We thank both reviewers for their detailed comments on our manuscript. We have responded to all the comments and made modifications to our manuscript. Our detailed response to the review is below (reviewer comments in red, our responses in black).

Reviewer 1:

In this manuscript, the authors use a global aerosol microphysics model and an offline radiative transfer model to study how the manner in which secondary organic aerosols (SOA) is added to the aerosol size distribution affects simulated changes in CCN-sized particles and the radiative effects of biogenic SOA. They show that the first aerosol indirect effect (AIE) due to biogenic SOA is sensitive to the SOA model treatment. This work highlights the importance of better representation of the impact of SOA on particle size distributions. The content of this work is within the scope of ACP. The following comments should be properly addressed before I can recommend it for final publication in ACP.

Major comments:

1. The authors used two different methods to treat the partitioning of biogenic organics into particle phase ("kinetic" and "equilibrium" approaches). In the "kinetic" approach (Eq. 9), all organics from the oxidation of monoterpene were assumed to be nonvolatile. This may significantly over-predict the growth rate of freshly nucleated particles as only the extremely low volatile part (a small fraction) of oxidation products can directly condense on the nucleated particles. In the "equilibrium" approach (Eq. 10), all SOA were also assumed to be non-volatile and the re-partition of SOA into gas phase were not allowed. This can't really be considered as "equilibrium" approach because it was not "equilibrium" at all (no reparation, no temperature-dependence). The authors should at least discuss the uncertainties associated with the non-volatile assumption of all oxidation products. A figure showing the global distribution of modeled Sorg based on the two approaches is needed to help the reader better understand the results of the work.

   We agree with the reviewer that our mass-based partitioning approach does not represent an "equilibrium" approach; we refer to this approach as "mimicking the thermodynamic" approach (p4152, lines 12-15), we do not specifically call it "equilibrium". To clarify this further we have changed the terminology throughout the manuscript to refer to this as the "mass-based" approach, rather than "thermodynamic"

We also agree that the 100% kinetic approach will overestimate the amount of very low volatility material that may condense in this way. However, this has been the standard approach used in our own model (Spracklen et al., 2006; Mann et al., 2010; Scott et al., 2014) and other global microphysics models (Makkonen et al., 2009; Pierce and Adams, 2009; Makkonen et al., 2012; D'Andrea et al., 2015).

We now emphasise that many models make this assumption, after line 7 on p4153:

"We note that the KinSOA simulation matches the approach used in a wide range of recent global aerosol models (Spracklen et al., 2006; Makkonen et al., 2009; Pierce and Adams, 2009; Mann et al., 2010; Makkonen et al., 2012; D'Andrea et al., 2015)."

We have included a sensitivity study to examine the impact of a 50%:50% split between the amount of SOA mass partitioned according to the particle surface area and according to the pre-existing organic mass (i.e., only allowing half of the SOA to condense kinetically). Our results suggest non-linear behaviour in terms of the fraction of SOA distributed kinetically and the impact on cloud droplet number. Future work from our group will examine in more detail the effect on particle growth rates of distributing a more realistic amount (between 0% (i.e. our mass-based approach) and 50% (our split approach)) of the SOA kinetically, based on new laboratory studies on the production of extremely low volatility organic oxidation products. We already discuss this uncertainty in the conclusions of our paper.

To isolate the impact of the two different approaches to partitioning, we calculate the amount of SOA condensing in the same way under each approach (i.e., determined by the available condensation sink); accordingly the amount of S_{org} present under the two different approaches will vary only as the size distribution changes. We now clarify this in our paper (at p4152, line 8). Because the amount of organic condensation is identical in our simulations, we don't feel that a figure of S_{org} concentrations would be of benefit to the paper.

2. Another concern is related to the uncertainties of this study associated with several other simplifications and assumptions: (1) Offline chemistry ("prescribe six-hourly mean offline oxidant"); (2) No nitrate and ammonium; (3) "secondary organic material is generated at a fixed molar yield (13 %) from the oxidation of monoterpenes". The formation of atmospheric particles and their growth to CCN sizes depend on the concentrations of precursors involved. The authors showed that the method to deal with organics lead to large difference in CCN and AIE. The above

simplifications and assumptions will surely impact CCN and AIE. The authors need to justify the usage of these simplifications in this study and discuss how these may affect the conclusions of this work.

Our objective was to understand the impact of partitioning of biogenic organics on aerosol and global radiative effects. We therefore chose to isolate this effect whilst keeping other variables constant (e.g., offline chemistry, fixed SOA yields). We now highlight these simplifications and add discussion as suggested by the referee. We have added the following (at p4153, line 3):

“To isolate the impact of the condensation of secondary organic material the SOA yield, the oxidant chemistry and the SOA condensation rate was identical in all simulations.”

Our treatment of SOA is similar to many other global aerosol models. We have added the following at p4148, line 11:

“The treatment of SOA in global aerosol models is summarised by Tsigaridis et al. (2014).”

To address the specific points:

1) We accept that the use of offline chemistry is a simplification and in the future we intend to examine the impact of coupled chemistry on our treatment of SOA. The lack of online chemistry here means that we are missing the feedback on oxidant concentrations due to BVOC emission, however, we are looking at the difference between two ways of distributing the SOA, once formed via BVOC oxidation, so we do not expect this aspect of our results to be very sensitive to our use of offline oxidants.

We have added the following at line 9, p4150:

“The use of offline oxidants means that we do not simulate the feedback on oxidant concentrations due to monoterpene emission.”

2) The version of GLOMAP-mode used here does not include ammonium or nitrate aerosol; a version of GLOMAP-mode containing ammonium and nitrate is under development but was not available at the start of this work. In the absence of nitrate and ammonium, our total mass concentrations are likely to be biased low – however, the focus of this study was to compare the two methods of distributing secondary organics across the size distribution.

We have added the following to our model description at line 2, p4150 to clarify that we do not include nitrate or ammonium:

"Material in the particle-phase is classified into four components: sulphate (SU), black carbon (BC), particulate organic matter (POM) and sea-salt (SS); this version of GLOMAP-mode does not include nitrate or ammonium aerosol."

3) Generating secondary organics from the oxidation of BVOCs, using a fixed molar yield, is a simple approach based on empirical relationships between the amount of organic material found to reside in the aerosol phase and the level of BVOC emission an air parcel has been exposed to (e.g., Tunved et al., 2004; Tunved et al., 2006). In reality these yields would be sensitive to the specific precursors and oxidants involved, but are poorly constrained.

Whilst the simulated amount of SOA formed could be different with different/variable yields, we were interested in the relative difference between two approaches that distribute the same amount of SOA across the size distribution.

3. GLOMAP-mode was employed for this study. The mode approach uses several longnormal to describe particle size distributions. Since this work focuses on the effect of particle growth associated with SOA on particle size distributions and CCN concentrations, I was wondering why the authors didn't use their more accurate GLOMAP-bin aerosol model for the work.

As with many aerosol-climate models, it is the modal version of GLOMAP that is to be included within HadGEM-ES (the UK's Earth System Model) so, in terms of global radiative effects, we wanted to explore this process within the modal scheme. In previous work we have demonstrated that the modal model is able to reproduce much of the behaviour of the sectional (GLOMAP-bin) model. We have added the following after line 10, p4150.

"In previous work (Mann et al., 2012) it has been demonstrated that the modal version of the model we use here is able to accurately simulate the aerosol size distribution simulated by a sectional version of the model (Spracklen et al., 2005)."

However, we agree that there is a need to explore these processes using global models with a spectrum of complexity; as the reviewer points out the process of particle growth is a particularly important process to examine using our more detailed sectional scheme and we will be addressing this in future work.

4. Page 4150, Equation (2). How [NucOrg] was calculated in the model? Is NucOrg the same as Sorg (Eq. 4)? You only mentioned that NucOrg represents monoterpene oxidation products but monoterpene oxidation should have many

products of different volatilities. Some details on the calculation of [NucOrg] and global distribution of [NucOrg] should be given.

Yes NucOrg is the same as S_{org}. We have corrected Equation 2 to clarify this. This was the approach taken when the Metzger scheme was originally implemented in GLOMAP (Metzger et al. 2010) and in Scott et al. 2014. However, we agree that monoterpene oxidation will produce products of differing volatilities and that only a fraction of these will be able to participate in the earliest stages of new particle formation. We have added a sensitivity study exploring the impact of a 50:50 split – see earlier response. Future work from our group will assess the impact of allowing differing amounts of the secondary organics (or those produced from particular pre-cursors via particular reactions) to participate in new particle formation.

5. Page 4150, Equation (2). Riccobono et al. (Science, 2014) gave a more updated formula for the organically mediated nucleation. Why not use the formula given by Riccobono et al.? What is the uncertainty associated with the usage of specific nucleation parameterizations? A figure showing the global distributions of nucleation rates predicted by ACT and ORG schemes should be provided.

The start of this work predated the Riccobono publication so we have used the organically mediated mechanism given by Metzger et al. 2010. Our intention here is to compare the two different treatments of SOA partitioning and we use the Metzger scheme as an example of an organically mediated mechanism. To demonstrate the sensitivity to nucleation parameterization we also completed simulations using the activation nucleation mechanism. Both the activation and organically mediated nucleation parameterizations showed consistent behaviour; we would not expect the Riccobono mechanism to differ greatly. We highlight the consistent response, in terms of CDNC change, between the activation and Metzger mechanisms in Section 3.1. The nucleation rates themselves are not the focus of this study; therefore we do not feel that a figure of global nucleation rates is necessarily of relevance to this paper.

6. Figure 1 shows the simulated and observed particle size distributions at a boreal forest site. The conclusion of this work is for global. Therefore, it is necessary to compare simulated CN and CCN number concentrations with those observed at different sites around the globe.

Our intention here was not to evaluate the model extensively (which we have done in other studies) but to compare these two different treatments using an example observed size distribution to put the modelled results into context. We have added a sentence on previous model evaluation after line 10, p4150.

"We have previously evaluated GLOMAP against observations of CN (Spracklen et al., 2010) and CCN (Spracklen et al., 2011)."

We have now added a comparison against measurements collected at a pristine Amazon rainforest location (Manaus, Brazil) to Figure 1 and related discussion to Section 3.

Minor comments:

1. Pages 4147-4148. As I understand, both kinetic approach (for low volatile organics) and equilibrium (for semi-volatile organics) were used in in the work of Yu (2011) cited here. This should be reflected and correctly described in the review of previous work in the Introduction.

We already include the following description at line 18 p4148:

"Yu (2011) found that allowing successive stages of oxidation to occur, and the generation of non-volatile products, increased simulated surface level CCN concentrations by 5-50%, over a version of the same model in which the thermodynamic assumption was applied."

So we have expanded this slightly to clarify that this involved using both a kinetic and thermodynamic approach:

"*Yu (2011) found that allowing successive stages of oxidation to occur, and the generation of non-volatile products which were distributed according to the kinetic approach, increased simulated surface level CCN concentrations by 5-50% over a version of the same model in which only an equilibrium approach was taken*."

2. Page 4149, line 12. Offline radiative transfer model was used. Please add some details on what aerosol (and gas) fields at what temporal resolutions were saved for the offline RT calculation.

We have added extra details to Section 2.2 (p4193, line 9 onwards) to clarify that our radiative transfer calculations are based on monthly mean aerosol fields and provide other further details. This section now reads:

"The changes to CDNC due to the inclusion of biogenic SOA (i.e., *KinSOA* - *NoSOA*) are calculated from the monthly mean aerosol distribution, using the parameterisation developed by Nenes and Seinfeld (2003), Fountoukis and Nenes

(2005) and Barahona et al. (2010); assuming a globally uniform updraught velocity of 0.2 m s^{-1}.

The first AIE due to biogenic SOA is then determined using the offline radiative transfer model of Edwards and Slingo (1996) with nine bands in the longwave and six bands in the shortwave; a monthly mean climatology based on ECMWF reanalysis data and cloud fields for the year 2000 from the ISCCP-D2 archive (Rossow and Schiffer, 1999) are used. To calculate the first AIE, a uniform control cloud droplet effective radius (r_{e1}) of 10 µm is assumed to maintain consistency with the ISCCP derivation of liquid water path, and for each perturbation experiment the effective radius (r_{e2}) is calculated as in Eqn. 11, from monthly mean cloud droplet number fields $CDNC_1$ and $CDNC_2$ respectively (where $CDNC_1$ represents the simulation including SOA, and $CDNC_2$ represents the simulation with no SOA).

The first AIE of biogenic SOA is then calculated by comparing net (SW + LW) radiative fluxes using the varying r_{e2} values derived for each perturbation experiment, to those of the control simulation with fixed r_{e1}. In these offline experiments, we do not calculate the second aerosol indirect (cloud lifetime) effect.

To determine the DRE, following the methodology described in Rap et al. (2013), the radiative transfer model is used to calculate the difference in net top-of-atmosphere all-sky radiative flux between experiments including SOA and the equivalent experiments without SOA. Aerosol optical properties are calculated from the monthly mean aerosol distribution. The refractive index for each mode is calculated as the volume-weighted mean refractive index of the components present (values for which are given at 550 nm in Table A1 of Bellouin et al., 2011), including water for the soluble modes. The optical properties (scattering and absorption coefficients, together with the dimensionless asymmetry parameter) are then obtained from look-up tables of all realistic combinations of refractive index and Mie parameter, as described in Bellouin et al. (2013).”

Reviewer 2:

The authors have investigated the effects of thermodynamic equilibrium and kinetic condensation treatments for partitioning biogenic SOA on the magnitude of the direct and first indirect effects. The effects of two new particle formation schemes – one based on activation rate of H2SO4 clusters and the other based on organically mediated cluster formation rate – are also investigated. While the topic of this study is within the scope of ACP, I am unable to recommend it for final publication in the current form due to several issues listed below.

Comments:

1. I had some difficulty in assessing what major insights this study provides that were not already provided by Riipinen et al., ACP, 2011 – that kinetic condensation leads to an increase in CCN while thermodynamic partitioning suppresses it. While this study computes CDNC from CCN and the radiative effects, I am not convinced that is enough to qualify it as a unique scientific contribution, especially when the thermodynamic approach used here seems somewhat flawed (see next comment). Comparing the effects of two new particle formation schemes is new, but that does not seem to be the main focus of the study.

We respectfully disagree with the reviewer here as we have made the first assessment on the global direct and indirect radiative effects. We demonstrate that the treatment of condensation is an important uncertainty in the calculation of global indirect effects, and this is the first time this process has been examined using the GLOMAP model. We feel that this is a sufficient contribution to justify our manuscript. This is highlighted in the Introduction and we now also highlight this novelty in the Conclusions.

2. The thermodynamic approach used in this study is not the one typically used in a thermodynamic partitioning model. It simply partitions the SOA mass (predicted by the kinetic approach) according to organic mass (MOA), and does not let it evaporate, undergo further oxidation in the gas phase, and repartition in subsequent time steps. While I understand the rationale behind this approach, it would be incorrect to call it thermodynamic approach.

We agree and although we had originally used this terminology to maintain consistency with Riipinen et al., 2011 and D'Andrea et al., 2013, we have changed the terminology throughout the manuscript to refer to this as the “mass-based” partitioning approach instead.

3. Comparison of observed size distribution with model predictions is shown for only one site. More comparisons at different locations are necessary as this is a global study.

Our intention here was not to evaluate the model extensively but to compare these two different treatments using an example observed size distribution to put the modelled results into context. In previous work we have made extensive evaluations of the model – we now detail this after line 10, p4150.

We have now added a comparison against measurements collected at a pristine Amazon rainforest location (Manaus, Brazil) and related discussion to Section 3. These two locations are chosen as they are relatively far from pollution sources and biogenic SOA is likely a dominant component of fine aerosol mass.

4. This study focuses biogenic SOA, but uses only monoterpenes as precursor VOCs. What about isoprene, which is also an important biogenic VOC that can produce substantial amounts of SOA in certain regions of the globe? Other sources such as anthropogenic VOCs and biomass burning VOCs can be important as well. Ignoring these key SOA precursors would lead to underprediction of global SOA budget and skew the magnitudes of direct and indirect effects, and hence the main results of this study

In this study we wanted to investigate the relative impact of two different approaches to partitioning for a given amount of SOA, which is formed here from a precursor with the spatial/temporal emission pattern of monoterpenes. But we agree with the reviewer that this approach will likely lead to an underestimate in the amount of SOA produced in our simulations and we accept that the amount of SOA included will affect the magnitude of the DRE and AIE we calculate.

In Scott et al., 2014, we showed that the global annual mean AIE (simulated using an activation nucleation mechanism) was very similar for simulations containing monoterpenes only (-0.07 W m^{-2}), isoprene only (-0.06 W m^{-2}) and both monoterpenes and isoprene (-0.06 W m^{-2}). However, we showed that increasing the amount of SOA further (by multiplying the yields at which the SOA is generated by a factor of 2 or 5) reduced the magnitude of the AIE (because the growth of smaller particles to CCN size was suppressed due to the enhanced condensation sink), but also reduced our model’s ability to capture observed N_{80} and CCN concentrations. This demonstrates that the magnitude of the AIE does not scale linearly with SOA formation.

Accordingly we have added the following to our model description at line 9 of p4150:

"*The inclusion of monoterpene emissions only will likely lead to an underestimate in the amount of SOA produced in our model simulations.*"

5. Page 4149, line 25: It is stated that 5 log-normal size modes are used in the model, implying that the model uses some sort of modal dynamics approach to simulate aerosol size distribution. This could be problematic if the mode widths are assumed to remain fixed after kinetic condensation, which produces a characteristic narrowing the mode. Please provide some details on the modal dynamics approach used and how this issue is handled in the model?

GLOMAP-mode uses a two-moment modal scheme, within which mode number and mass concentrations may vary but mode width is held fixed. We agree with the reviewer that the modal scheme may not fully capture the evolution of the aerosol size distribution during condensation.

Following condensation, the particle number concentration for a mode is held constant and the new geometric mean diameter for the mode is calculated according to the new particle volume (due to added mass). The standard deviation of the mode is fixed so the mode width would not change to reflect any change to the distribution of material within a mode.

In previous work we have demonstrated that our 2 moment modal model closely matches results from a sectional version of the model (see response to Reviewer #1). Our group also will be using the more detailed, sectional version of our model to examine particle growth due to the condensation of secondary organics.

To clarify this issue we have added the following before line 1, p4153:

"GLOMAP-mode uses a two-moment modal approach, within which mode number and mass concentrations vary but the mode width is held fixed. Following condensation, the particle number concentration for a mode is held constant and the new geometric mean diameter for the mode is calculated according to the updated volume per particle (Mann et al., 2010). Since the mode width is held fixed, this approach will not capture potential changes to the distribution of material within a mode following condensation."

6. Page 4150, line 4: It is mentioned that six-hourly mean offline oxidant concentrations are used to oxidise monoterpenes to form SOA at 13% molar yield. What time splitting interval is used to perform coagulation and condensation calculations? Also, in which order are these calculations done? And are the results sensitive to the order?

A flowchart of the microphysical operations performed within GLOMAP is given in Spracklen et al., 2005. Within each chemistry or microphysical time step (15 mins), there are 5 competition sub-steps, during which nucleation and condensation compete for the available sulphuric acid (and organic oxidation products when an organic nucleation mechanism is used). Condensation is performed first (then nucleation), then coagulation. Spracklen et al. (2005) found that shortening the length of the time-step, and changing the order of operations altered particle concentrations by less than 5%.

We have added the following to our model description, at line 4, p4150:

"Operator splitting is used to calculate the different microphysical processes: condensation is calculated followed by nucleation then coagulation with a time step of 3 minutes. Spracklen et al. (2005) found that shortening the length of the time-step, and changing the order of operations altered particle concentrations by less than 5%."

7. Editorial comment: Abstract, line 17: Change "medicated" to "mediated".

Thank you for pointing this out, we have now corrected this.

Additional changes:

The results presented initially for the ORG simulation were generated using a rate coefficient (*k* in Eq. 2) of 5 x 10^{-12} s^{-1} (not 5 x 10^{-13} s^{-1} as given on line 22 of p4150). We have updated our results throughout to reflect the lower rate coefficient of 5 x 10^{-13} s^{-1} specified in Metzger et al. (2010), but include the original results in Table 2 as a sensitivity study representing a faster nucleation rate. The effect of applying a mass-based approach, rather than a kinetic approach, on the global annual mean AIE is the same using either value for *k* (i.e., a 24% reduction).

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Impact of gas-to-particle partitioning approaches on the simulated radiative effects of biogenic secondary organic aerosol

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Abstract

The oxidation of biogenic volatile organic compounds (BVOCs) gives a range of products, from semi-volatile to extremely low-volatility compounds. To treat the interaction of these secondary organic vapours with the particle phase, global aerosol microphysics models generally use either a thermodynamic partitioning approach (assuming instant equilibrium between semi-volatile oxidation products and the particle phase) or a kinetic approach (accounting for the size-dependence of condensation). We show that model treatment of the partitioning of biogenic organic vapours into the particle phase, and consequent distribution of material across the size distribution, controls the magnitude of the first aerosol indirect effect (AIE) due to biogenic secondary organic aerosol (SOA). With a kinetic partitioning approach, SOA is distributed according to the existing condensation sink, enhancing the growth of the smallest particles, i.e., those in the nucleation mode. This process tends to increase cloud droplet number concentrations in the presence of biogenic SOA. By contrast, an ~~thermodynamic~~ approach that distributes SOA according to pre-existing organic mass~~,~~ restricts~~sing~~ the growth of the smallest particles, limiting the number that are able to form cloud droplets. With an organically medi~~c~~ated new particle formation mechanism, applying a mass-based~~thermodynamic~~ rather than a kinetic approach to partitioning reduces our calculated global mean AIE due to biogenic SOA by 24%. Our results suggest that the mechanisms driving organic partitioning need to be fully understood in order to accurately describe the climatic effects of SOA.

1 Introduction

Biogenic volatile organic compounds (BVOCs), such as monoterpenes and isoprene, are emitted into the atmosphere by vegetation (Guenther et al., 1995; Guenther et al., 2006) and are rapidly oxidised. The oxidation of BVOCs yields products with lower volatility, which may partition to the particle phase forming secondary organic aerosol (SOA). Organic compounds contribute a large fraction of submicron aerosol mass (Murphy et al., 2006; Zhang et al., 2007; Jimenez et al., 2009) with important impacts on air quality and climate (Fiore et al., 2012; Scott et al., 2014).

The part of the aerosol size distribution to which SOA is added affects the number, size and composition of particles in the atmosphere; in particular, the number of particles that are able to act as cloud condensation nuclei (CCN). The availability of CCN controls cloud droplet number concentrations (CDNC), and subsequently cloud albedo; therefore, the manner in which organics are distributed has potential implications for the first aerosol indirect effect (AIE) of biogenic SOA.

The presence of SOA can affect atmospheric CCN concentrations in several ways. Firstly, the condensation of SOA may grow particles to larger sizes, increasing CCN concentrations (Riipinen et al., 2012). However, this enhanced growth increases the condensation sink for potential nucleating vapours, and the coagulation sink for nucleation mode particles. The net change to CCN concentration therefore reflects the competition between particle growth, and the scavenging of particles and vapours. Secondly, condensation of water-soluble organic species can make hydrophobic particles more hydrophilic, providing an additional source of new CCN (Petters et al., 2006).

The transfer of semi-volatile gas-phase organic species into the condensed phase is often treated assuming thermodynamic equilibrium (Pankow, 1994; Odum et al., 1996). When simulating the evolution of the aerosol size distribution, a consequence of assuming instant equilibrium is that the net condensation of new organic mass scales with the existing organic aerosol mass size distribution (Kroll and Seinfeld, 2008; Pierce et al., 2011; Riipinen et al., 2011). Because aerosol mass scales with diameter cubed, small particles that require condensational growth to reach climatically relevant sizes receive only a trivial fraction of the new SOA and subsequently do not grow.

However, if the volatility of organic oxidation products in the atmosphere is further reduced (i.e., through gas or particle-phase chemistry (Jimenez et al., 2009; Donahue et al., 2011; Ehn et al., 2014)), they may condense kinetically according to the Fuchs-corrected surface area of existing particles and a larger proportion of the condensable mass will be added to the nucleation mode (Riipinen et al., 2011; Yu, 2011; Zhang et al., 2012).

Neither approach fully describes the behaviour of SOA; the kinetic approach neglects the re-evaporation of semi-volatile organics whilst the thermodynamic approach is unable to account for the observed growth of particles beyond the nucleation mode (Pierce et al., 2011; Riipinen et al., 2011; Yu, 2011; Pierce et al., 2012). The results of laboratory experiments indicate the presence of both semi-volatile organic aerosol components that evaporate upon heating or dilution (e.g., Robinson et al., 2007) as well as highly oxidised compounds with extremely low volatilities (Ehn et al., 2014) in atmospherically relevant SOA particles.

The treatment of SOA in global aerosol models is summarised by Tsigaridis et al., (2014). Global aerosol ~~microphysics~~ models typically use either the thermodynamic (partitioning proportional to existing organic mass e.g., Chung and Seinfeld, 2002; Heald et al., 2008; Pye and Seinfeld, 2010; O'Donnell et al., 2011) or the kinetic (condensation proportional to particle surface area e.g., Spracklen et al., 2006; Makkonen et al., 2009; Mann et al., 2010; Makkonen et al., 2012; D'Andrea et al., 2015) assumptions described above. Riipinen et al. (2011) and D'Andrea et al. (2013) both found that the simulated global annual mean concentration of CCN-sized particles increased by approximately 10% when the kinetic (rather than mass-based~~thermodynamic~~) assumption was used for SOA, with regional increases of over 50%. Yu (2011) found that allowing successive stages of oxidation to occur, and the generation of non-volatile products which were distributed according to the kinetic approach, increased simulated surface level CCN concentrations by 5-50%~~,~~ over a version of the same model in which only an equilibrium approach was taken ~~the thermodynamic assumption was applied~~.

Previous modelling studies have quantified the cloud albedo effect, or first AIE, of biogenic SOA, estimating global annual mean values that span from positive (+0.23 W m^{-2} (O'Donnell et al., 2011)) to negative (e.g. -0.02 W m^{-2} (Rap et al., 2013), and -0.77 W m^{-2} (Scott et al., 2014)). One difference between these studies is the method by which they represent the condensation of SOA, with O'Donnell et al. (2011) applying a mass-based ~~thermodynamic~~ approach to partitioning, whereas the other studies used the kinetic approach. We hypothesise that uncertainty in the sign and magnitude of the first AIE due to biogenic SOA may, in part, be due to the different approaches used to distribute SOA amongst the existing aerosol population.

Conversely, we hypothesise that the direct radiative effect (DRE) due to biogenic SOA is less sensitive to the way in which secondary organic material is partitioned across the size distribution. Previous studies agree on a negative global annual mean DRE due to biogenic SOA (-0.29 W m^{-2} (clear-sky; O'Donnell et al., 2011), -0.13 W m^{-2} (all-sky; Rap et al., 2013), -0.17 W m^{-2} (all-sky; Unger, 2014) and -0.18 W m^{-2} (all-sky; Scott et al., 2014)). Rap et al. (2013) explored the radiative effects associated with several natural aerosol sources and demonstrated that the DRE responds linearly to changes in emission source strength and is less sensitive to microphysical complexities than the first AIE.

Here we use a global aerosol microphysics model and offline radiative transfer model to explore how the assumed behaviour of secondary organic material affects simulated changes in CCN-sized particles, and for the first time, CDNC and the radiative effects of biogenic SOA.

2 Method

2.1 GLOMAP

We use the GLObal Model of Aerosol Processes (GLOMAP-mode) (Mann et al., 2010) which is an extension to the TOMCAT model (Chipperfield, 2006). ~~GLOMAP operates at a~~Here we use the model with a horizontal resolution of 2.8° x 2.8° with 31 σ-pressure levels from the surface to 10 hPa. Meteorology is obtained from European Centre for Medium-Range Weather Forecasts (ECMWF) reanalyses at six-hourly intervals and cloud fields from the International Satellite Cloud Climatology Project (ISCCP) archive (Rossow and Schiffer, 1999). The particle component masses and number concentrations are simulated in 5 log-normal size modes; four hydrophilic (nucleation, Aitken, accumulation and coarse), and a non-hydrophilic Aitken mode. Material in the particle-phase is classified into four components: sulphate (SU), black carbon (BC), particulate organic matter (POM) and sea-salt (SS); this version of GLOMAP-mode does not include nitrate or ammonium aerosol. GLOMAP includes representations of nucleation, particle growth via coagulation, condensation and cloud processing, wet and dry deposition and in/below cloud scavenging. Operator splitting is used to calculate the different microphysical processes: condensation is calculated followed by nucleation then coagulation with a time step of 3 minutes; Spracklen et al., (2005) found that shortening the length of the time-step, and changing the order of operations altered particle concentrations by less than 5%.

We prescribe six-hourly mean offline oxidant (OH, O_3, NO_3, HO_2, H_2O_2) concentrations, linearly interpolated to the model time step, from a previous TOMCAT simulation (Arnold et al., 2005). Monoterpene emissions are taken from the Global Emissions InitiAtive (GEIA) database (Guenther et al., 1995) and secondary organic material is generated at a fixed molar yield (13%) from the oxidation of monoterpenes by O_3, OH and NO_3; producing approximately 20 Tg(SOA) a^{-1}. The inclusion of monoterpene emissions only will likely lead to an underestimate in the amount of SOA produced in our model simulations; the use of offline oxidants means that we do not simulate the feedback on oxidant concentrations due to monoterpene emission. Further details of this model setup are given in Scott et al. (2014). In previous work (Mann et al., 2012) it has been demonstrated that the modal version of the model we use here is able to accurately simulate the aerosol size distribution simulated by a sectional version of the model (Spracklen et al., 2005). We have previously evaluated GLOMAP against observations of total particle number (Spracklen et al., 2010; Mann et al., 2012; Riccobono et al., 2014) and CCN concentrations (Spracklen et al., 2011; Mann et al., 2012; Schmidt et al., 2012; Scott et al., 2014).

2.1.1 New particle formation

All model experiments include a representation of binary homogeneous nucleation (BHN), which simulates the formation of particles from H_2SO_4 and H_2O; this occurs predominantly in the free troposphere, and is parameterised according to Kulmala et al. (1998). One set of experiments (*ACT*; Table 1), use an empirically derived mechanism for the activation rate (J^*_{ACT}) of H_2SO_4 clusters in the boundary layer (Eqn.1; Kulmala et al., 2006), with a value for A of 2 x 10^{-6} s^{-1} (Sihto et al., 2006).

$$J^*_{ACT} = A\,[H_2SO_4] \qquad (1)$$

In a second set of experiments (*ORG*; Table 1), new particle formation is parameterised according to Metzger et al. (2010). In these simulations, the cluster formation rate (J^*_{ORG}) is calculated according to Eqn. 2, where S_{org}~~NucOrg~~

represents monoterpene oxidation products and k = 5 x 10^{-13} s^{-1} (Metzger et al., 2010). In a sensitivity study (*ORG_x10*) we examine the impact of using a higher rate coefficient of 5 x 10^{-12} s^{-1}.

$$J^*_{ORG} = k\,[H_2SO_4][\cancel{NucOrg}\ S_{org}] \tag{2}$$

The initial stages of cluster growth are not simulated explicitly, rather the approximation of Kerminen and Kulmala (2002) as given in Eqn. 3, is used to determine the production rate (J_m) of particles at a measurable size (taken as d_m = 3 nm). The cluster dry-diameter (d^*) is taken as 0.8 nm for J^*_{ACT} and 1.5 nm for J^*_{ORG} (Metzger et al., 2010).

$$J_m = J^* \exp\left[0.23\left(\frac{1}{d_m} - \frac{1}{d^*}\right)\frac{CS'}{GR}\right] \tag{3}$$

J_m allows the growth of newly formed clusters (up to d_m) at a constant growth rate (GR); here GR is proportional to the gas-phase concentration of sulphuric acid, but other species could also contribute to growth at this size (Yli-Juuti et al., 2011; Kulmala et al., 2013). J_m also accounts for the scavenging of newly formed clusters by larger particles; the reduced condensation sink (CS') is calculated by integrating over the aerosol size modes, following (Kulmala et al., 2001).

2.1.2 Partitioning of secondary organic material

The rate of change of gas-phase molecular concentration of organics (S_{org}) due to condensation is calculated as in Eqn. 4 where C_i is the condensation coefficient for each mode i (Eqn. 5) and n_i is the corresponding particle number concentration. C_i is calculated for each mode i as described in Mann et al. (2010) using the diffusion coefficient for a typical gas-phase α-pinene oxidation product in air (D_s) and the condensation sink radius ($\overline{r_{i,cond}}$, calculated as in Eqn. A1 of Mann et al. (2012) which is based on Lehtinen et al. (2003)). C_i is corrected for molecular effects and limitations in interfacial mass transport by the terms $F(Kn_i)$ and $A(Kn_i)$ respectively (Eqn. 6 and 7), where s is the accommodation coefficient, or sticking efficiency. Here we assume a value of s equal to 1, therefore $A(Kn_i)$ is unity in this case. Kn_i is the Knudsen number for each mode i (Eqn. 8), calculated using the mean free path of the relevant condensable gas in air (MFP_{gas}).

$$\frac{\mathrm{d}S_{org}}{\mathrm{d}t} = -\left(\sum_i C_i N_i\right) S_{org} \tag{4}$$

$$C_i = 4\,\pi\,D_s\,\overline{r_{i,cond}}\,F(Kn_i)\,A(Kn_i) \tag{5}$$

$$F\,(Kn_i) = \frac{1 + Kn_i}{1 + 1.71Kn_i + 1.33(Kn_i)^2} \tag{6}$$

$$A\,(Kn_i) = \frac{1}{1 + 1.33Kn_i\,F(Kn_i)\left(\frac{1}{s} - 1\right)} \tag{7}$$

$$Kn_i = \frac{MFP_{gas}}{\overline{r_{i,cond}}} \tag{8}$$

We apply two different approaches to distribute SOA across the pre-existing aerosol size distribution. The rate of SOA condensation (dS_{org}/dt) is identical in both approaches. In GLOMAP the standard approach is to assume secondary organic mass (M_{SOA}) condenses as if it were non-volatile, to the Fuchs-corrected surface area ~~(i.e., the kinetic approach)~~ as in Eqn. 9; we refer to this as the “kinetic” approach.

$$\frac{dM_{SOA_i}}{dt} = \frac{C_i N_i}{\sum_{i=1,5} C_i N} \times \frac{dS_{org}}{dt} \tag{9}$$

Here, we apply a second approach in which the amount of secondary organic material entering the aerosol phase is partitioned between the size modes according to Eqn. 10, mimicking the thermodynamic approach; we refer to this as the “mass-based” approach. M_{OAi} is the pre-existing organic mass in mode *i*.

$$\frac{dM_{SOA_i}}{dt} = \frac{M_{OA_i}}{\sum_{i=1,5} M_{OA_i}} \times \frac{dS_{org}}{dt} \tag{10}$$

We complete one simulation without biogenic SOA (*NoSOA*), as well as simulations with biogenic SOA distributed according to the kinetic approach (*KinSOA*), the mass-based~~thermodynamic~~ approach (*Mass~~Therm~~SOA*), and a simulation in which 50% of the SOA mass is distributed according to each approach (*SplitSOA*). We note that the KinSOA simulation matches the approach used in a wide range of recent studies with global aerosol models (Spracklen et al., 2006; Makkonen et al., 2009; Pierce and Adams, 2009; Mann et al., 2010; D'Andrea et al., 2015).

GLOMAP-mode uses a two-moment modal approach, within which mode number and mass concentrations vary but the mode width is held fixed. Following condensation, the particle number concentration for a mode is held constant and the new geometric mean diameter for the mode is calculated according to the updated volume per particle (Mann et al., 2010). Since the mode width is held fixed, this approach will not capture potential changes to the distribution of material within a mode following condensation.

Because our aim is to quantify the impact of changes in the size of particles to which the SOA condenses we otherwise treat SOA identically between the two different approaches and do not allow SOA to re-partition into the gas phase. To isolate the impact of the condensation of secondary organic material the SOA yield, the oxidant chemistry and the SOA condensation rate was identical in all simulations.

2.2 Calculation of radiative effects

The changes to CDNC due to the inclusion of biogenic SOA (i.e., *KinSOA* - *NoSOA*) are calculated from the monthly mean aerosol distribution, using the parameterisation developed by Nenes and Seinfeld (2003), ~~and updated by~~ Fountoukis and Nenes (2005) and Barahona et al. (2010); assuming ~~, with~~ a globally uniform updraught velocity of 0.2 m s^{-1}.

The first AIE due to~~of~~ biogenic SOA is then determined using the offline radiative transfer model of Edwards and Slingo (1996) with nine bands in the longwave and six bands in the shortwave; a monthly mean climatology based on ECMWF reanalysis data and cloud fields for the year 2000 from the ISCCP-D2 archive (Rossow and Schiffer, 1999) are used. To calculate the first AIE, a uniform control cloud droplet effective radius (r_{e1}) of 10 µm is assumed to maintain consistency with the ISCCP derivation of the liquid water path~~cloud data~~, and for each perturbation experiment the effective radius (r_{e2}) is calculated as in Eqn. 11, from monthly mean cloud droplet number fields $CDNC_1$ and $CDNC_2$ respectively (where $CDNC_1$ represents the simulation including SOA, and $CDNC_2$ represents the simulation with no SOA).

$$r_{e_2} = r_{e_1} \times \left[\frac{CDNC_1}{CDNC_2}\right]^{\frac{1}{3}} \tag{11}$$

The first AIE of biogenic SOA is then calculated by comparing net (SW + LW) radiative fluxes using the varying r_{e2} values derived for each perturbation experiment, to those of the control simulation with fixed r_{e1}. In these offline experiments, we do not calculate the second aerosol indirect (cloud lifetime) effect.

To determine the DRE, following the methodology described in Rap et al. (2013), the radiative transfer model is used to calculate the difference in net top-of-atmosphere all-sky radiative flux between experiments including SOA and the equivalent experiments without SOA. Aerosol optical properties ~~scattering and absorption coefficients together with asymmetry parameters~~ are calculated from the monthly mean aerosol distribution ~~for each aerosol size mode and spectral band, as described in Bellouin et al. (2013)~~. The refractive index for each mode is calculated as the volume-weighted mean refractive index of the components present (values for which are given at 550 nm in Table A1 of Bellouin et al., 2011), including water for the soluble modes. The optical properties (scattering and absorption coefficients, together with the dimensionless asymmetry parameter) are then obtained from look-up tables of all realistic combinations of refractive index and Mie parameter, as described in Bellouin et al. (2013).

3 Results

Table 1 summarises how the treatment of SOA condensation in GLOMAP impacts the global flux of secondary organic material to the aerosol size distribution. The total global flux of secondary organic material to the particle phase is the same in each approach (~20.2 Tg(SOA) a^{-1}), but there are important changes to how the material is distributed across particles of different sizes. When the mass-based ~~thermodynamic~~ approach is applied, no SOA is added to the nucleation mode. Rather, SOA is added to larger particles with greater existing organic mass (more than 80% to particles with dry diameter greater than 100 nm, less than 20% to particles with dry diameter between 10 and 100 nm). Under the kinetic approach, most of the secondary organic material also condenses on the larger particles (~76-78% to particles with diameter greater than 100 nm, ~21-23% to particles with dry diameter between 10 and 100 nm). Additionally, a small fraction (0.26%-0.57%) of secondary organic material is added to the nucleation mode (i.e., particles with diameter less than 10 nm), under the kinetic approach. As we show below, this small amount of SOA (0.05-0.11 Tg(SOA) a^{-1}) adding to nucleation mode particles has important implications for the aerosol size distribution.

Figure 1 compares simulated and observed aerosol number size distributions at two~~a boreal~~ forest locations; ~~(~~Hyytiälä, Finland (24.3°E, 61.9°N; described in Hari and Kulmala, 2005)~~)~~ during the northern hemisphere summertime, and Manaus, Brazil (60.2°W, 2.6°S; described in Martin et al., 2010 and Rizzo et al., 2013) during the wet season. From Manaus, we include in our wet season mean only scanning mobility particle sizer (SMPS) data that could be validated (and agreed to within 15%) by comparison to particle number concentrations measured with a condensation particle counter (CPC). In boreal and tropical rainforests~~At Hyytiälä~~, the ~~simulated~~ aerosol size distribution will be ~~is~~ sensitive to a range of processes including particle formation rates, amount of SOA, ~~and~~ the characteristics of primary particles and in-cloud processing (e.g., Spracklen et al., 2008; Martin et al., 2010; Spracklen et al., 2010; Reddington et al., 2011). Our intention here is to demonstrate that the aerosol size distribution simulated by GLOMAP is also sensitive to the treatment of SOA condensation.

When the mass-based ~~thermodynamic~~ approach (~~*Therm*~~*MassSOA*; dashed lines in Fig. 1) is applied, the model simulates high concentrations of nucleation mode particles (smaller than 10 nm dry diameter). Under this approach no organic material condenses on these small particles and their growth is slow since it is limited by the availability of sulphuric acid (Riipinen et al., 2011). This slow growth rate means few particles can grow to larger sizes and the number of particles simulated between 30 – 100 nm diameter is far less than observed at both sites.

When the kinetic approach is applied, a small amount of SOA condenses onto particles in the nucleation mode (0.26% of the total global flux for *ACT* and 0.57% for *ORG*; Table 1), increasing the growth rate of these small particles. At Hyytiälä, ~~T~~the kinetic approach results in a greater number of particles in the 30 – 100 nm size range compared to the mass-based~~thermodynamic~~ approach, improving the match against observations over this size range

(*KinSOA*; full lines in Fig. 1). At Manaus, the number of particles in the 30 – 100 nm range is underestimated with either approach. Under the kinetic approach, the number of particles between 100 – 200 nm is greater than observed, when the organically mediated new particle formation mechanism is used (*KinSOA_ORG*), suggesting that the growth rate of particles in the Aitken mode may be over-estimated under these conditions.

At both sites, we simulate a similar size distribution when we assume ~~We find the best match between model and observations when we assume organically mediated new particle formation and~~ either completely kinetic condensation, or a combination of the kinetic and mass-based approaches ~~of organic material~~ (~~*KinSOA_ORG*;~~ full or dotted red lines in Fig. 1). In the *SplitSOA* experiments, some secondary organic material is able to condense onto newly formed particles (0.19% of the total flux for *ACT* and 0.44% for *ORG*; Table 1), resulting in a size distribution similar to that generated by the kinetic approach (*SplitSOA*; dotted lines in Fig. 1). ~~The faster nucleation rates under this mechanism combined with condensation of organic material on small particles under the kinetic condensation assumption increases the number of particles in the 30 – 100 nm size range.~~ This implies that it is not necessary to assume that all of the organic material generated has an extremely low volatility in order to account for the growth of particles to CCN relevant sizes, but that some fraction of the SOA does need to be treated in this way, consistent with the findings of Kulmala et al. (2013).The same relative response to the kinetic and ~~thermodynamic~~mass-based approaches was documented by D'Andrea et al. (2013) and is consistent with ~~the findings of~~ Yu (2011) who combined the kinetic condensation of low volatility organics with the equilibrium partitioning of semi-volatile organics.

3.1 Changes to Cloud Droplet Number Concentration

Table 2 reports the simulated changes to global CDNC due to biogenic SOA under the kinetic, mass-based~~thermodynamic~~ and split approaches, for both nucleation mechanisms. As we have reported previously, the impact of biogenic SOA on CDNC strongly depends on the nucleation mechanism used in the model, with the largest impact on CDNC simulated with an organically mediated new particle formation mechanism (Scott et al., 2014). We find that for both nucleation mechanisms, biogenic SOA leads to a larger global annual mean increase in CDNC under the kinetic condensation approach compared to the mass-based~~thermodynamic~~ approach. With the *ACT* nucleation mechanism, GLOMAP simulates a 3.4% increase in global annual mean CDNC with kinetic condensation but only a 1.4% increase when the mass-based approach is used~~with thermodynamic condensation~~. Similarly, with the *ORG* nucleation mechanism, GLOMAP simulates a 21.1% increase in global annual mean CDNC with kinetic condensation and a 16.8% increase when the mass-based approach is used~~ith thermodynamic condensation~~; the same relative response is observed in our sensitivity study (*ORG_x10*), in which the organically mediated nucleation rate is a factor of 10 higher. The *SplitSOA* approach increases the global annual mean CDNC by almost as much as the kinetic approach (+ 3.2% for *ACT* and +20.4% for *ORG*) because only a small amount of SOA is required to allow the smallest particles to grow sufficiently.

Simulated changes to CDNC (Fig. 2) are not restricted to the areas over which biogenic SOA is generated, or proportional to the amount of SOA being generated ~~(Fig. 2)~~, as discussed in Scott et al. (2014). Under the kinetic approach, GLOMAP simulates large fractional increases to CDNC over boreal regions and southern hemisphere oceans (greater than 20% for *ACT* and over 100% for *ORG*; Fig. 2). Using the mass-based ~~nder the thermodynamic~~ approach, the growth of particles to CCN-relevant size is suppressed and fewer regions experience such large increases in CDNC in response to the inclusion of biogenic SOA.

The inclusion of biogenic SOA can induce decreases in simulated CDNC due to an enhanced rate of ageing / scavenging of initially hydrophobic particles, or the suppression of nucleation in the free troposphere (and subsequent entrainment back into the boundary layer) due to an increased condensation sink at the surface (Scott et al., 2014). When the *ACT* mechanism for new particle formation is used with the kinetic approach, these effects combine to give small decreases to CDNC over tropical ocean regions (Fig. 2*a*); when the mass-based ~~thermodynamic~~ approach is used, much larger ocean regions experience a decrease in CDNC (Fig. 2*b*). In the *ORG* simulations, the contribution of organic oxidation products to new particle formation is sufficient to prevent any regional decreases in CDNC under either approach (Fig 2*c* & *d*).

To examine the sensitivity of this response to updraught velocity, CDNC were calculated a five globally uniform updraught velocities, from 0.1 m s^{-1} to 0.5 m s^{-1}, for the ACT set of experiments (Table 3). Under both approaches to SOA partitioning, increasing the updraught velocity increases the absolute and fractional change in CDNC at low-level cloud base due to biogenic SOA; however, the relative kinetic to ~~thermodynamic~~mass-based response remains consistent.

3.2 First Aerosol Indirect Effect

We explored the impact of the condensation approach on the first AIE due to biogenic SOA and report the global annual mean values in Table 2; Figure 3 shows the spatial patterns in annual mean first AIE for each nucleation mechanism and partitioning approach~~assumption~~. The global annual mean first AIE is calculated for an updraft velocity of 0.2 m s^{-1}; in Table 3 we show consistent results for a range of updraft velocities between 0.1 and 0.5 m s^{-1}.

Increases in CDNC lead to a negative first AIE (i.e., a cooling effect), and decreases in CDNC lead to a positive first AIE (i.e., a warming effect). When the *ACT* new particle formation mechanism is used, the kinetic approach gives a negative global annual mean first AIE of -0.07 W m^{-2}, with a negative first AIE in regions of CDNC increase, and a positive first AIE in regions of CDNC decrease (Fig. 3*a*). When the *ACT* mechanism is used with the mass-based~~thermodynamic~~ approach, spatially extensive decreases in CDNC (as compared to the kinetic approach) lead to large regions where a positive first AIE is simulated, and a positive global annual mean first AIE (+0.01 W m^{-2}) due to biogenic SOA (Fig. 3*b*).

When the *ORG* mechanism is used with the kinetic approach, the inclusion of biogenic SOA generates a global annual mean first AIE of -0.66 W m^{-2}, due to widespread increases in CDNC (Fig. 2*c*), which is reduced to -0.50 W m^{-2} under the mass-based~~thermodynamic~~ approach (Table 2). A global annual mean negative first AIE is maintained under the mass-based~~thermodynamic~~ approach because the contribution of organic oxidation products to new particle formation is sufficient to outweigh the impact of suppressed growth on CDNC (Fig 2*d*). The same relative response between the two partitioning approaches (-0.78 W m^{-2} for kinetic, as compared to -0.59 W m^{-2} for the mass-based approach) is observed for our *ORG_x10* sensitivity simulations, in which the organically mediated nucleation rate is a factor of 10 higher.

For both nucleation mechanisms, the *SplitSOA* approach gives a negative first AIE (-0.05 W m^{-2} for *ACT* and -0.63 W m^{-2} for *ORG*), of similar magnitude to the kinetic approach due to similar changes to global annual mean CDNC.

3.3 Direct Radiative Effect

The direct radiative effect is less sensitive to the distribution of secondary organic material across the aerosol size distribution (Table 2). When the *ACT* new particle formation mechanism is used, the kinetic approach gives a global annual mean DRE of -0.10 W m^{-2}, as compared to -0.11 W m^{-2} with the kinetic approach. When the *ORG* mechanism for new particle formation is used, the inclusion of biogenic SOA generates a global annual mean DRE that varies between ~~of~~ -0.08 and -0.09 W m^{-2} across all three approaches to partitioning.~~under both the kinetic and thermodynamic approaches.~~

This lack of sensitivity can be explained in part by the fact that, under the mass-based~~thermodynamic~~ approach, the shift in SOA mass from smaller (< 100 nm dry diameter) to larger (> 100 nm dry diameter) particles represents a much smaller fractional change to the amount of SOA the larger particles receive. Using the *ACT* mechanism, particles greater than 100 nm dry diameter receive approximately 20% more secondary organic mass per particle under the mass-based~~thermodynamic~~ approach, relative to the amount they received under the kinetic approach. Whereas, particles smaller than 100 nm dry diameter receive approximately 40% less secondary organic mass per particle under the mass-based~~thermodynamic~~ approach, relative to the amount they received under the kinetic approach (Table 2).

4 Conclusions

Using a global aerosol microphysics model we have shown that the manner in which secondary organic material is added to the aerosol size distribution is important in determining its impact on the number and size of climatically relevant particles in the atmosphere. We tested two assumptions about the way secondary organic material is added to existing particles – a kinetic approach where material condenses according to the surface area of existing particles and a mass-based approach where the material condenses according to the organic mass present in existing particles. We calculate the impact of these assumptions on the direct radiative effect (DRE) and aerosol indirect effect (AIE) due to biogenic secondary organic aerosol (SOA).

The kinetic approach to partitioning, which enables organic oxidation products to condense upon the smallest particles, facilitating their growth to larger sizes, increases global annual mean CDNC when either an activation or organically mediated new particle formation mechanism is applied (by 3.4% for *ACT* and 21.1% for *ORG*). These global annual mean increases in CDNC result in a negative global annual mean first AIE (-0.07 W m^{-2} for *ACT* and -0.66 W m^{-2} for *ORG*).

Applying a mass-based approach to partitioning ~~the thermodynamic approach~~ suppresses the growth of the smallest particles, resulting in a smaller global annual mean increase in CDNC (+1.4% for *ACT* and +16.8% for *ORG*). When an activation mechanism is applied to new particle formation, the mass-based ~~thermodynamic~~ approach results in a small positive first AIE (+0.01 W m^{-2}) due to biogenic SOA. When an organically mediated new particle formation mechanism is applied, a negative first AIE is maintained because the contribution of organic oxidation products to new particle formation is sufficient to outweigh the impact of suppressed growth on CDNC, but the magnitude of the first AIE is reduced by 24% to -0.50 W m^{-2}; we see a consistent response when the organically mediated nucleation rate is a factor of 10 higher.

Neither approach adequately describes the complex behaviour of secondary organic material in the atmosphere. Ultimately, a combination of ~~the~~ thermodynamic and kinetic approaches will be required to accurately represent the behaviour of SOA in global models. Improving on existing first attempts by e.g., Riipinen et al. (2011), Yu (2011), and the *SplitSOA* approach described here, will require a more detailed understanding of the pathways by which organic compounds of differing volatilities are generated, and their relative contributions to the growth of particles of different sizes.

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Table 1: Global annual mean fluxes of secondary organic material to the aerosol size distribution in GLOMAP. D_g is the geometric mean diameter for each mode.

Comment [CS[1]: Values in Table updated to reflect updated results for ORG simulation

New particle formation	**Distribution of secondary organic material**		**Smaller than 100 nm**		**Larger than 100 nm**	
			Nucleation (D_g < 10 nm)	Aitken (10 < D_g < 100 nm)	Accumulation (100 nm < D_g < 1µm)	Coarse (D_g > 1µm)
ACT	*Kinetic (KinSOA)*	Percentage of total flux	0.26 %	20.94 %	78.26 %	0.55 %
		Annual total flux	4.28 Tg(SOA) a^{-1} 6.77 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		15.92 Tg(SOA) a^{-1} 1.50 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	
	Mass based ~~Thermodynamic~~ (~~Therm~~MassSOA)	Percentage of total flux	0.00 %	18.71 %	81.24 %	0.04 %
		Annual total flux	3.77 Tg(SOA) a^{-1} 4.06 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		16.38 Tg(SOA) a^{-1} 1.81 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	
	50% kinetic 50% mass based ~~thermodynamic~~ (SplitSOA)	Percentage of total flux	0.19 %	20.92 %	78.49 %	0.40 %
		Annual total flux	4.27 Tg(SOA) a^{-1} 6.10 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		15.94 Tg(SOA) a^{-1} 1.53 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	
ORG	*Kinetic (KinSOA)*	Percentage of total flux	0.57 %	23.43 %	75.52 %	0.48 %
		Annual total flux	4.86 Tg(SOA) a^{-1} 4.63 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		15.40 Tg(SOA) a^{-1} 1.17 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	
	Mass based ~~Thermodynamic~~ (Mass~~Therm~~SOA)	Percentage of total flux	0.00 %	18.76 %	81.16 %	0.08 %
		Annual total flux	3.79 Tg(SOA) a^{-1} 2.12 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		16.40 Tg(SOA) a^{-1} 1.73 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	
	50% kinetic 50% mass based ~~thermodynamic~~ (SplitSOA)	Percentage of total flux	0.44 %	22.94 %	76.26 %	0.36 %
		Annual total flux	4.73 Tg(SOA) a^{-1} 4.00 x 10^{-12} ng(SOA) particle^{-1} sec^{-1}		15.52 Tg(SOA) a^{-1} 1.21 x 10^{-11} ng(SOA) particle^{-1} sec^{-1}	

Table 2: Global annual mean change to CDNC, calculated using a globally uniform updraught velocity of 0.2 m s^{-1}, in the model level corresponding to low-level cloud base (mean pressure of approx. 900 hPa), and first AIE, due to biogenic SOA in GLOMAP using the kinetic and mass-based ~~thermodynamic~~ approaches.

Nucleation mechanism	**Background (without biogenic SOA) global annual mean CDNC** (cm^{-3})	**Distribution of secondary organic material**	ΔCDNC	**AIE** (W m^{-2})	**DRE** (W m^{-2})
ACT	185.2	*Kinetic*	+6.3 (+3.4%)	-0.07	-0.10
		Mass based	+2.6 (+1.4%)	+0.01	-0.11
		50 % kinetic 50% mass based	+5.9 (+3.2%)	-0.05	-0.11
ORG	165.2	*Kinetic*	+34.8 (+21.1%)	-0.66	-0.09
		Mass based	+27.8 (+16.8%)	-0.50	-0.08
		50 % kinetic 50% mass based	+33.77 (+20.4%)	-0.63	-0.09
ORG_x10	165.2	*Kinetic*	+41.5 (+25.1%)	-0.78	-0.08

		Mass based	+33.0 (+20.0%)	-0.59	-0.08
		50% kinetic *50% mass based*	+40.3 (+24.4%)	-0.75	-0.09

Table 3: Global annual mean change to cloud droplet number concentration (CDNC), calculated using five globally uniform updraught velocities, in the model level which corresponds to low-level cloud base (mean pressure of approximately 900 hPa), and first aerosol indirect effect (AIE), reported to 2 decimal places, resulting from the inclusion of biogenic SOA in GLOMAP using the kinetic and mass-based ~~thermodynamic~~ approaches. The mean values are calculated assuming that all updraught velocities are equally likely.

Nucleation mechanism	**Updraught velocity ($\mathrm{m\ s^{-1}}$)**	**Distribution of secondary organic material**			
		Kinetic		*Thermodynamic*	
		ΔCDNC ($\mathrm{cm^{-3}}$)	**AIE ($\mathrm{W\ m^{-2}}$)**	**ΔCDNC ($\mathrm{cm^{-3}}$)**	**AIE ($\mathrm{W\ m^{-2}}$)**
ACT	0.1	+2.7 (+2.0%)	-0.04	+0.6 (+0.5%)	+0.02
	0.2	+6.3 (+3.4%)	-0.07	+2.6 (+1.4%)	+0.01
	0.3	+9.1 (+4.3%)	-0.08	+4.4 (+2.1%)	0.00
	0.4	+11.3 (+4.9)	-0.08	+6.0 (+2.6%)	-0.01
	0.5	+12.9 (+5.3%)	-0.08	+7.2 (+3.0)	-0.01
	Mean	**+8.4 (+4.0%)**	**-0.07**	**+4.2 (+1.9%)**	**+0.004**

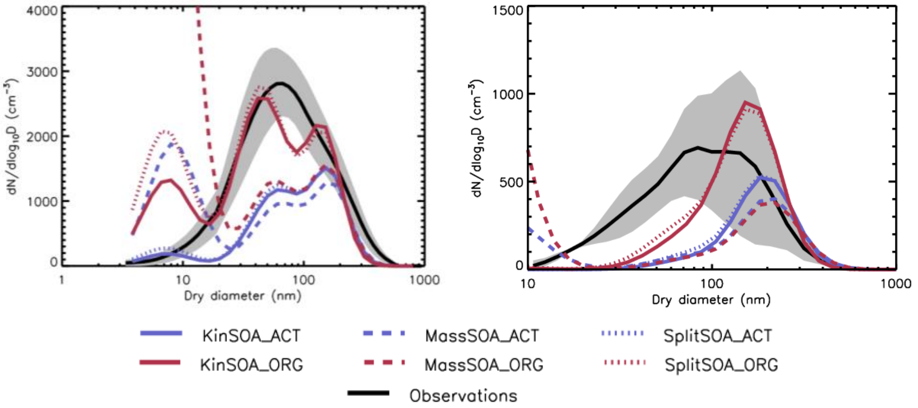

Figure 1: Simulated and observed mean aerosol number size distributions at two~~a boreal~~ forested sites. Left: ~~(~~Hyytiälä, Finland~~)~~ during June-July-August (multi-annual; 1996-2006). Right: Manaus, Brazil during the wet season (multi-annual; Jan-Jun, 2008-2009). The grey shaded regions indicate ± 1 standard deviation from the seasonal mean, calculated from the observed monthly mean size distributions (over all years). In each figure, ~~S~~simulations show the sensitivity to nucleation mechanism: activation (blue), organic (red) and condensation assumptions: kinetic approach (solid), mass-based approach ~~thermodynamic~~ (dashed), 50% split kinetic and mass-based approaches- ~~thermodynamic~~ (dotted).

Comment [CS[2]: Figure updated to include new site and reflect updated results for ORG simulations

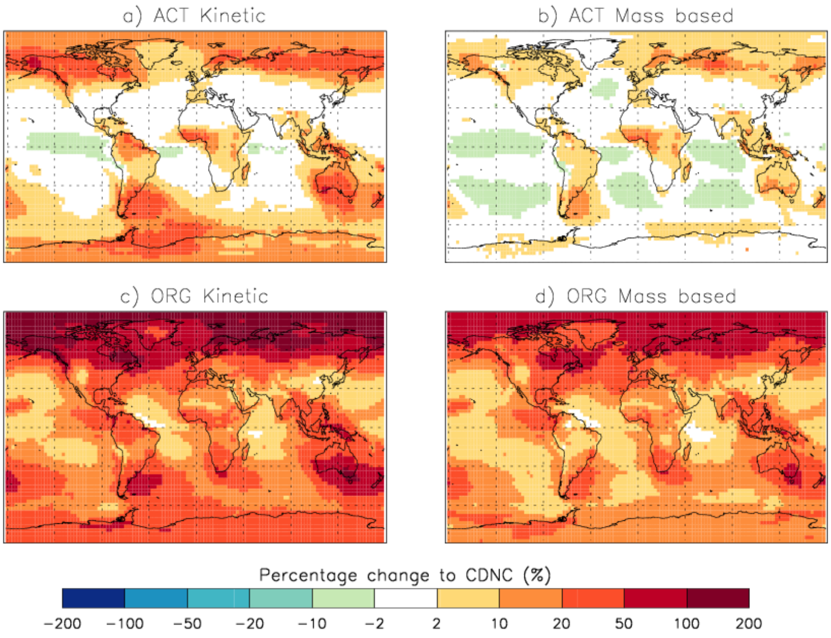

Figure 2: Annual mean percentage change to CDNC (using a uniform updraught velocity of 0.2 m s^{-1}) from biogenic SOA in GLOMAP, in the model level which corresponds to low-level cloud base (mean pressure of approximately 900 hPa); SOA is distributed according to the kinetic~~ally~~ approach (*a* and *c*)~~,~~ and the mass-based approach ~~thermodynamically~~ (*b* and *d*). Simulations use either an activation (*a* and *b*) or organically mediated (*c* and *d*) new particle formation mechanism.

Comment [CS[3]: Figure updated to reflect updated results for ORG sims

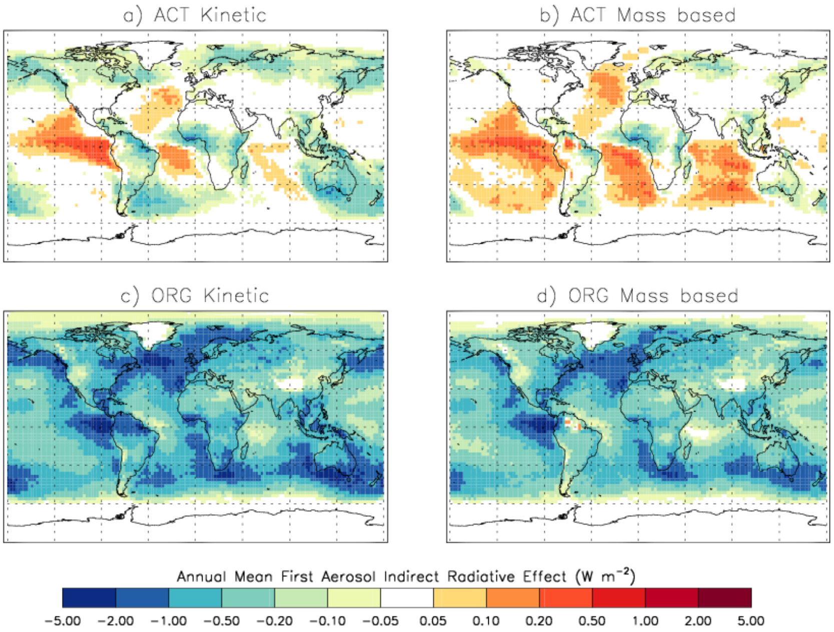

Figure 3: Annual mean first AIE (W m^{-2}) from biogenic SOA in GLOMAP when SOA is distributed according to the kinetic~~ally~~ approach (*a* and *c*) and the mass-based approach ~~, thermodynamically~~ (*b* and *d*). Simulations use either an activation (*a* and *b*) or organically mediated (*c* and *d*) new particle formation mechanism.

Comment [CS[4]: Figure updated to reflect new results for ORG simulations