



# Weak global sensitivity of cloud condensation nuclei and the aerosol indirect effect to Criegee + SO<sub>2</sub> chemistry

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**Abstract.** H<sub>2</sub>SO<sub>4</sub> 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 SO<sub>2</sub> may be an important source of H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub>, 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+SO<sub>2</sub>, we find that the addition of this chemistry increases the global production of H<sub>2</sub>SO<sub>4</sub> by 4%. H<sub>2</sub>SO<sub>4</sub> 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+SO<sub>2</sub> chemistry, but the change is generally negligible elsewhere. The predicted changes in CCN were strongly dampened to the CI+SO<sub>2</sub> changes in H<sub>2</sub>SO<sub>4</sub> 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<sup>-2</sup>. The model global sensitivity of CCN and the AIE to CI+SO<sub>2</sub> 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+SO<sub>2</sub> 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  $> 30\text{--}100\text{ nm}$  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  $\sim 1\text{ nm}$  particles occurs (via clustering of sulfuric acid and likely organic  $\text{NH}_3$  and  $\text{H}_2\text{O}$  molecules), with these particles also growing via condensation to CCN sizes (Merikanto et al., 2009; Pierce and Adams, 2009c). However, not all ultrafine ( $D_p < 100\text{ nm}$ ) 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 coagulation losses must be accurately represented in models in order to predict CCN.

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 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  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  concentrations (e.g. Sihto et al., 2006). In many locations, such as the polluted boundary layer, remote oceans and the free troposphere,  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  vapor (via gas phase oxidation of  $\text{SO}_2$ ) may lead to uncertainties in CCN predictions.

$\text{SO}_2$ , the precursor of  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{O}_2$  or  $\text{O}_3$  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  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  (Berglen et al., 2004; Chin et al., 1996; Koch et al., 1999; Sofen et al., 2011). Thus, there are uncertainties in the

production of  $\text{H}_2\text{SO}_4$  vapors in models that may lead to errors in the aerosol microphysical processes associated with  $\text{H}_2\text{SO}_4$ .

Traditionally, the sole pathway of  $\text{H}_2\text{SO}_4$  vapor production in models was via the reaction of  $\text{SO}_2$  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  $\text{SO}_2$  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  $\text{O}_2$  or  $\text{N}_2$ ), we will explicitly state that it is the energetic Criegee.) The CI+ $\text{SO}_2$  reaction has gained much attention because of the possibility of these reactions creating  $\text{H}_2\text{SO}_4$ . 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 ( $\sim$  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,  $\text{SO}_2$ , NO,  $\text{NO}_2$ , 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,  $\text{H}_2\text{COO}$ , with  $\text{SO}_2$  and  $\text{NO}_2$  was significantly faster ( $3.9 \times 10^{-11}$  and  $7.0 \times 10^{-12}\text{ cm}^3\text{ s}^{-1}$ , respectively) than previously considered (e.g.  $7.0 \times 10^{-14}$  and  $1 \times 10^{-15}\text{ cm}^3\text{ s}^{-1}$ , Jenkin et al., 1997). These reaction rates published by Welz et al. (2012) suggest that the CI could be an additional important oxidant for  $\text{SO}_2$  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,  $\text{H}_2\text{COO}$ , 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  $\text{SO}_2$  to reach closure for  $\text{H}_2\text{SO}_4$  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  $\alpha$ -pinene) enhanced the production of CIs and  $\text{H}_2\text{SO}_4$ . Mauldin et al. (2012) deduced that the reaction rate constants of  $\text{SO}_2$  with CIs from ozonolysis of  $\alpha$ -pinene and limonene were  $6 \times 10^{-13}\text{ cm}^3\text{ s}^{-1}$  and  $8 \times 10^{-13}\text{ cm}^3\text{ s}^{-1}$ , respectively, under boundary-layer atmospheric conditions.

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.  $7.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ , 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  $\text{SO}_2$  oxidation and  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  oxidation at these locations.

Theoretical calculations of the reaction of CIs with  $\text{SO}_2$  by Vereecken et al. (2012) showed that while smaller CIs (e.g.  $\text{H}_2\text{COO}$ ) produce  $\text{H}_2\text{SO}_4$  from the reaction with  $\text{SO}_2$ , 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  $\text{SO}_2$  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+ $\text{SO}_2$  chemistry. The theoretical findings of Vereecken et al. (2012) conflict with the measurements of Mauldin et al. (2012), and the CI+ $\text{SO}_2$  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  $\text{H}_2\text{COO}$  by Welz et al. (2012). However, while these uncertainties in CI+ $\text{SO}_2$  chemistry persist, scoping studies of the potential importance of CI chemistry on CCN and climate can be performed to determine how critical these CI+ $\text{SO}_2$  reactions may be.

In this paper, we attempt to provide an upper bound for the potential of CI+ $\text{SO}_2 \rightarrow \text{H}_2\text{SO}_4$  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+ $\text{SO}_2$  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  $4^\circ \times 5^\circ$  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; Trivitanurak 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  $\mu\text{m}$ . 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  $\text{Tg yr}^{-1}$ . In this paper, we perform sensitivity studies where we add 100  $\text{Tg yr}^{-1}$  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; Riipinen et al., 2011; 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 (Sihto et al., 2006) in the boundary layer with an A-factor of  $2 \times 10^{-6} \text{ s}^{-1}$  (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  $0.2 \text{ m s}^{-1}$ , but test values between 0.1 and  $0.5 \text{ m s}^{-1}$  to examine the sensitivity of the AIE to this assumption. We employ a 1983–2008 multi-annual 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+ $\text{SO}_2$  chemistry, the total AIE (when cloud lifetime effects are included) may be larger.

We updated the standard GEOS-Chem alkene- $\text{O}_3$  chemistry scheme following the methodology used in the Master Chemical Mechanism (MCM) (Jenkin et al., 1997) ([\[www.atmos-chem-phys.net/13/3163/2013/\]\(http://www.atmos-chem-phys.net/13/3163/2013/\)](http://</a></p></div><div data-bbox=)

**Table 1.** Overview of the GEOS-Chem-TOMAS simulations performed in this study.

Simulation name	CI+SO <sub>2</sub>	Extra 100 Tg SOA yr <sup>-1</sup>
BASE	no	no
BASE-CI	yes	no
XSOA	no	yes
XSOA-CI	yes	yes

//mcm.leeds.ac.uk) for propene and isoprene (the only primary emitted compounds with double bonds considered by the standard GEOS-Chem chemistry scheme) and for methyl vinyl ketone (MVK) and methacrolein (MACR) (isoprene degradation products). Additionally, we added the initial oxidations steps (OH, NO<sub>3</sub> and O<sub>3</sub>) of monoterpene chemistry into the scheme (monoterpenes are used for SOA in standard GEOS-Chem simulations but not considered in the standard gas-phase chemistry scheme), and we treat the chemistry for all monoterpenes as if they are  $\alpha$ -pinene (the dominant monoterpene). The initial ozonolysis of each of these compounds (isoprene, MVK, MACR, propene and monoterpenes) results in a primary, energetic Criegee intermediate, which may either decompose or form a stabilized Criegee intermediate. The net reactions to form the stabilized Criegee intermediates are shown in Table 2. These stabilized Criegee radicals (CIs) then react with CO, NO, NO<sub>2</sub>, SO<sub>2</sub> and water vapor to form stable products. The rate constants for CO and NO are taken from the MCM and are  $1.2 \times 10^{-15}$  and  $1.00 \times 10^{-14}$ , respectively, for all CIs. The rate constant for reaction with water vapor is again taken from the MCM and depends upon the structure of the Criegee radical and varies from  $6 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$  to  $1.6 \times 10^{-17}$ . For SO<sub>2</sub> and NO<sub>2</sub>, we use the fast CI oxidation rates of  $3.9 \times 10^{-11}$  and  $7.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , respectively, from Welz et al. (2012) for all CIs. This rate constant for SO<sub>2</sub> allows us to determine a probable 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-spun-up restart file. The first month of the simulation was used as additional spin-up to let the different simulations tested here diverge.

## 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<sup>-1</sup> that is correlated with anthropogenic CO emissions based on Spracklen et al. (2011b). The XSOA cases allow us to determine if the effect of the extra H<sub>2</sub>SO<sub>4</sub> formed by CI+SO<sub>2</sub> chemistry on CCN is stronger/weaker in the presence of extra SOA, which is a major uncertainty in global aerosol models. The extra SOA in the XSOA cases is added as condensable material in

**Table 2.** Sources and sinks of CIs in the BASE-CI and XSOA-CI simulations (same for both simulations).

Sources of CIs	Rate [Gmol yr <sup>-1</sup> ]
ISOP + O <sub>3</sub> → MACROO	48.4
ISOP + O <sub>3</sub> → MVKOO	32.2
MACR, MVK + O <sub>3</sub> → MGLOO	21.8
PRPE + O <sub>3</sub> → CH <sub>3</sub> CHOO	21.5
ISOP, MACR, MVK, PRPE + O <sub>3</sub> → CH <sub>2</sub> OO	137.7
*MO + O <sub>3</sub> → APINOO	85.2
Total sources	346.8
Sinks of CIs	Rate [Gmol yr <sup>-1</sup> ]
CI + CO	0.326
CI + NO	0.00072
CI + NO <sub>2</sub>	1.44
CI + H <sub>2</sub> O	335.0
CI + SO <sub>2</sub>	10.05
Total sinks	346.8

ISOP = isoprene, MACR = methacrolein, MVK = methyl vinyl ketone, MGL = methylglyoxal, PRPE = propene, MO = all monoterpenes, APIN =  $\alpha$ -pinene, CIs end in "OO".

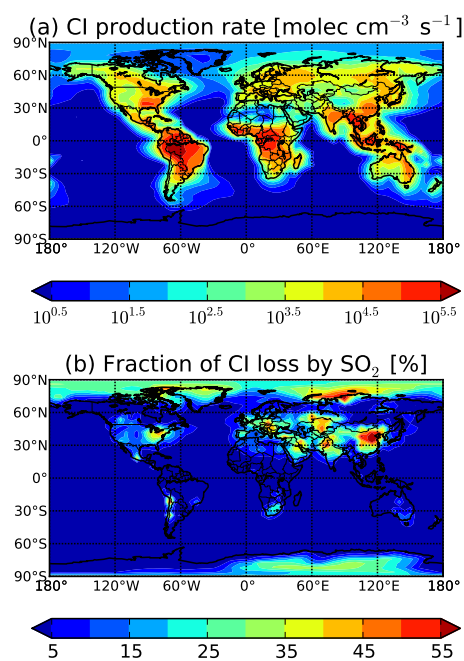
\* Criegees from all monoterpenes are assumed to take the form of the  $\alpha$ -pinene criegee.

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<sub>2</sub> 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<sub>2</sub> 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 CCN impacts of CI+SO<sub>2</sub> → H<sub>2</sub>SO<sub>4</sub> chemistry. Because the extra SOA in the XSOA cases have no impact on the CI chemistry, the BASE-CI and XSOA-CI cases have the same CI budgets (described in the next section).

## 3 Results

### 3.1 Criegee intermediate budget

Table 2 shows the sources and sinks of CIs in the BASE-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

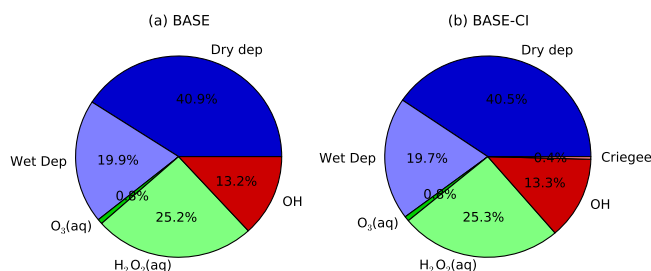


**Fig. 1.** (a) The annual-average boundary-layer production rate of CIs in the BBASE-CI (and XSOA-CI, same for both simulations) simulation. (b) The annual-average fraction of CI loss via reaction with  $\text{SO}_2$  in the same simulation in the boundary layer.

of propene. In the calculation of these fractions we have assumed that isoprene (and MVK and MACR) accounts for 83 % of  $\text{CH}_2\text{OO}$  production and propene for 17 % of  $\text{CH}_2\text{OO}$  production (this is the same ratio as isoprene (and MVK and MACR) versus propene forming other CIs (i.e.  $\text{MACROO}+\text{MVKOO}+\text{MGLOO}$  versus  $\text{CH}_3\text{CHOO}$ )).

Globally, the loss of CIs in our model is dominated ( $\sim 96.6\%$ ) by reaction with water vapor (Table 2). Reaction with  $\text{SO}_2$  represents 2.9 % of the CI loss, and the total summed loss by reaction with CO, NO and  $\text{NO}_2$  is 0.5 %. In our simulations, we use the fast  $\text{CI}+\text{SO}_2$  and  $\text{CI}+\text{NO}_2$  reaction rates presented in Welz et al. (2012) for all CIs. This  $\text{CI}+\text{SO}_2$  rate constant is over 1 order-of-magnitude faster than the rate constants published in Mauldin et al. (2012) and over 2 orders-of-magnitude faster than what is currently used in the MCM (Jenkin et al., 1997). Thus, the CI loss by reaction with water vapor could be over 99 % of the total CI loss if the slower reaction rates were used. However, the  $\text{CI}+\text{H}_2\text{O}$  rate constant is also highly uncertain with significant differences (about a factor of 10) between studies (Calvert et al., 2000); thus, the rate of even this dominant sink processes for CIs is currently highly uncertain.

Figure 1a shows the annual-average boundary-layer production rate of CIs in the BASE-CI (or XSOA-CI) simulation (the same in both simulations). CI production rates exceed  $10^5 \text{ molec cm}^{-3} \text{ s}^{-1}$  in the tropics and a portion of the southeastern US, and exceed  $10^4 \text{ molec cm}^{-3} \text{ s}^{-1}$  in many NH boreal and broad-leaf forest regions. Outside of CI-precursor

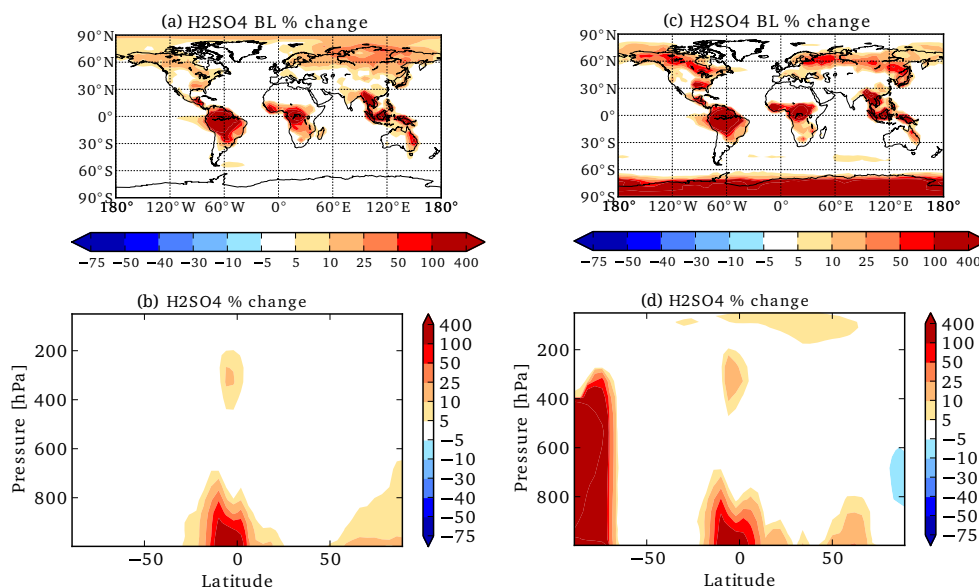


**Fig. 2.** Fractional contributions of  $\text{SO}_2$ -loss pathways predicted for the BASE and BASE-CI simulations (XSOA and XSOA-CI simulations give the same respective  $\text{SO}_2$  budgets).

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  $\text{SO}_2$  in the boundary layer. Regions with high  $\text{SO}_2$  concentrations and/or low absolute humidities have the highest fractional loss of CIs by  $\text{SO}_2$ . In the mid-latitudes, the fraction of CI loss by  $\text{SO}_2$  can be more important, and it exceeds 40 % in several  $\text{SO}_2$ -rich regions. Additionally, the poles have large regions where CI loss by reaction with  $\text{SO}_2$  exceeds 30 % due to low absolute humidities. In the tropical regions, the loss of CIs is almost entirely (over 95 %) by reaction with  $\text{H}_2\text{O}$  due to the high absolute humidity and generally low  $\text{SO}_2$  concentrations. Since the tropics have the highest CI production rates (Fig. 1a), the global-mean loss of CIs by reaction with  $\text{SO}_2$  is low, 2.9 % (Table 2).

### 3.2 Effect of CIs on $\text{SO}_2$ -loss pathways

Figure 2 shows the global relative contributions to the various  $\text{SO}_2$ -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  $\text{SO}_2$  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  $\text{SO}_2$  is removed through aqueous chemistry, and this aqueous removal is dominated by chemistry with  $\text{H}_2\text{O}_2$ . The balance of the  $\text{SO}_2$  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  $\text{SO}_2$  from the atmosphere. The CIs also indirectly affect the fractional  $\text{SO}_2$  loss pathways by increasing oxidant concentrations (via  $\text{CI}+\text{NO}_x$  reactions) such that the OH and  $\text{H}_2\text{O}_2$  pathways each increase by 0.1 %. To compensate for the fractional 0.6 % increase in the chemical loss of  $\text{SO}_2$  in BASE-CI, the fractional deposition pathway is reduced by 0.6 %. The decrease in the fractional contribution of deposition to  $\text{SO}_2$  loss is driven by a 1.2 % decrease in the lifetime and burden of  $\text{SO}_2$  due to the  $\text{CI}+\text{SO}_2$  chemistry. Overall, there is a net global increase

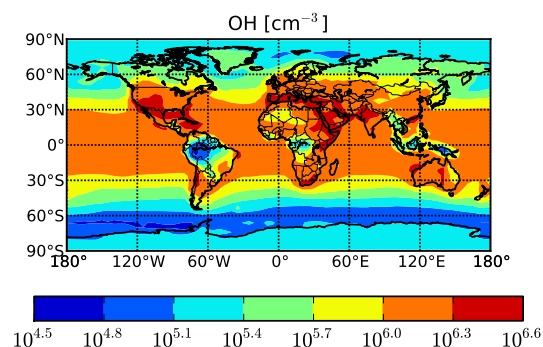


**Fig. 3.** Percent change in gas-phase  $\text{H}_2\text{SO}_4$  concentration due to the addition of the CI+ $\text{SO}_2$  chemistry (BASE-CI-BASE). The left column (a and b) is annual-mean values, and the right column (c and d) is for July. The top panels (a and c) show the boundary-layer values, and the bottom panels (b and d) show zonal-mean values.

in the fraction of  $\text{SO}_2$  that forms  $\text{H}_2\text{SO}_4$  vapor by 0.5 % due to the addition of Criegee chemistry in GEOS-Chem, which corresponds to a 4 % increase in the production of  $\text{H}_2\text{SO}_4$  vapor in the model. However, the global  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  (and aerosols) will be explored next.

### 3.3 CI influence on global aerosol microphysics

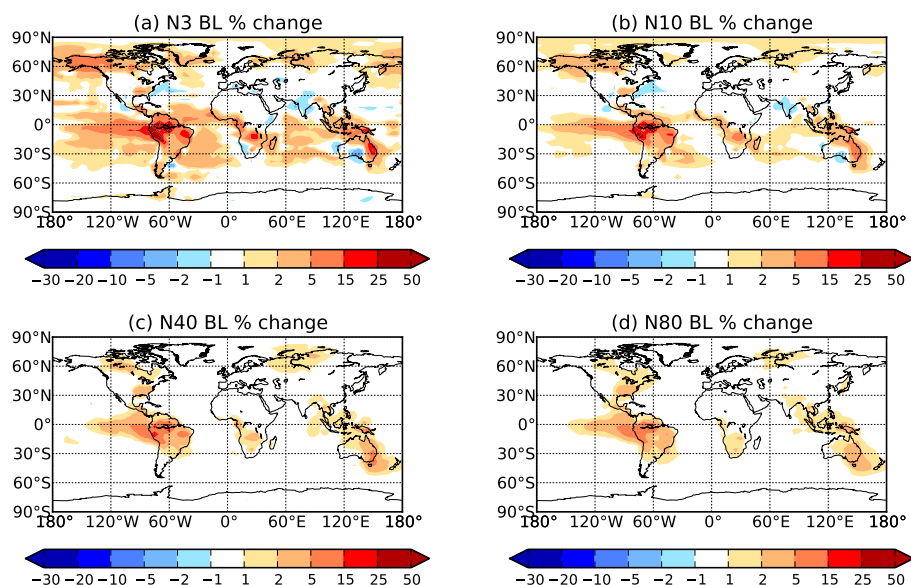
Figure 3 shows the BL- and zonal-mean percent changes in the gas-phase  $\text{H}_2\text{SO}_4$  concentrations between the BASE and BASE-CI cases (red denotes higher concentrations in the BASE-CI case) for both an annual average and the month of July (when alkene emissions from the Northern Hemispheric (NH) boreal forests are highest). The annual-mean boundary-layer plot (Fig. 3a) shows  $\text{H}_2\text{SO}_4$  more than doubling in tropical forests due to the addition of CI+ $\text{SO}_2$  chemistry. The large fractional change in  $\text{H}_2\text{SO}_4$  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  $\text{SO}_2$  to  $\text{H}_2\text{SO}_4$  is slow in these regions in the BASE simulation. The annual-average changes in  $\text{H}_2\text{SO}_4$  in the NH bo-



**Fig. 4.** Annual-mean boundary-layer OH concentrations in the BBASE simulation.

real and broad-leaf (e.g. southeastern US) forest regions are generally 10–25 % increases. The  $\text{H}_2\text{SO}_4$ -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  $\text{H}_2\text{SO}_4$  enhancement is in the boundary layer due to the short lifetime (several hours to  $\sim 1$  day) of the CI precursor gases. There is some enhancement in the tropical tropopause region due to transport of CI precursors, ozone and  $\text{SO}_2$  in deep convection.

In July (Fig. 3c, d), the  $\text{H}_2\text{SO}_4$  enhancements in the tropics due to CI+ $\text{SO}_2$  chemistry are nearly identical to the annual-mean plots. On the other hand, the NH forests show a much larger sensitivity of  $\text{H}_2\text{SO}_4$  concentrations to CI chemistry due to increased isoprene and monoterpene emissions in the



**Fig. 5.** The annual-mean boundary-layer change in  $N_3$ , 10, 40 and 80 due to the addition of CI+SO<sub>2</sub> chemistry (BASE-CI-BASE).

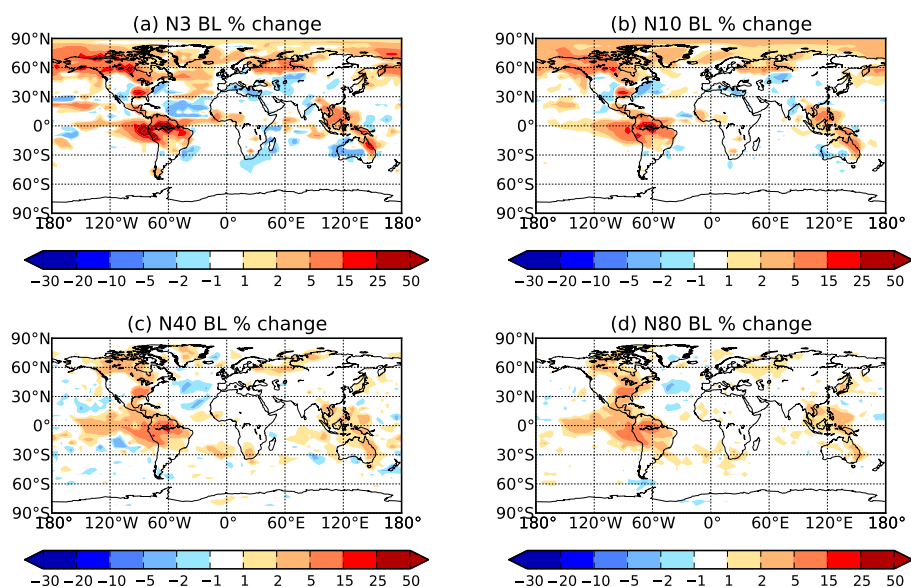
summer. H<sub>2</sub>SO<sub>4</sub> concentrations change by over 100 % in the southeastern US and by over 50 % in many regions of the boreal forests, which means that CI+SO<sub>2</sub> is responsible for about 50 % and 35 % of the H<sub>2</sub>SO<sub>4</sub> in the BASE-CI simulation in these regions, respectively. This increase in the boreal forest regions is slightly lower than the estimates of the summertime H<sub>2</sub>SO<sub>4</sub> enhancements due to CI chemistry calculated by Boy et al. (2012), where CI+SO<sub>2</sub> chemistry was found to explain up to 50 % of the gas-phase H<sub>2</sub>SO<sub>4</sub> production in Hyytiälä, Finland and Hohenpeissenberg, Germany (as opposed to ~35 % in this study) even though a faster CI+SO<sub>2</sub> 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 H<sub>2</sub>SO<sub>4</sub> production through CI+SO<sub>2</sub> chemistry, and we will discuss this possibility in our conclusions. In July, the H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> differences between the XSOA and XSOA-CI cases (not shown) are nearly identical to Fig. 3. While the H<sub>2</sub>SO<sub>4</sub> concentrations in XSOA are lower than BASE due to a larger condensation sink for H<sub>2</sub>SO<sub>4</sub> in XSOA (and a similar difference for XSOA-CI versus BASE-CI), the fractional

changes in H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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+SO<sub>2</sub> chemistry improves modeled H<sub>2</sub>SO<sub>4</sub> concentrations. However, (1) the model overpredicts H<sub>2</sub>SO<sub>4</sub> by a factor of 2 at Hyytiälä even without CI+SO<sub>2</sub> 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 H<sub>2</sub>SO<sub>4</sub> is more sensitive to the condensation sink (80 % reduction in H<sub>2</sub>SO<sub>4</sub> concentrations at Hyytiälä due to the addition of the extra 100 Tg of SOA per year in the XSOA simulation) than the CI+SO<sub>2</sub> chemistry (25 % increase in H<sub>2</sub>SO<sub>4</sub> 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+SO<sub>2</sub> chemistry on improving H<sub>2</sub>SO<sub>4</sub> 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 SO<sub>2</sub> concentrations, did predict that CI+SO<sub>2</sub> chemistry was needed for the closure of H<sub>2</sub>SO<sub>4</sub> 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+SO<sub>2</sub> in generating H<sub>2</sub>SO<sub>4</sub>.

Figures 5 and 6 show the annual-mean and July-mean, respectively, boundary-layer changes in  $N_3$ ,  $N_{10}$ ,  $N_{40}$  and  $N_{80}$  (the total number of particles larger than 3 nm, 10 nm, 40 nm and 80 nm, respectively) due to CI+SO<sub>2</sub> chemistry (BASE-CI – BASE).  $N_{40}$  and  $N_{80}$  represent a rough bound



**Fig. 6.** The July-mean boundary-layer change in  $N_3$ , 10, 40 and 80 due to the addition of CI+SO<sub>2</sub> chemistry (BASE-CI-BASE).

for the CCN concentrations for most clouds. Similar to the enhancements in H<sub>2</sub>SO<sub>4</sub> 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  $N_3$  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  $N_3$  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  $N_3$  and  $N_{10}$ . These are due to chemical feedbacks in SO<sub>2</sub> 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.

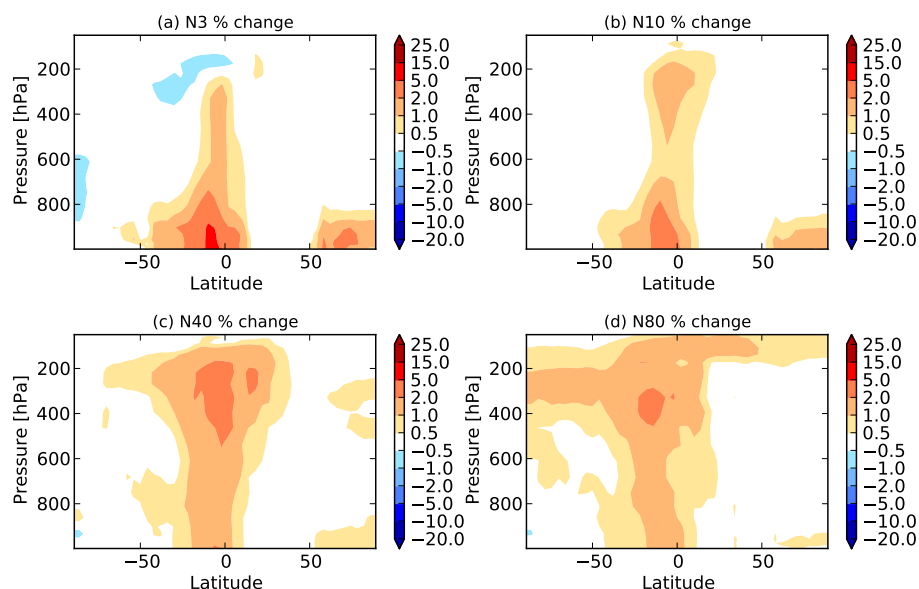
Figure 7 shows the annual- and zonal-mean change in  $N_3$ ,  $N_{10}$ ,  $N_{40}$  and  $N_{80}$  concentrations due to CI chemistry (BASE-CI – BASE), and unlike the similar plots for H<sub>2</sub>SO<sub>4</sub> (Fig. 3b and d), the influence of the tropical CIs extend to the upper troposphere due to 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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> in these locations. Although H<sub>2</sub>SO<sub>4</sub> 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 Hyytiälä, 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<sub>2</sub>SO<sub>4</sub>, a 50 % increase in H<sub>2</sub>SO<sub>4</sub> due to CI+SO<sub>2</sub> chemistry only represents a ~5 % increase in condensable



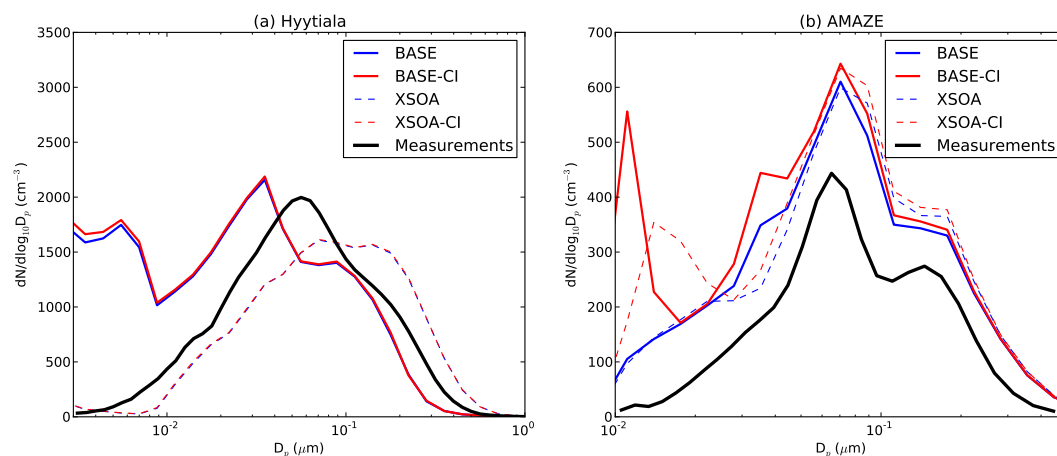


**Fig. 7.** The annual- and zonal-mean change in  $N3$ , 10, 40 and 80 due to the addition of CI+SO<sub>2</sub> chemistry (BASE-CI-BASE).

material. Thus, the enhancement in H<sub>2</sub>SO<sub>4</sub> has only a minor influence on the growth of the particles. Nucleation, on the other hand, is linear with H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub>SO<sub>4</sub> due to CI+SO<sub>2</sub> 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-Kroppla 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 condensable 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 condensable 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<sub>2</sub>SO<sub>4</sub>.

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<sub>2</sub> 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<sub>2</sub> chemistry (e.g. the sensitivity of H<sub>2</sub>SO<sub>4</sub> to CI+SO<sub>2</sub> chemistry was larger in Boy et al., 2012), the effect of CI+SO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> chemistry did not greatly change). Thus, while the CI+SO<sub>2</sub> chemistry is predicted to be important for CCN in some locations, particularly the Amazon, improving our understanding of CI+SO<sub>2</sub> chemistry will likely not significantly improve our estimates of CCN globally.



**Fig. 8.** (a) Measured and modelled (BASE, BASE-CI, XSOA and XSOA-CI) annual-mean aerosol size distribution at Hyytiälä for 2001. (b) The same but for the AMAZE campaign in the central Amazon during February and March.

### 3.4 Comparison to size distribution measurements

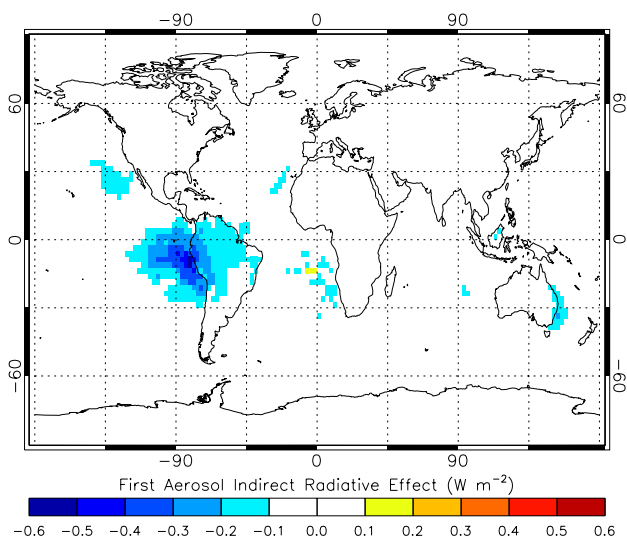
In Fig. 8, we evaluate the model size distributions in two locations that are both affected by the CI chemistry, Hyytiälä, Finland, and the AMAZE field station in the central Amazon, Brazil. Figure 8a shows the annual-average size distributions at Hyytiälä, Finland ( $61^{\circ}51' \text{N}$ ,  $24^{\circ}17' \text{E}$ , 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  $100 \text{Tg yr}^{-1}$  was used. A more detailed and general evaluation on the additional SOA (beyond the CI+SO<sub>2</sub> 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 ( $02^{\circ}36' \text{S}$ ,  $60^{\circ}13' \text{W}$ , 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  $50\text{--}100 \text{cm}^{-3}$  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 emis-

sion 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+SO<sub>2</sub> 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+SO<sub>2</sub> chemistry to the model (radiative perturbation between the BASE-CI and BASE cases). Throughout most of the globe, the AIE change is very small ( $< 0.1 \text{W m}^{-2}$ ), as would be expected by the small changes in  $N_{40}$  and  $N_{80}$  throughout most of the boundary layer. The strongest cooling due to the CI+SO<sub>2</sub> 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  $-0.5 \text{W m}^{-2}$  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  $-0.031 \text{W m}^{-2}$  for the BASE case (and  $-0.034 \text{W m}^{-2}$  for the XSOA case, not



**Fig. 9.** Annual-mean cloud albedo AIE due to inclusion of CI+SO<sub>2</sub> chemistry with an assumed updraft velocity of 0.2 m s<sup>-1</sup> (radiative perturbation between the BASE and BASE-CI simulations).

shown but similar spatial patterns) when the updraft velocities are assumed to be 0.2 m s<sup>-1</sup>. When the updraft velocities are varied between 0.1 and 0.5 m s<sup>-1</sup>, the range of AIE was  $-0.025$  to  $-0.031$  W m<sup>-2</sup> for the BASE case (and  $-0.028$  to  $-0.036$  W m<sup>-2</sup> 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<sub>2</sub> on present-day H<sub>2</sub>SO<sub>4</sub>, 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<sub>2</sub> 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<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>. We used the fast CI+SO<sub>2</sub> rates measured by Welz et al. (2012) in an attempt to provide an upper bound for CI+SO<sub>2</sub> 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<sub>2</sub> represented most of the remaining loss (2.9 %). However, SO<sub>2</sub> 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<sub>2</sub> reactions, these estimates of CI+SO<sub>2</sub> were likely an upper bound, and could be over an order-of-magnitude lower if other published rate constants were used. We also note there are significant uncertainties on the rate constant of CI+H<sub>2</sub>O, leading to large uncertainties on the atmospheric fate of CI radicals.

The addition of the CI+SO<sub>2</sub> chemistry increased the production of H<sub>2</sub>SO<sub>4</sub> globally by 4 %. However, the H<sub>2</sub>SO<sub>4</sub> increases were driven almost entirely by increases over forested continental regions with large fluxes of biogenic alkene emissions. The annually averaged H<sub>2</sub>SO<sub>4</sub> 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 *N*<sub>3</sub>, *N*<sub>10</sub>, *N*<sub>40</sub> and *N*<sub>80</sub> (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<sub>2</sub>SO<sub>4</sub>. The annually averaged changes in CCN (*N*<sub>40</sub> and *N*<sub>80</sub>) 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<sub>2</sub> chemistry. The relatively small sensitivity of CCN compared to the larger sensitivity of H<sub>2</sub>SO<sub>4</sub> to CI chemistry is due, in part, to CI chemistry generally being only important in forested locations where SOA (as opposed to H<sub>2</sub>SO<sub>4</sub>) is the dominant species contributing to ultrafine particle growth. Thus, increasing H<sub>2</sub>SO<sub>4</sub> in these locations increased nucleation rates but did not significantly increase growth rates, and CCN were dampened to changes in H<sub>2</sub>SO<sub>4</sub> 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<sub>2</sub> 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, 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). Subsequently, the uncertainty in the cloud albedo AIE change due to CI+SO<sub>2</sub> chemistry was about 0.03 W m<sup>-2</sup> (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 CI+SO<sub>2</sub> chemistry on CCN and the AIE (e.g. we found a smaller sensitivity of H<sub>2</sub>SO<sub>4</sub> to CI+SO<sub>2</sub> 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<sub>2</sub>SO<sub>4</sub> concentrations to CI+SO<sub>2</sub> 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<sub>2</sub> emissions with biogenic alkene emissions in the coarse grid boxes could lead to a larger fraction of anthropogenic SO<sub>2</sub> being oxidized by CIs in the model than in reality, which could bias the model-predicted impacts of CI+SO<sub>2</sub> 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 CI+SO<sub>2</sub> 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 CI+SO<sub>2</sub> chemistry would not lead to significant improvements in present-day CCN predictions. However, it is possible that CI+SO<sub>2</sub> 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<sub>2</sub> that is oxidized by CIs. However, additional biogenic alkenes may also yield more SOA. Additional SOA coupled with potential future reductions in SO<sub>2</sub> emissions would mean that H<sub>2</sub>SO<sub>4</sub> would be even less important for ultrafine particle growth, and the sensitivity of CCN to CI+SO<sub>2</sub> chemistry could be even less than in the present day.

One possible outcome of CI+SO<sub>2</sub> 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<sub>2</sub> to the CI could lead to a reduction in vapor pressure of the CI, SO<sub>2</sub>+CI 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 CI+SO<sub>2</sub> → stable sulfur-bearing secondary ozonide, and we assume that 0 % of the CI would have formed SOA if it had not reacted with SO<sub>2</sub> (an obvious underestimate) and 100 % of the stable sulfur-bearing sec-

ondary ozonide forms SOA, we find that the enhancement of SOA would be several to 10 s of Tg SOA yr<sup>-1</sup>. While this calculation is likely an upper bound, it shows that CI+SO<sub>2</sub> chemistry might be important through this pathway, and this should be explored in future work.

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