**Atmospheric
Chemistry
and Physics
Discussions**

Weak sensitivity of cloud condensation nuclei and the aerosol indirect effect to Criegee + SO$_2$ chemistry

J. R. Pierce[1,2], M. J. Evans[3], C. E. Scott[4], S. D. D'Andrea[2,1], D. K. Farmer[5], E. Swietlicki[6], and D. V. Spracklen[4]

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

Abstract

H_2SO_4 vapor is important for the nucleation of atmospheric aerosols and the growth of ultrafine particles to cloud condensation nuclei (CCN) sizes. Recent studies have found that reactions of stabilized Criegee intermediates (CIs, formed from the ozonolysis of alkenes) with SO_2 may be an important source of H_2SO_4 that has been missing from atmospheric aerosol models. In this paper, 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_2SO_4, 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_2, we find that the addition of this chemistry increases the global production of H_2SO_4 by 4 %. H_2SO_4 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_2 chemistry, but the change is generally negligible elsewhere. The predicted changed in CCN were strongly dampened to the CI + SO_2 changes in H_2SO_4 in these 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 + SO_2 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 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_2 chemistry would not likely to lead to significant improvements in present-day CCN and AIE predictions.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

1   Introduction

Atmospheric aerosol particles regulate climate by scatting/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 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 the 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–$100\,\mathrm{nm}$ 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 $\sim 1\,\mathrm{nm}$ particles occurs (via clustering of sulfuric acid and likely organic, NH_3 and H_2O molecules) with these particles also growing via condensation to CCN sizes (Merikanto et al., 2009; Pierce and Adams, 2009c). However, not all ultrafine ($D_p < 100\,\mathrm{nm}$) particles will survive to grow to become 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 (H_2SO_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 H_2SO_4 is not the only species involved in tropospheric nucleation,

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

nucleation rates measured in all parts of the troposphere have been shown to have at least linear dependence on H_2SO_4 concentrations (e.g. Sihto et al., 2006). In many locations, such as the polluted boundary layer, remote oceans and the free troposphere, H_2SO_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 H_2SO_4 vapor (via gas phase oxidation of SO_2) may lead to uncertainties in CCN predictions.

SO$_2$, the precursor of H_2SO_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 H_2O_2 or 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 H_2SO_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 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 H_2SO_4 vapors in models, which may lead to errors in the aerosol microphysical processes associated with H_2SO_4.

Traditionally, the sole pathway of H_2SO_4 vapor production in models was via the reaction of 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 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 O_2 or N_2), we will explicitly state that it is the energetic Criegee.) The CI + SO_2 reaction has gained much attention because of the possibility of these reactions creating H_2SO_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, SO_2, NO, 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, H_2COO, with SO_2 and NO_2 was significantly faster (3.9×10^{-11} and 7.0×10^{-12} $cm^3 s^{-1}$, respectively) than previously considered (e.g. 7.0×10^{-14} and 1×10^{-15} $cm^3 s^{-1}$, Jenkin et al., 1997). These reaction rates published by Welz et al. (2012) suggest that the CI could be an additional important oxidant for 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, H_2COO, 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 SO_2 to reach closure for H_2SO_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 α-pinene) enhanced the production of CIs and H_2SO_4. Mauldin et al. (2012) deduced that the reaction rate constants of SO_2 with CIs from ozonolysis of α-pinene and limonene were 6×10^{-13} $cm^3 s^{-1}$ and 8×10^{-13} $cm^3 s^{-1}$, 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. 7.0×10^{-14} $cm^3 s^{-1}$, Jenkin et al., 1997). A recent study by Boy et al. (2012) used measurements and modeling of Hyytiälä, Finland and Hohenpeissenberg, Ger-

many 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 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 $CI + SO_2 \rightarrow H_2SO_4$ 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 $4° \times 5°$ horizontal resolution and has 30 vertical layers from the surface to 0.01 hPa. 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–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; 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 radiative perturbation due to the cloud albedo AIE using the offline version of the Edwards and Slingo (1996) radiative transfer model. Our method

is described in detail in Spracklen et al. (2011a). Cloud droplet number concentrations (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). We assume a uniform updraft velocity of 0.2 m s-1; the calculated radiative effect is generally insensitive to updraft velocities in the range of 0.2–0.5 m s^{-1} (Spracklen et al., 2011a).

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://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_3 and O_3) 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 α-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_2, SO_2 and water vapor to form stable products. The rates constants for CO, NO and water vapor are taken from the MCM and are 1.2×10^{-15}, 1.00×10^{-14} and 1.6×10^{-17} cm^3 s^{-1}, respectively, for all CIs. For SO_2 and NO_2, we use the fast CI oxidation rates of 3.9×10^{-11} and 7.0×10^{-12} cm^3 s^{-1}, respectively, from Welz et al. (2012) for all CIs. This rate constant for SO_2 allows us to determine a probable upper bound for the impact of CI chemistry on CCN and the aerosol indirect effect.

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

2.1 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 $100\,Tg\,SOA\,yr^{-1}$ 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_2SO_4 formed by $CI + SO_2$ 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 has no effect on the CI chemistry. The simulations without "CI" in the 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 CCN impacts of $CI + SO_2 \rightarrow H_2SO_4$ chemistry.

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 propene. In the calculation of these fractions we have assumed that isoprene (and MVK and MACR) accounts for 83 % of CH_2OO production and propene for 17 % of CH_2OO production (this is the

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

same ratio as isoprene (and MVK and MACR) versus propene forming other CIs (i.e. MACROO + MVKOO + MGLOO versus CH_3CHOO)).

Globally, the loss of CIs in our model is dominated ($\sim 96.6\%$) by reaction with water vapor (Table 2). Reaction with SO_2 represents 2.9% of the CI loss, and the total summed loss by reaction with CO, NO and NO_2 is 0.5%. In our simulations, we use the fast $CI + SO_2$ and $CI + NO_2$ reaction rates presented in Welz et al. (2012) for all CIs. This $CI + SO_2$ 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 $CI + H_2O$ 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 BBASE-CI (or XSOA-CI) simulation. CI production rates exceed $10^5\,\mathrm{molec\,cm^{-3}\,s^{-1}}$ in the tropics and a portion of the southeastern US, and exceed $10^4\,\mathrm{molec\,cm^{-3}\,s^{-1}}$ in many NH boreal and broad-leaf forest regions. Outside of CI-precursor 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_2O 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_2O_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_2O_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 SO_2 that forms H_2SO_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 H_2SO_4 vapor in the model. However, the global H_2SO_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 H_2SO_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 H_2SO_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 H_2SO_4 concentrations between the BASE and BASE-CI cases (red denotes higher concentra-

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

tions 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 H_2SO_4 more than doubling in tropical forests due to the addition of CI + SO_2 chemistry. The large fractional change in H_2SO_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 SO_2 to H_2SO_4 is slow in these regions in the BASE simulation. The annual-average changes in H_2SO_4 in the NH boreal and broad-leaf (e.g. southeastern US) forest regions are generally 10–25 % increases. The H_2SO_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 H_2SO_4 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 SO_2 in deep convection.

In July (Fig. 3c, d), the H_2SO_4 enhancements in the tropics due to CI + SO_2 chemistry are nearly identical to the annual-mean plots. On the other hand, the NH forests show a much larger sensitivity of H_2SO_4 concentrations to CI chemistry due to increased isoprene and monoterpene emissions in the summer. H_2SO_4 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_2 is responsible for about 50 % and 35 % of the H_2SO_4 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_2SO_4 enhancements due to CI chemistry calculated by (Boy et al., 2012), where CI + SO_2 chemistry was found to explain up to 50 % of the gas-phase H_2SO_4 production in Hyytiälä, Finland and Hohenpeissenberg, Germany (as opposed to ∼ 35 % in this study) even though a faster CI + SO_2 rate constant for large CIs was used here than in their work. This lower sensitivity in our model may be due to the coarse hori-

zontal 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_2SO_4 production through CI + SO_2 chemistry, and we will discuss this possibility in our conclusions. In July, the H_2SO_4 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_2SO_4 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_2SO_4 differences between the XSOA and XSOA-CI cases (not shown) are nearly identical to Fig. 3. While the H_2SO_4 concentrations in XSOA are lower than BASE due to a larger condensation sink for H_2SO_4 in XSOA (and a similar difference for XSOA-CI versus BASE-CI), the fractional changes in H_2SO_4 between XSOA and XSOA-CI are similar to the fractional changes between BASE and BASE-CI.

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 + SO_2 chemistry (BASE-CI–BASE). N40 and N80 represent a rough bound for the CCN concentrations for most clouds. Similar to the enhancements in H_2SO_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 N3 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 N3 is nearly always less than a 15 % enhancement, and CCN enhancements are generally less than 2 % except for the southeast US for both N40 and N80 and part of Canada for N40. There are a few regions where the addition of CI chemistry causes a decrease in N3 and N10. 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. N3 are enhanced by over 15 % in many parts of Canada and southeastern US and over 5 % over in northeastern Europe. In general, the enhancements in N40 and N80 are about a factor of 3 lower due to microphysical dampening (and don't 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 N3, N10, N40 and N80 concentrations due to CI chemistry (BASE-CI-BASE), and unlike the similar plots for H_2SO_4 (Fig. 3b, 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_2SO_4 in the upper troposphere were minor (Fig. 3b, d), but may have contributed to the enhancements in N3 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 N3, N10, N40 and N80 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_2SO_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_2SO_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_2SO_4 in these locations. Although H_2SO_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 Hyytiälä, Finland, the measurements show and model predicts that SOA condensation is responsible for over 90 % of the particle growth. If 90 % of the condensible material in a region is SOA and the remaining 10 % is H_2SO_4, a 50 % increase in H_2SO_4 due to $CI + SO_2$ chemistry only represents a ~ 5 % increase in condensible material. Thus, the enhancement in H_2SO_4 has only a minor influence on the growth of the particles. Nucleation, on the other hand, is linear with H_2SO_4 concentrations in the boundary layer in the model (i.e. Fig. 3a, c also show the relative change in nucleation rates due to CI chemistry), and a 50 % increase in H_2SO_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 coagulational 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 coagulational 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_2SO_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

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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;
5   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
10 the impact of $CI + SO_2$ chemistry (e.g. the sensitivity of H_2SO_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. Thus, while the $CI + SO_2$ chemistry is predicted to be important for CCN in some locations, particularly the Amazon,
15 improving our understanding of $CI + SO_2$ chemistry will likely not significantly improve our estimates of CCN globally.

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
20 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
25 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 + SO_2 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 is 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, 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_2 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_2 chemistry to the model (BASE-CI–BASE). 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 $CI + SO_2$ chemistry occurs off of the coast of Peru, where there Amazon-influenced CCN increases meet the persistent susceptible marine straticumulus clouds of the eastern subtropical South Pacific ocean. In this region, the AIE changes exceed $-1\,W\,m^{-2}$ in some locations. There is also some cooling in other subtropical marine cloud regions (and even some patchy warming in the South Atlantic due to reductions in CCN in these regions during some months). Overall the regions of cooling occupy a small fraction of the earth, so the global mean AIE change is only $-0.029\,W\,m^{-2}$ (same for XSOA-CI–XSOA). Similar to the results with CCN, this 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 manuscript, we tested the sensitivity of the reaction of stabilized Criegee intermediates (CIs) with SO_2 on present-day H_2SO_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 α-pinene) were added to the model. CIs were lost by reaction with CO, NO, NO_2, H_2O and SO_2. We used the fast $CI + SO_2$ rates measured by Welz et al. (2012) as an attempt at the 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 repre-

senting 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 are used. We also note the there are significant uncertainties on the rate constant of CI + H_2O leading to large uncertainties on the atmospheric fate of CI radicals.

The addition of the CI + SO_2 chemistry increased the production of H_2SO_4 globally by 4 %. However, the H_2SO_4 increases were driven almost entirely by increases over forested continental regions with large fluxes of biogenic alkene emissions. The annually averaged H_2SO_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_2SO_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_2SO_4 to CI chemistry is due, in part, to CI chemistry generally being only important in forested locations where SOA (as opposed to H_2SO_4) is the dominant species contributing to ultrafine particle growth. Thus, increasing H_2SO_4 in these locations increased nucleation rates, but did not significantly increase growth rates, and CCN were dampened to changes in H_2SO_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.,

5 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 deposi-

10 tion (Croft et al., 2012). Subsequently, the uncertainty in the cloud albedo AIE change due to CI + SO$_2$ chemistry was less than 0.03 W m^{-2}, which is also significantly less than the other model uncertainties described above. While the simulations presented here may not be a true upper bound on the impact of CI + SO$_2$ chemistry on CCN and the AIE (e.g. we found a smaller sensitivity of H$_2$SO$_4$ to CI + SO$_2$ chemistry than Boy

15 et al. (2012) at the two sites that they investigated), it would take an order-of-magnitude increase in the CCN sensitivity to CI + 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,

20 we conclude that improvements in our understanding of CI + SO$_2$ chemistry would not lead to significant improvements in present-day CCN predictions. However, it is possible that CI + 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.

25 One possible outcome of CI + 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 CI could lead to a reduction in vapor pressure of the CI, SO$_2$ + 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 $CI + SO_2 \rightarrow$ stable sulfur-bearing secondary ozonide, and we assume that 0 % of the CI would have formed SOA if it had not reacted with SO_2 (an obvious underestimate) and 100 % of the stable sulfur-bearing secondary ozonide forms SOA, we find that the enhancement of SOA would be several to 10s of $Tg\,SOA\,yr^{-1}$. While this calculation is likely an upper bound, it shows that $CI + SO_2$ chemistry might be important through this pathway, and this should be explored in future work.

References

Adams, P. J. and Seinfeld, J. H.: Predicting global aerosol size distributions in general circulation models, J. Geophys. Res.-Atmos., 107, 4310–4370, 2002.

Adams, P. J. and Seinfeld, J. H.: Disproportionate impact of particulate emissions on global cloud condensation nuclei concentrations, Geophys. Res. Lett., 30, 1210–1239, 2003.

Albrecht, B. A.: Aerosols, cloud microphysics, and fractional cloudiness, Science, 245, 1227–1230, 1989.

Bauer, S. E., Menon, S., Koch, D., Bond, T. C., and Tsigaridis, K.: A global modeling study on carbonaceous aerosol microphysical characteristics and radiative effects, Atmos. Chem. Phys., 10, 7439–7456, doi:10.5194/acp-10-7439-2010, 2010.

Berglen, T. F., Berntsen, T. K., Isaksen, I. S. A., and Sundet, J. K.: A global model of the coupled sulfur/oxidant chemistry in the troposphere: the sulfur cycle, J. Geophys. Res., 109, D19310, doi:10.1029/2003JD003948, 2004.

Boy, M., Mogensen, D., Smolander, S., Zhou, L., Nieminen, T., Paasonen, P., Plass-Dülmer, C., Sipilä, M., Petäjä, T., Mauldin, L., Berresheim, H., and Kulmala, M.: Oxidation of SO_2 by stabilized Criegee Intermediate (sCI) radicals as a crucial source for atmospheric sulphuric acid concentrations, Atmos. Chem. Phys. Discuss., 12, 27693–27736, doi:10.5194/acpd-12-27693-2012, 2012.

Calvert, J. R., Atkinson, R., Kerr, J. A., Madronich, S., Moortgat, G. K., Wallington, T. J., and Yarwood, G.: Mechanisms of Atmospheric Oxidation of the Alkenes, Oxford University Press, NY, USA, , 2000.

Charlson, R. J., Schwartz, S. E., Hales, J. M., Cess, R. D., Coakley, J. A., Hansen, J. E., and Hofman, D. J.: Climate forcing by anthropogenic aerosols, Science, 255, 423–430, 1992.

Chin, M. A., Jacob, D. J., Gardner, G. M., Foreman-Fowler, M. S., Spiro, P. A., and Savoie, D. L.: A global three-dimensional model of tropospheric sulfate, J. Geophys. Res.-Atmos., 101, 18667–18690, 1996.

Croft, B., Pierce, J. R., Martin, R. V., Hoose, C., and Lohmann, U.: Uncertainty associated with convective wet removal of entrained aerosols in a global climate model, Atmos. Chem. Phys., 12, 10725–10748, doi:10.5194/acp-12-10725-2012, 2012.

van Donkelaar, A., Martin, R. V., Leaitch, W. R., Macdonald, A. M., Walker, T. W., Streets, D. G., Zhang, Q., Dunlea, E. J., Jimenez, J. L., Dibb, J. E., Huey, L. G., Weber, R., and Andreae, M. O.: Analysis of aircraft and satellite measurements from the Intercontinental Chemical Transport Experiment (INTEX-B) to quantify long-range transport of East Asian sulfur to Canada, Atmos. Chem. Phys., 8, 2999–3014, doi:10.5194/acp-8-2999-2008, 2008.

Edwards, J. M. and Slingo, A.: Studies with a flexible new radiation code. I: Choosing a configuration for a large-scale model, Q. J. Roy. Meteor. Soc., 122, 689–719, 1996.

Forster, P., Ramaswamy, V., Artaxo, P., Berntsen, T., Betts, R., Fahey, D. W., Haywood, J., Lean, J., Lowe, D. C., Myhre, G., Nganga, J., Prinn, R., Raga, G., Schulz, M. and Dorland, R. V: Changes in atmospheric constituents and in radiative forcing, in Climate change 2007: the physical science basis. contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change, edited by: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor, and H. L. Miller, 129–234, Cambridge University Press, Cambridge, UK and New York, NY, USA., 2007.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem – Atmosphere Relations (SMEAR II), Boreal Environ. Res., 10, 315–322, 2005.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81–104, doi:10.1016/S1352-2310(96)00105-7, 1997.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin,

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U. and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.

Jung, J. G., Adams, P. J., and Pandis, S. N.: Simulating the size distribution and chemical composition of ultrafine particles during nucleation events, Atmos. Environ., 40, 2248–2259, 2006.

Kazil, J., Stier, P., Zhang, K., Quaas, J., Kinne, S., O'Donnell, D., Rast, S., Esch, M., Ferrachat, S., Lohmann, U., and Feichter, J.: Aerosol nucleation and its role for clouds and Earth's radiative forcing in the aerosol-climate model ECHAM5-HAM, Atmos. Chem. Phys., 10, 10733–10752, doi:10.5194/acp-10-10733-2010, 2010.

Koch, D., Jacob, D., Tegen, I., Rind, D., and Chin, M.: Tropospheric sulfur simulation and sulfate direct radiative forcing in the Goddard Institute for Space Studies general circulation model, J. Geophys. Res., 104, 23799–23822, 1999.

Kulmala, M., Vehkamaki, H., Petajda, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Lee, Y. H. and Adams, P. J.: Evaluation of aerosol distributions in the GISS-TOMAS global aerosol microphysics model with remote sensing observations, Atmos. Chem. Phys., 10, 2129–2144, doi:10.5194/acp-10-2129-2010, 2010.

Lee, Y. H., Chen, K., and Adams, P. J.: Development of a global model of mineral dust aerosol microphysics, Atmos. Chem. Phys., 9, 2441–2458, doi:10.5194/acp-9-2441-2009, 2009.

Makkonen, R., Asmi, A., Korhonen, H., Kokkola, H., Järvenoja, S., Räisänen, P., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., Järvinen, H., Lohmann, U., Bennartz, R., Feichter, J., and Kulmala, M.: Sensitivity of aerosol concentrations and cloud properties to nucleation and secondary organic distribution in ECHAM5-HAM global circulation model, Atmos. Chem. Phys., 9, 1747–1766, doi:10.5194/acp-9-1747-2009, 2009.

Martin, S. T., Andreae, M. O., Althausen, D., Artaxo, P., Baars, H., Borrmann, S., Chen, Q., Farmer, D. K., Guenther, A., Gunthe, S. S., Jimenez, J. L., Karl, T., Longo, K., Manzi, A.,

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Müller, T., Pauliquevis, T., Petters, M. D., Prenni, A. J., Pöschl, U., Rizzo, L. V., Schneider, J., Smith, J. N., Swietlicki, E., Tota, J., Wang, J., Wiedensohler, A., and Zorn, S. R.: An overview of the Amazonian Aerosol Characterization Experiment 2008 (AMAZE-08), Atmos. Chem. Phys., 10, 11415–11438, doi:10.5194/acp-10-11415-2010, 2010.

Mauldin, R. L., Berndt, T., Sipilä, M., Paasonen, P., Petäjä, T., Kim, S., Kurtén, T., Stratmann, F., Kerminen, V.-M., and Kulmala, M.: A new atmospherically relevant oxidant of sulphur dioxide, Nature, 488, 193–196, doi:10.1038/nature11278, 2012.

Merikanto, J., Spracklen, D. V., Mann, G. W., Pickering, S. J., and Carslaw, K. S.: Impact of nucleation on global CCN, Atmos. Chem. Phys., 9, 8601–8616, doi:10.5194/acp-9-8601-2009, 2009.

Nenes, A. and Seinfeld, J. H.: Parameterization of cloud droplet formation in global climate models, J. Geophys. Res.-Atmos., 108, 4415, doi:10.1029/2002JD002911, 2003.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961–1971, doi:10.5194/acp-7-1961-2007, 2007.

Pierce, J. R. and Adams, P. J.: Global evaluation of CCN formation by direct emission of sea salt and growth of ultrafine sea salt, Journal of Geophysical Research-Atmospheres, 111, D06203, doi:10.1029/2005JD006186, 2006.

Pierce, J. R. and Adams, P. J.: Efficiency of cloud condensation nuclei formation from ultrafine particles, Atmos. Chem. Phys., 7, 1367–1379, doi:10.5194/acp-7-1367-2007, 2007.

Pierce, J. R. and Adams, P. J.: A computationally efficient aerosol nucleation/condensation method: pseudo-steady-state sulfuric acid, Aerosol Sci. Tech., 43, 216–226, doi:10.1080/02786820802587896, 2009a.

Pierce, J. R. and Adams, P. J.: Can cosmic rays affect cloud condensation nuclei by altering new particle formation rates?, Geophys. Res. Lett., 36, 1–6, doi:10.1029/2009GL037946, 2009b.

Pierce, J. R. and Adams, P. J.: Uncertainty in global CCN concentrations from uncertain aerosol nucleation and primary emission rates, Atmos. Chem. Phys., 9, 1339–1356, doi:10.5194/acp-9-1339-2009, 2009c.

Pierce, J. R., Chen, K., and Adams, P. J.: Contribution of primary carbonaceous aerosol to cloud condensation nuclei: processes and uncertainties evaluated with a global aerosol microphysics model, Atmos. Chem. Phys., 7, 5447–5466, doi:10.5194/acp-7-5447-2007, 2007.

Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petäjä, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmos. Chem. Phys., 11, 9019–9036, doi:10.5194/acp-11-9019-2011, 2011.

Pierce, J. R., Theodoritsi, G., Adams, P. J., and Pandis, S. N.: Parameterization of the effect of sub-grid scale aerosol dynamics on aerosol number emission rates, J. Aerosol Sci., 40, 385–393, doi:10.1016/j.jaerosci.2008.11.009, 2009.

Reddington, C. L., Carslaw, K. S., Spracklen, D. V., Frontoso, M. G., Collins, L., Merikanto, J., Minikin, A., Hamburger, T., Coe, H., Kulmala, M., Aalto, P., Flentje, H., Plass-Dülmer, C., Birmili, W., Wiedensohler, A., Wehner, B., Tuch, T., Sonntag, A., O'Dowd, C. D., Jennings, S. G., Dupuy, R., Baltensperger, U., Weingartner, E., Hansson, H.-C., Tunved, P., Laj, P., Sellegri, K., Boulon, J., Putaud, J.-P., Gruening, C., Swietlicki, E., Roldin, P., Henzing, J. S., Moerman, M., Mihalopoulos, N., Kouvarakis, G., Ždímal, V., Zíková, N., Marinoni, A., Bonasoni, P., and Duchi, R.: Primary versus secondary contributions to particle number concentrations in the European boundary layer, Atmos. Chem. Phys., 11, 12007–12036, doi:10.5194/acp-11-12007-2011, 2011.

Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.: Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, Atmos. Chem. Phys., 11, 3865–3878, doi:10.5194/acp-11-3865-2011, 2011.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä, T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, Atmos. Chem. Phys., 6, 4079–4091, doi:10.5194/acp-6-4079-2006, 2006.

Snow-Kropla, E. J., Pierce, J. R., Westervelt, D. M., and Trivitayanurak, W.: Cosmic rays, aerosol formation and cloud-condensation nuclei: sensitivities to model uncertainties, Atmos. Chem. Phys., 11, 4001-4013, doi:10.5194/acp-11-4001-2011, 2011.

Sofen, E. D., Alexander, B., and Kunasek, S. A.: The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core Delta^{17}O(SO$_4^{2-}$), Atmos. Chem. Phys., 11, 3565–3578, doi:10.5194/acp-11-3565-2011, 2011.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Spracklen, D. V, Carslaw, K. S., Kulmala, M., Kerminen, V. M., Sihto, S. L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W., and Lihavainen, H.: Contribution of particle formation to global cloud condensation nuclei concentrations, Geophys. Res. Lett., 35, D06808, doi:10.1029/2007GL033038, 2008.

5 Spracklen, D. V., Carslaw, K. S., Pöschl, U., Rap, A., and Forster, P. M.: Global cloud condensation nuclei influenced by carbonaceous combustion aerosol, Atmos. Chem. Phys., 11, 9067–9087, doi:10.5194/acp-11-9067-2011, 2011a.

Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., Zhang, Q., Canagaratna, M. R., Allan, J., Coe, H., McFiggans, G., Rap, A., and Forster, P.:

10 Aerosol mass spectrometer constraint on the global secondary organic aerosol budget, Atmos. Chem. Phys., 11, 12109–12136, doi:10.5194/acp-11-12109-2011, 2011b.

Trivitayanurak, W., Adams, P. J., Spracklen, D. V., and Carslaw, K. S.: Tropospheric aerosol microphysics simulation with assimilated meteorology: model description and intermodel comparison, Atmos. Chem. Phys., 8, 3149–3168, doi:10.5194/acp-8-3149-2008, 2008.

15 Twomey, S.: Pollution and the planetary albedo, Atmos. Environ., 8, 1251–1256, 1974.

Vehkamäki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res.-Atmos., 107, 4610–4622, 2002.

Vereecken, L., Harder, H., and Novelli, A.: The reaction of Criegee intermediates with NO,

20 RO(2), and SO(2), and their fate in the atmosphere, Phys. Chem. Chem. Phys., 14, 14682–14695, doi:10.1039/c2cp42300f, 2012.

Wang, M. and Penner, J. E.: Aerosol indirect forcing in a global model with particle nucleation, Atmos. Chem. Phys., 9, 239–260, doi:10.5194/acp-9-239-2009, 2009.

Welz, O., Savee, J. D., Osborn, D. L., Vasu, S. S., Percival, C. J., Shallcross, D. E., and Taat-

25 jes, C. A.: Direct kinetic measurements of Criegee intermediate (CH_2OO) formed by reaction of CH_2I with O_2, Science, 335, 204–207, doi:10.1126/science.1213229, 2012.

Westervelt, D. M., Riipinen, I., Pierce, J. R., Trivitayanurak, W., and Adams, P. J.: Formation and growth of nucleated particles: observational constraints on cloud condensation nuclei budgets, Atmos. Chem. Phys. Discuss., 12, 11765–11822, doi:10.5194/acpd-12-11765-2012,

30 2012.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

Simulation name	Cl + SO$_2$	Extra 100 Tg SOA yr^{-1}
BASE	no	no
BASE-CI	yes	no
XSOA	no	yes
XSOA-CI	yes	yes

Table 2. Sources and sinks of CIs in the BASE-CI and XSOA-CI simulations.

Sources of CIs	Rate [Gmol yr^{-1}]
$\text{ISOP} + O_3 \rightarrow \text{MACROO}$	48.4
$\text{ISOP} + O_3 \rightarrow \text{MVKOO}$	32.2
$\text{MACR,MVK} + O_3 \rightarrow \text{MGLOO}$	21.8
$\text{PRPE} + O_3 \rightarrow \text{CH}_3\text{CHOO}$	21.5
$\text{ISOP,MACR,MVK,PRPE} + O_3 \rightarrow \text{CH}_2\text{OO}$	137.7
[*] $\text{MO} + O_3 \rightarrow \text{APINOO}$	85.2
Total sources	346.8

Sinks of CIs	Rate [Gmol yr^{-1}]
$\text{CI} + \text{CO}$	0.326
$\text{CI} + \text{NO}$	0.00072
$\text{CI} + \text{NO}_2$	1.44
$\text{CI} + \text{H}_2\text{O}$	335.0
$\text{CI} + \text{SO}_2$	10.05
Total sinks	346.8

ISOP = isoprene, MACR = methacrolein, MVK = mthyl vinyl ketone,
MGL = methylglyoxal, PRPE = propene, MO = all monoterpenes,
APIN = a-pinene.
CIs end in "OO".
[*] Criegees from all monoterpenes are assumed to take the form of of the
a-pinene criegee.

(a) CI production rate [molec cm^{-3} s^{-1}]

(b) Fraction of CI loss by SO$_2$ [%]
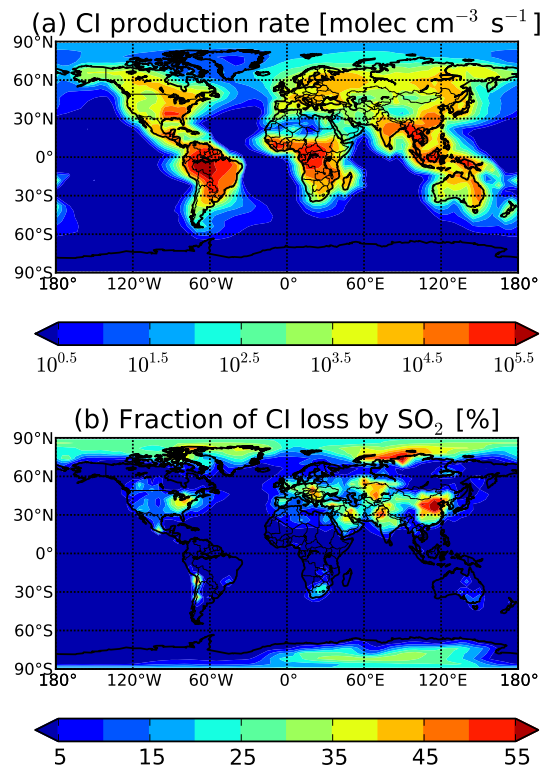
Fig. 1. (a) The annual-average boundary-layer production rate of CIs in the BBASE-CI (and XSOA-CI) simulation. **(b)** The annual-average fraction of CI loss via reaction with SO$_2$ in the same simulation in the boundary layer.
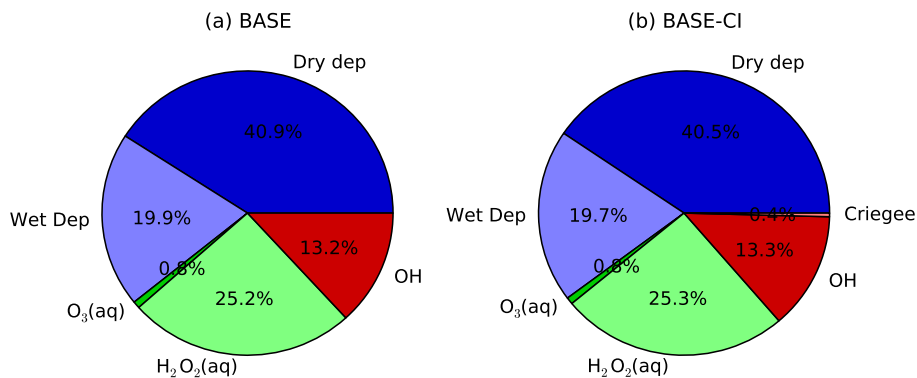
Fig. 2. Fractional contributions of SO$_2$-loss pathways predicted for the BASE and BASE-CI simulations (XSOA and XSOA-CI simulations give the same respective SO$_2$ budgets).
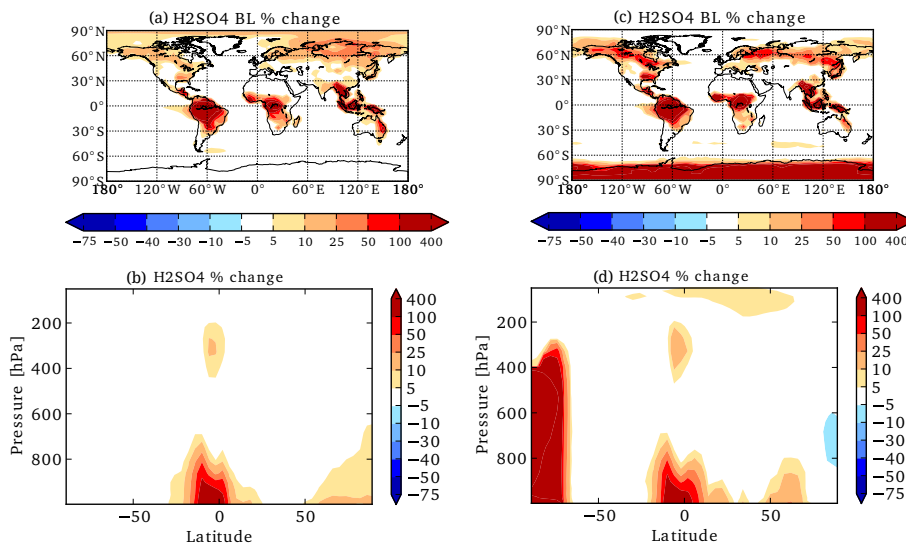
Fig. 3. Percent change in gas-phase H2SO4 concentration due to the addition of the CI + SO$_2$ chemistry (BASE-CI-BASE). The left column (**a** and **b**) is annual-mean values, and the right column (**c** and **d**) is for July. The top panels (**a** and **c**) show the boundary-layer values, and the bottom panels (**b** and **d**) show zonal-mean values.

Weak sensitivity of aerosols to Criegee chemistry

J. R. Pierce et al.

Title Page

Abstract · Introduction

Conclusions · References

Tables · Figures

◄ · ►

Back · Close

Full Screen / Esc

Printer-friendly Version

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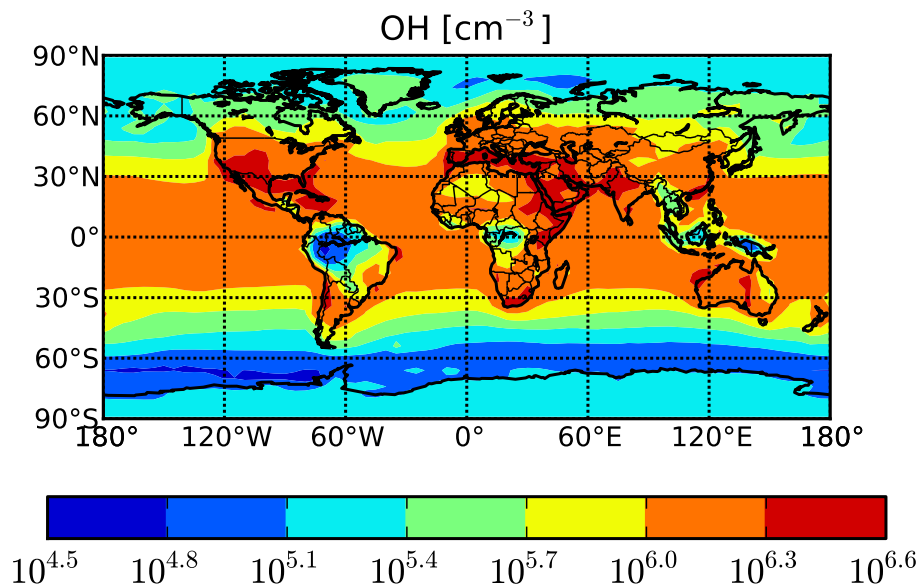
Fig. 4. Annual-mean boundary-layer OH concentrations in the BBASE simulation.

(a) N3 BL % change

(b) N10 BL % change

(c) N40 BL % change

(d) N80 BL % change
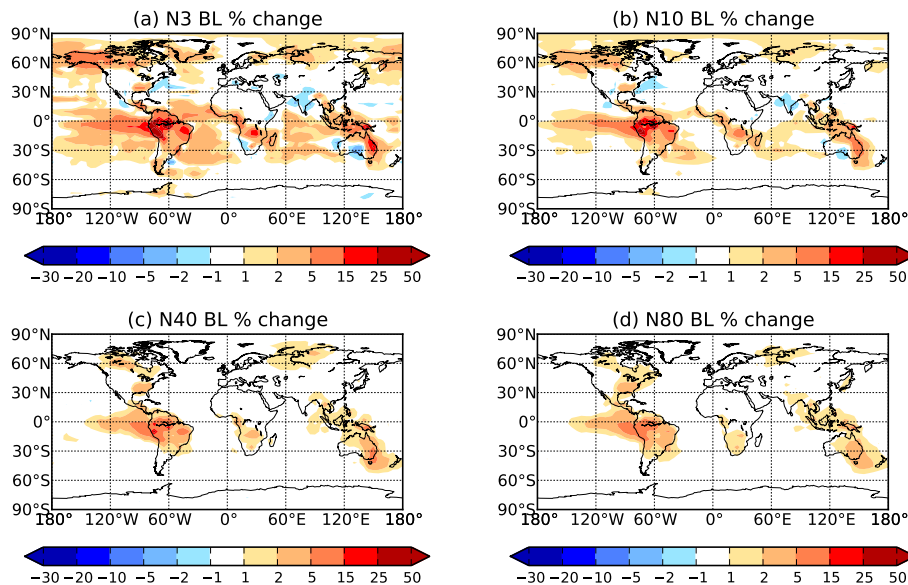
Fig. 5. The annual-mean boundary-layer change in N3, 10, 40 and 80 due to the addition of CI + SO_2 chemistry (BASE-CI-BASE).

Fig. 6. The July-mean boundary-layer change in N3, 10, 40 and 80 due to the addition of CI + SO_2 chemistry (BASE-CI-BASE).
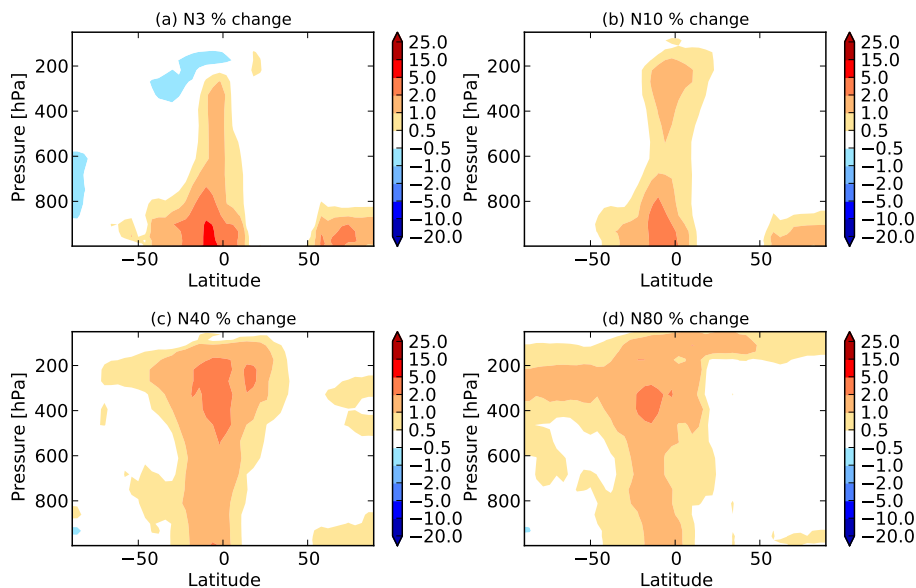
Fig. 7. The annual- and zonal-mean change in N3, 10, 40 and 80 due to the addition of CI + SO_2 chemistry (BASE-CI-BASE).
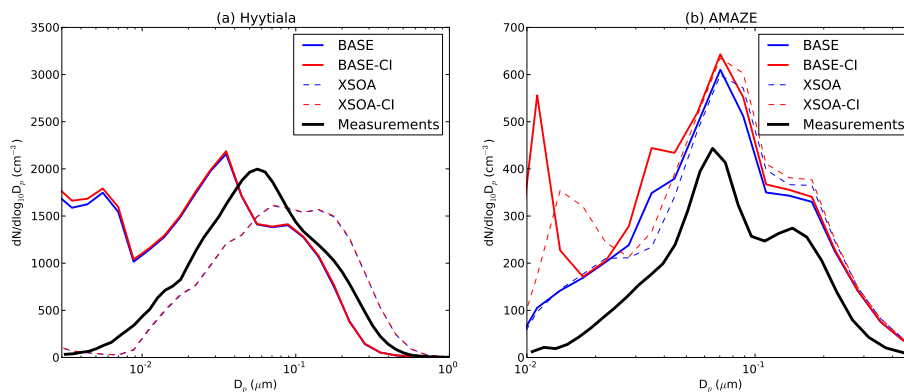
Fig. 8. (a) Measured and modelled (BASE, BASE-CI, XSOA and XSOA-CI) annual-mean aerosol size distribution at Hyytiälä for 2001. **(b)** The same but for the AMAZE campaign in the central Amazon during February and March.
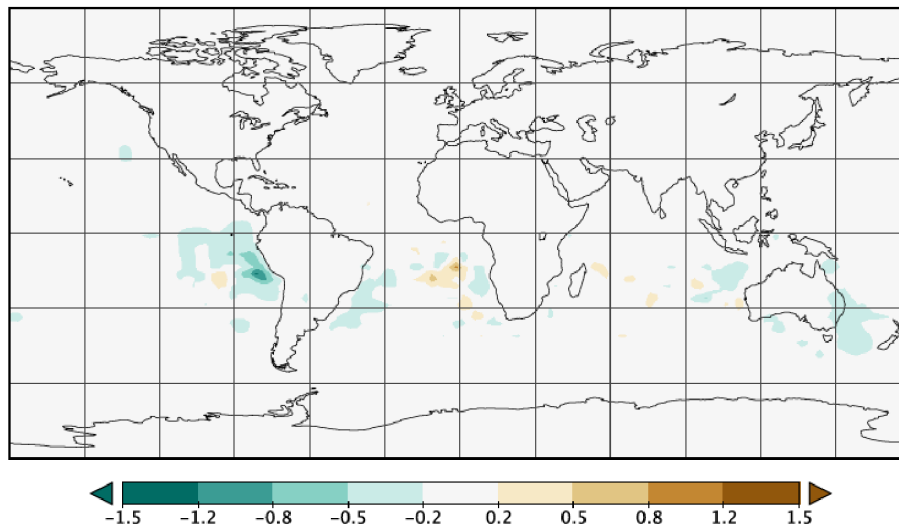
Fig. 9. Annual-mean cloud albedo AIE due to inclusion of CI + SO$_2$ chemistry (radiative perturbation between the BASE and BASE-CI simulations, BASE-CI-BASE).

Printer-friendly Version

Interactive Discussion