucleation. However, the fractional change in CCN is strongly dampened to fractional changes in nucleation rate, which has been shown in several modeling studies (Makkonen et al., 2009; Pierce and Adams, 2009b, c; Snow-Kropla et al., 2011; Spracklen et al., 2008; Wang and Penner, 2009). This dampening occurs because an increase in the nucleation rate increases the total surface area of particles. The condensation and coagulation sinks are both roughly proportional to the surface area, so (1) the growth rates are inversely proportional to the change in condensation sink since the condensible material is spread across more particle surface area, and (2) the coagulation loss rates of the new particles are proportional to the coagulation sink. Thus, an increase in the nucleation rate (in the absence of a significant increase in condensible material) reduces the probability of particles surviving to reach CCN sizes due to increased coagulation losses and longer growth times (Pierce and Adams, 2007, 2009c; Westervelt et al., 2012), and in this study, fractional changes in CCN are significantly smaller than fractional changes in H$_2$SO$_4$.

The global boundary-layer averaged change in CCN (both N40 and N80) was just under 1% between the BASE and BASE-CI simulations as well as between the XSOA and XSOA-CI simulations. The tropospheric-averaged changes in CCN were also just under 1%. This globally averaged CCN sensitivity to CI+SO$_2$ chemistry is significantly lower than the sensitivity in CCN predictions to uncertainties in nucleation mechanisms (Merikanto et al., 2009; Pierce and Adams, 2009c; Reddington et al., 2011; Spracklen et al., 2008; Wang and Penner, 2009), SOA amount (Pierce and Adams, 2009c; Spracklen et al., 2008), primary emissions amount (Adams and Seinfeld, 2003; Pierce and Adams, 2006, 2009c; Reddington et al., 2011; Spracklen et al., 2011a) and size (Pierce and Adams, 2006, 2007; Reddington et al., 2011; Spracklen et al., 2011a), SOA condensational behavior (Riipinen et al., 2011) and wet deposition (Croft et al., 2012). Many of these other uncertain factors lead to CCN uncertainties larger than 10%. Even if the simulations tested here do not represent a true upper bound for the impact of CI+SO$_2$ chemistry (e.g. the sensitivity of H$_2$SO$_4$ to CI+SO$_2$ chemistry was larger in Boy et al., 2012), the effect of CI+SO$_2$ chemistry on CCN would need to be an order-of-magnitude larger globally than predicted here in order to compete with some of the uncertain parameters listed above. Similarly, we did not test the sensitivity of CCN changes to CI+SO$_2$ chemistry under different nucleation-rate, primary-emissions or deposition assumptions; however, while uncertainties in each of these assumptions affect the CCN predictions, their effect on the sensitivity of CCN to CI+SO$_2$ chemistry is likely minimal (as was the case with the XTRA-SOA simulations, where CCN changed greatly due to the additional SOA, but the sensitivity of CCN to CI+SO$_2$ chemistry did not greatly change). Thus, while the CI+SO$_2$ chemistry is predicted to be important for CCN in some locations, particularly the Amazon, improving our understanding of CI+SO$_2$ chemistry will likely not significantly improve our estimates of CCN globally.

Fig. 7. The annual- and zonal-mean change in N3, 10, 40 and 80 due to the addition of CI+SO$_2$ chemistry (BASE-CI-BASE).
3.4 Comparison to size distribution measurements

In Fig. 8, we evaluate the model size distributions in two locations that are both affected by the CI chemistry, Hyytiälä, Finland, and the AMAZE field station in the central Amazon, Brazil. Figure 8a shows the annual-average size distributions at Hyytiälä, Finland (61°51′N, 24°17′E, 181 m a.s.l., Hari and Kulmala, 2005; Riipinen et al., 2011) predicted by the BASE, BASE-CI, XSOA and XSOA-CI simulations as well as the average-size distribution measured 2001 (the same year as the simulations). The simulated size distributions show a much larger sensitivity to the additional SOA (i.e. the difference between BASE and XSOA) than the sensitivity to the CI chemistry. The size distribution is biased towards smaller sizes in the BASE and BASE-CI simulations and biased towards larger sizes in the XSOA and XSOA-CI simulations. It appears that the model could best match the measured size distribution in Hyytiälä if a smaller amount of extra SOA than 100 Tg yr⁻¹ was used. A more detailed and general evaluation on the additional SOA (beyond the CI+SO₂ context) is currently being performed; however, it is clear that uncertainties in the amount of SOA have a much larger affect on the size distribution and CCN in Hyytiälä than CI chemistry, and any error in the representation of CI chemistry will have little effect on the performance of the model in the Hyytiälä grid box.

Figure 8b shows the same values as Fig. 8a, but for the central Amazon (02°36′S, 60°13′W, 110 m a.s.l.) in Brazil during the AMAZE campaign (Martin et al., 2010). The AMAZE campaign took place during February and March 2008, and the model data plotted are for February and March 2001. All model simulations overpredict the size distribution by 50–100 cm⁻³ throughout all sizes (with a few exceptions in the nucleation/Aitken modes where model biases are even higher). In the central Amazon, there is a much smaller sensitivity to extra SOA correlated with anthropogenic CO emission than in Hyytiälä due to the remoteness of the AMAZE station. Conversely, the sensitivity to CI chemistry is much larger than in Hyytiälä; thus, the uncertainties in the size distribution due to the two factors are similar. The CI chemistry causes significant (>25%) increases in the number of nucleation/Aitken-mode particles, which is consistent with the Amazon region in Fig. 5a and b. However, the errors in the modeled size distribution are larger than could be explained by errors in CI chemistry. Therefore, some other source of error (e.g. primary emissions, biogenic SOA or unresolved sub-grid variability) must be responsible for the model bias. Even in the region with the strongest effect of CI+SO₂ chemistry, improvement of our representation of this chemistry would not significantly improve model performance.

3.5 Aerosol indirect effect

Figure 9 shows the annual mean cloud albedo AIE change due to the addition of CI+SO₂ chemistry to the model (radiative perturbation between the BASE-CI and BASE cases). Throughout most of the globe, the AIE change is very small (<0.1 W m⁻²), as would be expected by the small changes in N₄₀ and N₈₀ throughout most of the boundary layer. The strongest cooling due to the CI+SO₂ chemistry occurs over South America and to the west of Peru, where there Amazon-influenced CCN increases meet the persistent susceptible marine stratocumulus clouds of the eastern subtropical South Pacific ocean. In this region, the AIE changes exceed −0.5 W m⁻² in some locations. There is also some minor cooling in other subtropical marine cloud regions, over the South Atlantic and the eastern coast of Australia. Overall, the regions of cooling occupy a small fraction of Earth, so the global annual mean AIE change due to the inclusion of CI chemistry is only −0.031 W m⁻² for the BASE case (and −0.034 W m⁻² for the XSOA case, not
shown but similar spatial patterns) when the updraft velocities are assumed to be 0.2 m s$^{-1}$. When the updraft velocities are varied between 0.1 and 0.5 m$^{-1}$, the range of AIE was $-0.025$ to $-0.031$ W m$^{-2}$ for the BASE case and $-0.028$ to $-0.036$ W m$^{-2}$ for XSOA. As these estimates are only for the cloud albedo AIE, the total AIE may be higher if aerosol lifetime effects were included. Similar to the results with CCN, this cloud albedo AIE change is significantly smaller than the uncertainties due to nucleation mechanisms (Pierce and Adams, 2009c; Wang and Penner, 2009; Kazil et al., 2010). SOA amount (Pierce and Adams, 2009c), primary emissions amount (Adams and Seinfeld, 2003; Pierce and Adams, 2009c; Spracklen et al., 2011a) and size (Bauer et al., 2010; Spracklen et al., 2011a), SOA condensational behavior (Riipinen et al., 2011) and wet deposition (Croft et al., 2012).

4 Conclusions

In this study, we tested the sensitivity of the reaction of stabilized Criegee intermediates (CIs) with SO$_2$ on present-day H$_2$SO$_4$, total aerosol number, and CCN concentrations as well as the cloud albedo aerosol indirect effect (AIE). Aerosol size distributions were predicted with and without CI+SO$_2$ chemistry in the GEOS-Chem-TOMAS global aerosol microphysics model. The production of CIs from the ozonolysis of isoprene, methyl vinyl ketone, methacrolein, propene, and monoterpenes (treated as if they were $\alpha$-pinene) were added to the model. CIs were lost by reaction with CO, NO, NO$_2$, H$_2$O and SO$_2$. We used the fast CI+SO$_2$ rates measured by Welz et al. (2012) in an attempt to provide an upper bound for CI+SO$_2$ chemistry.

The ozonolysis of isoprene and its products (methyl vinyl ketone, methacrolein) represented about 62 % of the CI production, with the ozonolysis of monoterpenes representing 25 % and the rest by the ozonolysis of propene. Water vapor was the dominant loss for CIs globally (96.6 %), and SO$_2$ represented most of the remaining loss (2.9 %). However, SO$_2$ was a more significant sink of CIs in the polluted and/or dry NH regions (up to 60 % in some regions). Because we used the fast Welz et al. (2012) rate constant for all CI+SO$_2$ reactions, these estimates of CI+SO$_2$ were likely an upper bound, and could be over an order-of-magnitude lower if other published rate constants were used. We also note the there are significant uncertainties on the rate constant of CI+H$_2$O, leading to large uncertainties on the atmospheric fate of CI radicals.

The addition of the CI+SO$_2$ chemistry increased the production of H$_2$SO$_4$ globally by 4 %. However, the H$_2$SO$_4$ increases were driven almost entirely by increases over forested continental regions with large fluxes of biogenic alkene emissions. The annually averaged H$_2$SO$_4$ increases were over 100 % in the tropics and were more than 10 % in mid-latitude forests (though over 50 % in many mid-latitude forests in July). The increases in N3, N10, N40 and N80 (the total particle number with diameters larger than 3, 10, 40 and 80 nm, respectively) due to the addition of CI chemistry were generally co-located with, but were much smaller than, the increases in H$_2$SO$_4$. The annually averaged changes in CCN (N40 and N80) were less than 25 % in the tropics and less than 5 % in most mid-latitude locations. In July, when biogenic alkene emissions from mid-latitude forests are at their peak, many mid-latitude regions showed up to a 15 % sensitivity in CCN due to CI+SO$_2$ chemistry. The relatively small sensitivity of CCN compared to the larger sensitivity of H$_2$SO$_4$ to CI chemistry is due, in part, to CI chemistry generally being only important in forested locations where SOA (as opposed to H$_2$SO$_4$) is the dominant species contributing to ultrafine particle growth. Thus, increasing H$_2$SO$_4$ in these locations increased nucleation rates but did not significantly increase growth rates, and CCN were dampened to changes in H$_2$SO$_4$ similar to previous studies looking at the sensitivity of CCN to changes in the nucleation rate (Makkonen et al., 2009; Pierce and Adams, 2009b, c; Snow-Kropla et al., 2011; Spracklen et al., 2008; Wang and Penner, 2009).

The global-averaged boundary-layer and free-tropospheric changes to CCN due to the addition of CI+SO$_2$ chemistry were both less than 1 %, which is a significantly smaller CCN sensitivity than the uncertainty in CCN due to uncertainty in nucleation mechanisms (Merikanto et al., 2009; Pierce and Adams, 2009c; Reddington et al., 2011; Spracklen et al., 2008; Wang and Penner, 2009). SOA amount (Pierce and Adams, 2009c; Spracklen et al., 2008), primary emissions amount (Adams and Seinfeld, 2003; Pierce and Adams, 2009c; Reddington et al., 2011), and size (Pierce and Adams, 2006, 2007; Reddington et al., 2011; Spracklen et al., 2011a), SOA condensational behavior (Riipinen et al., 2011) and wet deposition (Croft et al., 2012).
behavior (Riipinen et al., 2011) and wet deposition (Croft et al., 2012). Subsequently, the uncertainty in the cloud albedo AIE change due to Cl + SO$_2$ chemistry was about 0.03 W m$^{-2}$ (depending on the assumed updraft velocity and SOA assumption), which is also significantly less than the other model uncertainties described above. The simulations presented here may not be a true upper bound on the impact of Cl + SO$_2$ chemistry on CCN and the AIE (e.g. we found a smaller sensitivity of H$_2$SO$_4$ to Cl + SO$_2$ chemistry than Boy et al. (2012) at the two sites that they investigated). It is possible that the model sensitivity may be biased either low or high due to the coarse model resolution. At the two European sites investigated by Boy et al. (2012), the model-predicted sensitivity of H$_2$SO$_4$ concentrations to Cl + SO$_2$ chemistry was biased low, which may have been due to not explicitly resolving the alkene-rich forested observation regions. On the other hand, the instant mixing of anthropogenic SO$_2$ emissions with biogenic alkene emissions in the coarse grid boxes could lead to a larger fraction of anthropogenic SO$_2$ being oxidized by Cls in the model than in reality, which could bias the model-predicted impacts of Cl + SO$_2$ chemistry on CCN high (however, we have no evidence of this). Regardless, it would take an order-of-magnitude increase in the CCN sensitivity to Cl + SO$_2$ chemistry to be similar in importance to many of the other uncertain model parameters listed above. Similarly, comparisons to size-distribution measurements at boreal-forest and tropical-forest locations showed that other model uncertainties dominated errors in the aerosol size distribution. Thus, we conclude that improvements in our understanding of Cl + SO$_2$ chemistry would not lead to significant improvements in present-day CCN predictions. However, it is possible that Cl + SO$_2$ chemistry has a stronger effect on pre-industrial CCN predictions (not tested here), and thus could be important for determining the radiative forcing change between pre-industrial and present-day. Additionally, a warmer future climate could bring additional biogenic alkene emissions, which may increase the fraction of SO$_2$ that is oxidized by Cls. However, additional biogenic alkenes may also yield more SOA. Additional SOA coupled with potential future reductions in SO$_2$ emissions would mean that H$_2$SO$_4$ would be even less important for ultralight particle growth, and the sensitivity of CCN to Cl + SO$_2$ chemistry could be even less than in the present day.

One possible outcome of Cl + SO$_2$ chemistry that we did not explore here is the formation of stable sulfur-bearing secondary ozonides (Vereecken et al., 2012). As the addition of an SO$_2$ to the Cl could lead to a reduction in vapor pressure of the Cl, SO$_2$ + Cl could lead to an increase in SOA and may be one of the reasons that anthropogenic pollution has been shown to increase the abundance of biogenic SOA (Spracklen et al., 2011b). If the reaction rates of Welz et al. (2012) are applied to Cl + SO$_2$ → stable sulfur-bearing secondary ozone, and we assume that 0 % of the Cl would have formed SOA if it had not reacted with SO$_2$ (an obvious underestimate) and 100 % of the stable sulfur-bearing sec-

secondary ozonide forms SOA, we find that the enhancement of SOA would be several to 10 s of Tg SOA yr$^{-1}$. While this calculation is likely an upper bound, it shows that Cl + SO$_2$ chemistry might be important through this pathway, and this should be explored in future work.

Acknowledgements. We thank the Atlantic Computational Excellence Network (ACEnet) and the Canadian Foundation for Innovation (CFI) for the computing resources used in this study. We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Electric Power Research Institute (EPRI) for funding.

Edited by: V.-M. Kerminen

References


www.atmos-chem-phys.net/13/3163/2013/


