Interactive comment on "The effects of hygroscopicity of fossil fuelcombustion aerosols on mixed-phase clouds" by Yun et al.

In this manuscript, a new parameterization scheme of ice nucleation was proposed and implemented in the CAM-IMPACT model, which was then applied to study the influence of elevated emissions on anthropogenic forcing. Sensitivity studies were also carried through comparison among different schemes). The parameterization of ice nucleation and mixed phase clouds is an important and challenging issue in climate modeling. I appreciate the authors' scientific work and I find their results interesting and promising. My major concern is if the new parameterization scheme makes more sense compared with the empirical equations. It seems that the provided experimental results are not sufficient to significantly improve the scheme (see general comments 1). Overall, I find the manuscript meets the scope of the journal and I would recommend publication of this work after the authors have seriously considered my comments/suggestions.

(Review comments in plain font, Replies in *italics*)

General comments

1. Ice nucleation activity of BC particles.

In the 3-ffBC/OM scheme, ice nucleation activity (INA) is considered as a function of the coating thickness of sulfuric acid. This assumption is based on (1) INA measurements of soot particles with different hygroscopicity and (2) the dependence of soot hygroscopicity on the coating thickness of sulfuric acid.

Besides sulfate, secondary organic matter, which comprises a major fraction of aerosol particle mass (Zhang, Jimenez et al. 2007), can also contribute to the coating and the change of aerosol hygroscopicity (Gunthe, Rose et al. 2011) and INA (Crawford, Möhler et al. 2011, as mentioned by the authors). The effects of organics could be as important as sulfate for both real atmosphere and laboratory studies. I am not sure if the scheme can be really improved by considering the coating of sulfuric acid alone. It seems that there is no comparable (to sulfuric acid) study about the effect of organics on INA. Therefore, I encourage the authors to provide complimentary information about all IN (ice nuclei, 3 kinds of BC, dust) under different schemes (1BC, 3BC_SCO and 3BC_noSCO), e.g. something like Fig. C1 (Phillips, DeMott et al. 2008) and Fig. C2 (Hoose, Kristjánsson et al. 2010). By adding such information, the readers could judge the scheme and conclusions themselves.

Reply: We agree with the reviewer that coating or mixing with secondary organic matter is also important. The effects of organic coverage may change the particle hygroscopicity as was shown in laboratory simulations performed in Popovicheva et al., (2009). Measurements of water uptake showed that non-polar organics (aliphatic and aromatic hydrocarbons) lead to hydrophobization of the soot surface. Acidic properties of organic compounds such as those of oxidized PAHs, ethers, ketones, aromatic and aliphatic acids are related to higher water uptake, while inorganic acids, like sulfuric acid, and ionic compounds, like salts of organic acids, are responsible for the soot surface becoming more

hydrophilic. Popovicheva et al. (2009) found that with the same amount of coverage, the impact of organic acid on soot hygroscopicity is weaker than that from sulfuric acid (Figure 7 in Popovicheva et al. 2009).

The issue with organics is that our model does not follow the organic functional groups. To do it right would take a far more sophisticated model as well as better quantification of the role of different organic functional groups in ice formation. This study is only a first step in more sophisticated treatment of ice nucleation. We have added the following discussion to the introduction: "Coating or mixing with secondary organic matter may also change the particle hygroscopicity as was shown in laboratory simulations performed in Popovicheva et al., (2009) and Crawford et al. (2011), among others. However, it has been shown by Popovicheva et al., (2009) that with the same amount of coverage, the impact of organic acid on soot hygroscopicity is weaker than that from sulfuric acid. Also, our model currently does not follow the organic functional groups. To do so would require a sophisticated organic chemistry-aerosol model that accounted for formation of secondary organic aerosols (as in, for example, Lin et al., 2012) as well as a better quantification of the role of different organic functional groups in ice formation. Thus, this study, which only considers the coating of soot by sulfuric acid, should be viewed as an exploratory step toward a more sophisticated treatment of ice nucleation."

We have added a figure similar to Fig. C1 in Phillips, DeMott et al. 2008 to show the ice nucleation ability of all IN in 1-ffBC/OM and 3-ffBC/OM schemes.

2. Mixing state of BC.

The mixing state of BC is a crucial parameter for its CCN, IN activity and optical properties. It is not explicitly explained how the mixing state of BC is treated in this study. Do you consider BC as externally mixed or internally mixed with other component (SO_4^{2-}, organics)? The authors state that BC and OM are assumed to be internally mixed (P19991 line 17, 'Although BC and OM are treated as distinct species in the model, they are assumed to be internally mixed'), how about BC and sulfate? The use of coating thickness (ncoat) seems to imply that the transition from externally mixed to internally mixed BC has been considered but I didn't find any details in this paper.

Reply: Fossil fuel BC and OM were emitted as externally mixed with sulfate. They become internally mixed with sulfate by three processes in the model: sulfuric acid condensation, coagulation with sulfate aerosol, and aqueous sulfuric acid formation in liquid droplets. The details can be found in Herzog et al., (2004). We have added more details to section 2.1.

In the new scheme, hygroscopic BC is defined as BC particles with ncoat>3. Is there any upper limit of ncoat confining hygroscopic BC? Field measurements have found internally mixed particles with more coating materials (sulfate, organics) than a small BC cores, which is actually often the case in remote areas or even polluted areas (Cheng, Su et al. 2012). INA of such particles (thickly coated BC) is more closer to the coating material sulfate/organics. If there is no upper limit of ncoat, even a small BC core can make the whole particles to be BC, which has subsequent impact on the concentration of ice nuclei and mixed-phase clouds.

Reply: We think (if we understood correctly) the reviewer is concerned that if there is no upper limit of ncoat, then with a lot of coating (ncoat is large), how do we know that the internally mixed particle still freeze like BC, but not the coating material (sulfate in our case). The answer is that we do not set an upper limit for ncoat, but we consider both possibilities. The sensitivity experiment of hygroscopic BC freeze homogeneously, instead of heterogeneously is intended to take into account that a lot of coating will make the soot particle act in a similar fashion to the coating material sulfate. While the sensitivity experiment in which we treat hygroscopic BC as freezing heterogeneously means their freezing property is still "like BC". We have not added anything, since this is already stated in the last paragraph in section 2.2.

3. Hygroscopicity or IN activity

It might not be appropriate to use the current title considering the scope of this paper. It is more about ice nucleation ability rather than hygroscopicity. According to the current title, I would expect impact on the CCN activation, hygroscopic growth and deposition/life time of BC particles.

'The effects of hygroscopicity of fossil fuel combustion aerosols on mixed-phase clouds' changed to 'The effects of ice nucleation ability of fossil fuel combustion aerosols on mixed-phase clouds'

Reply: We partially agree with this comment. However, we are also dealing with hygroscopicity effects. The title will be changed to "The effect of hygroscopicity on ice nucleation of fossil fuel combustion aerosol in mixed-phase clouds".

Specific comments

1. Abstract: Page 19988, line 7; Table 1

'The new scheme results in significant changes …'

Please specify which scheme (3BC_SCO or 3BC_noSCO) you meant. Also in Table 1, 3BC SCO scheme is described as '*3-ffBC/OM scheme and hygroscopic particles as heterogeneous ice nuclei*', do you mean hygroscopic soot particles as heterogeneous ice nuclei?

Reply: "The new scheme" here refers to the 3-ffBC/OM scheme in general (includes both 3BC_SCO and 3BC_noSCO). "soot" is added to the scheme description in Table 1.

2. Abstract: Page 19988, line 10

'but could be more positive if hygroscopic soot particles are allowed to nucleate ice particles.'

I suggest the authors to give exact numbers for the case when hygroscopic soot particles are allowed to nucleate ice, 'but could be more positive (x W m-2 and y W m-2)…'

Reply: We have carried out a one-year online simulation of the 3BC_SCO case, and estimated the net whole-sky anthropogenic aerosol forcing for this case to be -1.28 W/m². Therefore, we changed this sentence to: "The total anthropogenic cloud forcing and whole-sky forcing with the new scheme is 0.06 W/m² and -2.45 W/m², respectively, but could be more positive (by about 1.17 W/m²) if hygroscopic soot particles are allowed to nucleate ice particles." We have also added the following discussion to section 3.2: "Based on a one-year simulation using the online model the net whole-sky anthropogenic aerosol forcing for 3BC_SCO case is -1.28 W/m²."

3. Introduction: Page 19988, line 15

'Soot aerosols produced by fossil fuel and biomass burning contain both black carbon (BC) and organic matter (OM)…'

It is not appropriate to state that soot particles contain black carbon and organic matter, both of 'which act to absorb solar radiation'. Black carbon could contain compounds (grey carbon) which don't belong to soot particles. Also many/or probably most organic matters in the atmosphere is not actively involved in the absorption of solar radiation. I suggest the author to reformulate these claims and refer to the paper of (Andreae and Gelencsér 2006).

Reply: We agree that "It is not appropriate to state that soot particles contain black carbon and organic matter, both of 'which act to absorb solar radiation', but not because "Black carbon could contain compounds (grey carbon) which don't belong to soot particles". According to the general definition BC is the highly absorbing part of soot related to elemental carbon (Watson et al., 2005). It can not contain any "grey" carbon or others.

We agree because some organics mostly scatter the solar radiation while some other organic (like high molecular weight organic compounds such as those found in biomass burning - produced aerosols) can absorb quite well, especially at UV wavelengths.

We reformulate this statement as "Soot aerosols produced by incomplete combustion of fossil fuel and biomass, containing black carbon (BC) and organic matter (OM), can absorb solar radiation, thereby changing vertical temperature profiles and decreasing surface radiation (Andreae and Gelencsér 2006)."

4. Page 19989, line 3

'During the lifetime of soot aerosols in the atmosphere their hygroscopicity can be altered through coating by sulfate (Zhang et al., 2008).'

Besides sulfate, hygroscopicity can also be modified through coating by organics (Petters and Kreidenweis 2007; Gunthe, Rose et al. 2011).

Reply: Thank you. The sentence is changed to "During the lifetime of soot aerosols in the atmosphere their hygroscopicity can be altered through coating by sulfate and organics (Zhang et al., 2008; Petters and Kreidenweis, 2007; Gunthe et al., 2011)."

5. Page 19990, line 18

'Popovicheva et al. (2008, 2010) suggested that the hygroscopicity of soot could be quantified by the amount of water film extended over the soot surface at relative humidity < 80%.'

Is the difference in hygroscopicity sufficient to explain the contrasting/different results of previous experiments? Considering the parameterization scheme, is there any other factor that we should include for future studies?

Reply: We believe this is the primary cause of the differences in nucleation ability of different soots reported in Koehler et al. (2009). However, there can always be something that we have left out. Other possible factors may include differences in the bare soot particle, as we pointed out in the paragraph before this sentence, "These studies all lead to different conclusions about the effect of adding a soluble coating to soot. One possible reason for the differences in nucleation is the differences in the properties of the bare soot particles, for example, the organic content, porosity, surface area, etc."

6. Page 19991, Line 8

'The coupled model (inline simulation) provides …'

Do you mean 'online simulation'?

Reply: Yes. We think both are used in the literature, but we changed it to "online" to reduce confusion.

7. Page 19991, Line 8,

'The coupled model (inline simulation) provides the aerosol fields and meteorology fields for the offline model, and is used to calculate the total anthropogenic forcing.'

I am wondering why both offline and online simulations are used. Could you please give some explanations?

Reply: The analysis of the effect of hygroscopicity on ice nucleation of soot particles is done mainly with the offline simulation. The reason for using offline simulation is to fix the aerosol field. With the online simulation, using the 1-ffBC/OM scheme or 3-ffBC/OM scheme will produce changes to the aerosol field. Therefore the amount of ffBC/OM entering the ice nucleation scheme could be different. So the resulting differences cannot be attributed to the treatment of hygroscopicity in the ice nucleation scheme only. We added the following clarifying sentence to this paragraph: *"Using the offline model ensures that a fixed amount of ffBC/OM aerosol enters the ice nucleation scheme, and that changes in the cloud field and radiation is solely from the treatment of hygroscopicity in the ice nucleation scheme."*

8. Page 19991, Sect 2.1

'The University of Michigan IMPACT aerosol model … a two-moment microphysics scheme … The PH08 parameterization was modified …

It is good scientific practice to briefly describe the method first and then complement it by references. It would be helpful to include brief introduction about the aerosol model, microphysics, etc.

Reply: We've added more description about the aerosol model to section 2.1.

9. Page 19991, Line 10

'The offline model reads the aerosol and meteorology fields and examines the cloud water fields and mixed-phase cloud anthropogenic forcing without involving feedbacks to the cloud fields from changes in aerosols.'

It is not clear to me how the offline model works. Since hydrometers (both liquid and frozen water) generally belong to meteorology fields, 'reading meteorology fields' for me means that the model has got all information about mixed-clouds through input meteorological data. How aerosols change the prescribed meteorological fields in the offline model?

Reply: The advantage of using an offline model is that we can decide ourselves what is fixed and what is not. Even though we can read in all meteorology variables, for example the ice number, ice water content, and liquid water content, we can still choose to predict the ice number using the read-in aerosol field. By doing that and fixing the ice water content, we can get an aerosol indirect effect in mixed-phase cloud that's similar to the 1st indirect effect in warm clouds. However, in our offline model, we also chose to allow the ice water and liquid water change from Bergeron-Findensen process and contact freezing. All other meteorology variables are fixed.*

We have added the following explanation to the offline model in section 2.1: "In the offline radiation model, we predict the ice number concentration from nucleation using aerosol concentrations from an

on-line calculation that are read-in. The ice/liquid number/mass concentration change from contact freezing and the Bergeron-Findeisen process (the conversion of liquid to ice) was also implemented, due to its importance to radiative forcing (Storelvmo et al., 2008b). Other meteorology variables are fixed and no further processing of ice particles takes place (no sedimentation, coagulation, or precipitation formation)."

10. Page 19992, line 16

'The accommodation coefficient for the,'

Remove the comma

Reply: We think it was not in original draft that we submitted.

11. Page 19992, Sect 2.2

I suggest the authors to express the new scheme by a series of equations. It is difficult for me to figure out how the new scheme works exactly.

Reply: We added a diagram to show how the new 3-ffBC/OM scheme works, and also add a figure that shows the frozen fraction of hydrophobic, hydrophilic, and hygroscopic ffBC/OM as a function of temperature.

12. P19993, line 13

'Therefore, we made two assumptions to treat the freezing of hygroscopic particles at higher temperatures. The first is … The second is that they freeze heterogeneously, and we scale the frozen fraction of PH08 by a factor of 15.'

Could you please specify the conditions when they are assumed to freeze homo- or hetero-geneously? Otherwise these assumptions seem to be contradictory.

Reply: They are contradicting assumptions. The reason we make these assumptions is because there are contradicting observational results regarding whether multi-layer coated BC freeze heterogeneously or homogeneously (Crawford et al., 2011; DeMott et al., 1999). And we want to cover this range of sensitivity. We did not change the manuscript since this is addressed in section 2.2.

13. Page 19994, line 13-17

'Hydrophobic ffBC/OM is confined… The lifetime of the ffBC/OM particles increases with hygroscopicity from 0.45 to 0.95 to 4.55 days.'

Do you consider the impact of soot hygroscopicity on its lifetime/removal in your model simulations? If so, please add some descriptions. If not, difference in lifetime should be the cause and difference in hygroscopicity the effect. In the current manuscript, it is expressed the other way round.

Reply: The impact of hygroscopicity on the lifetime of soot is considered through wet and removal rates, since the wet scavenging efficiency is larger when the soluble material fraction is larger in a particle. The aging process that transforms hydrophobic soot to hydrophilic and hygroscopic soot as a result of additional increases in sulfate coating is considered as a sink of the hydrophobic and hydrophilic soot particles while the only sink of hygroscopic soot is via wet and dry deposition. Therefore hydrophobic particles have the shortest lifetime and least coating accumulation, and hygroscopic soot has the longest lifetime and the most coating accumulation. We've added the following explanation to this paragraph: "The aging process that transforms hydrophobic soot to hydrophilic and hygroscopic soot as a result of additional increases in sulfate coating is considered as a sink of the hydrophobic and hydrophilic soot particles while the only sink of hygroscopic soot is via wet and dry deposition. Therefore the hydrophobic soot particles have the shortest lifetime of 0.45 days. The lifetimes of the hydrophilic and hygroscopic ffBC/OM particles are 0.95 and 4.55 days, respectively."

14. Page 19995, line 4,16

'Figure 3 shows the grid-mean ice number concentration (Ni) change from PI to PD' … 'An increase in Ni causes a net conversion of liquid to ice'

Is Ni the number concentration of ice nuclei or the hydrometer - ice? 'An increase in Ni causes a conversion *of liquid to ice'* seems to imply Ni is the ice nuclei concentration. I suggest the authors to clarify this.

Reply: Ni is the number concentration of the hydrometeor ice. Increase in the ice number concentration will lead to reduction of liquid water mass, and increase of ice water mass due to the Bergeron-Findeisen process. We have revised the sentence as follows to clarify: "An increase in Ni causes a net conversion of liquid to ice <u>mass</u> in mixed-phase clouds, as a result of the Bergeron-Findeisen process."

15. Page 20002, Table 2

If 'off-line forcings are for mixed-phase clouds' only, should the forcings of Net Whole-Sky be left blank?

Reply: We do not think it is necessary to leave net whole-sky forcing blank for offline simulations. Keeping it there is helpful for two reasons. The first is that it shows no clear sky changes are included in the offline simulations. The second is to compare with the net whole-sky forcing from online simulations.

16. Page 20003, Fig. 1

The resolution of the figure is too low.

Reply: We have increased the size and resolution of the figures.

17. Page 20003, Fig.1, 2, etc

I suggest using the same format for all units, i.e. using either mg/m2 or mg m-2, not both. See figure titles and captions.

Reply: We are sorry that we did not find mg m-2 in our figure titles and captions.

Reference:

Andreae, M. O. and A. Gelencsér (2006). "Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols." Atmos.Chem. Phys.**6**(10): 3131-3148.

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Crawford, I., O. Möhler, et al. (2011). "Studies of propane flame soot acting as heterogeneous ice nuclei in conjunction with single particle soot photometer measurements." Atmos. Chem. Phys.**11**(18): 9549-9561.

Gunthe, S. S., D. Rose, et al. (2011). "Cloud condensation nuclei(CCN) from fresh and aged air pollution in the megacity region of Beijing." ATMOSPHERIC CHEMISTRY AND PHYSICS**11**(21): 11023-11039.

Hoose, C., J. E. Kristjánsson, et al. (2010). "How important is biological ice nucleation in clouds on a global scale?" Environmental Research Letters**5**(2): 024009.

Koehler, K. A., DeMott, P. J., Kreidenweis, S. M., Popovicheva, O. B., Petters, M. D., Carrico, C. M., Kireeva, E. D., Khokhlova, T. D., and Shonija, N. K.: Cloud condensation nuclei and ice nucleation activity of hydrophobic and hydrophilic soot particles, Phys Chem Chem Phys, 11(36), 7906-7920, 2009.

Lin, G., Penner J. E.,Sillman S., Taraborrelli D., and Lelieveld J.: Global modeling of SOA formation from dicarbonyls, epoxides, organic nitrates and peroxides, Atmospheric Chemistry and Physics, 12(10), 4743-4774, doi:10.5194/acp-12-4743-2012, 2012

Petters, M. D. and S. M. Kreidenweis (2007). "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity." Atmos. Chem. Phys.**7**(8): 1961-1971.

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Popovicheva et al. (2009). Water interaction with laboratory-simulated fossil fuel combustion particles. J.Phys. Chem.A., 113 (39), pp 10503–105

Watson et al. (2005). Summary of Organic and Elemental Carbon/Black Carbon Analysis Methods and Intercomparisons, Aerosol and Air Quality Research, Vol. 5, No.1, pp. 65-102

Zhang, Q., J. L. Jimenez, et al. (2007). "Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes." Geophys. Res. Lett.**34**(13): L13801.