Response to reviewer #1:

We thank Reviewer #1 for his/her valuable and thoughtful comments. Our responses to the comments are provided below, with the reviewer's comments italicized and our responses in plain and bold fonts.

Huang et al. investigate how carbonaceous aerosols are affected by an experiment based aging parameterization that is a function of the concentrations of ozone and water vapor. Overall this paper is within the scope of ACP and deals with an important issue (aging process), but I have several comments including a few major comments are listed below. After addressing these issues carefully, this paper should be published.

Major comments

1. *This study attempted to evaluation their BC and OC predictions with two BC/OC measurement sites and showed some improvement using the updated aging parameterization. The authors may intend to show the updated aging process as a more realistic mechanism than the fixed aging case, but their evaluation results (section 3.1) were not so convincing mainly because of too few measurement sites used. I strongly encourage including more observation sites.*

Response :

Point well taken. We have included more observational data from multiple networks (IMPROVE, CAWNET, EMEP, etc) in the text (now the new section 3.4).

"3.4 Comparison with observations

Ground-based Interagency Monitoring of Protected Visual Environments (IMPROVE) observational data in 2005 (http://views.cira.colostate.edu/web/), surface observations from China Atmosphere Watch Network (CAWNET) in 2006 (Zhang et al., 2008) and BC/OC campaign during 2002-2003 in Europe by the European Monitoring and Evaluation Programme (EMEP) (http://www.nilu.no/projects/ccc/emepdata.html) are employed to evaluate the global carbonaceous aerosol simulation results from the control run and updated aging scheme simulations. Additionally, we use aircraft campaign, Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) in 2001, to compare with the vertical distributions of model calculated carbonaceous aerosols by the above aging schemes. For the purpose of comparison to measurements, we treat BC equivalent to EC in this study although different measurement techniques, such as thermal technique for EC and photo-absorption for BC, could sometimes result in significant mass concentration differences (Jeong et al., 2004). Observational sites from these three observational networks

are shown in Figure 22. We use the annual mean data for BC and OC in 2005 to compare with observations by assuming that the interannual variability is small.

Surface concentrations of BC and OC from models and selected sites of IMPROVE are shown in Figure 23a and 23b. Annual mean BC and OC from control simulations are generally underestimated by a factor of 2, which are consistent with other model findings (Park et al., 2003; Liu et al., 2011). With the updated aging schemes, model simulated BC and OC improve the underestimate within a factor of 1.5. The comparisons of BC surface concentrations against observations from EMEP are shown in Figure 23a. Model generally captures well BC concentrations, except fours sites located at Italy, Belgium, Portugal and Great Britain. Without these four sites, our updated aging schemes, especially the combined and TRIPLE aging schemes, almost bring model simulated BC equals to observations. By contrast, the control simulation largely underestimates OC (more than 6 times), even the updated aging schemes only slightly improve the model performance within a factor of 6 (Figure 23b). This can be explained that open fire emissions are probably underestimated by the model emission inventory because open fires are the dominant source of OC. The scenario is even worse at the CAWNET of China. The control simulation significantly underestimates BC and OC by a factor of 7 and 16, respectively (Figs. 23a and 23b). This is mainly due to the underestimates of anthropogenic emissions and seasonal fire activities in South Asia (Wang et al. 2011). Wang et al. (2011) doubled the anthropogenic emissions in Asia but still get low bias of model simulated BC, compared with CAWNET observations. This implies that the anthropogenic emission sources in China should more than double.

Model simulated BC and OC concentrations in surface air at three remote sites are compared with the observational data from IMPROVE network: the Hawaii Volcanoes National Park (HAVO) (19.4°N, 155.3°W), the Haleakala National Park (HALE) (20.8°N, 156.3°W) and Denali National Park (DENALI) (63.7°N, 149°W). All the values are annual means for 2005. Compared to the control run, the simulation with oxidation aging scheme increases the annual mean concentration of BC and OC at HAVO by approximately 38% and 30%, respectively (Figs. 23a and 23b). The TRIPLE aging scheme performs the best, followed by the combined aging scheme, increasing BC and OC by 80% and 59%, 60% and 48% respectively, compared with the control run. This considerably improves the model performance, although it still underestimates the observations by a factor 2. Identifying the sources for the remaining model underestimates of carbonaceous aerosols is beyond the scope of this study, but it has been reported that there are around 10% of sea salt aerosols containing organic compounds during the First Aerosol Characterization Experiment (ACE 1) by analyzing the composition of marine particles under various environmental conditions (Middlebrook et al., 1998). Cavalli et al. (2004) reported even higher fraction of organic compounds in marine aerosols during phytoplankton bloom period at North Atlantic, with 54% and 4% of organic compounds in marine aerosols under submicron and supermicron modes, respectively. Global models estimate that the

marine OC emission source is around 8-9 Tg C yr^{-1} (Meskhidze et al., 2011; Spracklen et al., 2008), which is further confirmed by ship campaigns (9 Tg C yr^{-1}) reported by Lapina et al. (2011).

In an attempt to compare the model simulated vertical profiles of BC and OC with observations, aircraft campaign ACE-Asia during spring 2001 is employed to compare with our model simulations (Huebert et al., 2004). With the TRIPLE aging scheme, model simulated BC and OC are observed to increase by ~64% and ~45% in 4-6 km altitude, compared with the control run (Figure 24). By contrast, model simulated BC and OC by the oxidation aging scheme are found to increase by ~15% and ~13% at the same altitude range, with similar results for the condensation-coagulation and combined aging schemes. However, the updated aging schemes only slightly improve the model performance by a few percent below 4 km altitude. Due to missing a large amount of BC and OC sources in the free troposphere that originate from Asia emissions, model simulations significantly underestimate BC and OC by a factor of 10-100 (Heald et al., 2005). In particular, an important source of secondary organic aerosols that is produced in Asia source regions transports to the free troposphere of Pacific Ocean that GEOS-Chem doesn't capture, which leads to large model bias against observations."

2. *Did the control run use 1-day e-folding aging timescale? - I couldn't find the exact description for this. If so, I'd like to recommend adding another simulation that uses a longer e-folding aging timescale because 1-day e-folding is the shortest value used in global aerosol models, in my knowledge. This can give a better perspective on the potential biases in the BC/OC predictions using existing fixed aging timescales.*

Response :

Thanks for pointing this out. The control run simulation uses 1.15 days e-folding aging timescale. Based on the reviewer's suggestion, we triple the fixed e-folding lifetime for sensitivity study as well. We now add the text

Section 2 Approach and model descriptions-"In addition to the control run using the a priori τ_0 fixed at 1.15 days in the standard version of GEOS-Chem, we also carried out a sensitivity run by simply tripling the fixed conversion lifetime to 3.45 days (referred as TRIPLE run). Results from the TRIPLE run are compared to the control run as well as the new aging schemes to offer an additional quick reference point for model simulations of carbonaceous aerosols."

Section 3.3-"With TRIPLE aging scheme, the global average atmospheric lifetimes of BC and OC (8.32 days for BC and 5.70 days for OC), similar to the results from the combined aging scheme, are significantly higher than those calculated in the control simulation, by 43% and 24%, respectively (Table 1). Meanwhile, BC and OC burdens are calculated to be

0.167 Tg and 0.667 Tg, which are also quite close to the results of the combined aging scheme, but higher than both the oxidation and condensation-coagulation aging schemes.

We examine the impacts of the TRIPLE aging scheme on model simulated surface BC concentrations in Fig. 18. Increases of surface BC concentrations are found to be at the source regions by up to 0.19 μg C m^{-3}. Ratio plot shows that largest perturbations are observed at remote areas (more than double), which implies the importance of the long-range transport. Similar results are found for model calculated global OC surface concentrations (Fig. 19), with largest increases found to be 0.85 μg C m^{-3} at South Asia, which implies that model performance is highly sensitive to the τ values at source regions.

With the TRIPLE aging scheme, global distributions of model simulated BC and OC are shown in Figs. 20 and 21, respectively. BC and OC concentrations, at lower troposphere of northern Hemisphere, are found to increase by up to 0.018 μg C m^{-3} and 0.058 μg C m^{-3}, respectively, with the largest perturbations found in the upper troposphere for both BC and OC (more than double)."

3. *In my understanding, the new aging mechanism is chemistry-based aging, which doesn't include microphysics-based aging (via coagulation and condensation). If this is correct, this paper should state this clearly in the introduction/method section and also discuss carefully how model predictions with the new aging parameterization could be affected by missing microphysics-based aging mechanisms - one sentence in the conclusion section (P 29003; L 15) is not enough. This is an important issue because Riemer et al. (2004) present the microphysics-based aging process as the important aging process and neglect the photo-chemical-based aging based on results from Saathoff et al (2003). If the microphysics-based aging is significant, your BC/OC evaluation with the observation might be affected by missing microphysics-based aging process.*

Response :

Point well taken. We have expanded our work and included the condensation-coagulation aging scheme in our model.

We have added text for the condensation-coagulation aging scheme as follows.

Section 1 Introduction-"In addition, physical processes, such as condensation and coagulation, also make important contributions to the aging of aerosols. The aging of soot particles by these processes at a polluted region is simulated by Riemer et al. (2004), with condensation of sulfuric acid onto the surface of soot particles dominant during daytime while coagulation being an important process during nighttime. The e-folding aging lifetimes are approximate 8 h below 250 m during day time, with 2 h between 250 m and

3000 m. During nighttime, the aging timescale was found to be 10-40 h on average. These aging time scales are further employed by Croft et al. (2005) in a global model to estimate the global lifetime and burden of BC. However, the parameterization for this scheme tends to strongly depend on the regional case that was chosen by Riemer et al. (2004), which is not appropriate for global model parameterization and thus could result in larger uncertainties at GCM scales. By contrast, Liu et al. (2011) proposed a new condensation-coagulation scheme to globally simulate the aging rate of BC by assuming it is proportional to the gas concentration of sulfuric acid that are produced from the oxidation of SO_2 by hydroxyl radicals (OH) in the ambient air. As a result, the lifetime of BC in the model is predicted to be temporally and spatially variable, which improved the model performance in terms of comparisons to surface observations as well as aircraft campaigns."

Section 1 Introduction-"We also follow Liu et al. (2011) to account for the condensation-coagulation aging effects."

Section 2 Approach and model descriptions-"Following Liu et al. (2011), condensation-coagulation aging scheme is also investigated. The condensation of sulfuric acid gas onto the surface of particles leads to the conversion of carbonaceous aerosols from hydrophobic to hydrophilic. The conversion rate of particles by condensation is proportional to the sulfuric acid gas concentration, which is

$$k_{CC} = (D_g M/\rho R\delta_c) \cdot [H_2SO_4]_g, \quad (3)$$

where k_{CC} is the rate coefficient for condensation-coagulation aging scheme; subscript of CC represents condensation-coagulation; $[H_2SO_4]_g$ is the gas concentration of H_2SO_4 in the air; Dg is the diffusivity of H_2SO_4 in the atmosphere; M and ρ are the molecular weight and particle-phase density of H_2SO_4; R is the mass median radius of hydrophobic carbonaceous aerosols; δ_c is the equivalent coating thickness for the carbonaceous aerosols to take the critical soluble mass into account).

The reaction of SO_2 with OH produces H_2SO_4 in the air. The steady state concentration of H_2SO_4 in the air is derived as

$$[H_2SO_4]_g = \frac{k_1[OH][SO_2]}{\sum_i 4\pi D_g r_i}, \quad (4)$$

where k_1 is the reaction rate coefficient for SO_2 + OH; [OH] and $[SO_2]$ are gas concentrations of hydroxyl radicals and sulfur dioxide in the ambient air; i represents each particle in the air and r_i is the particle radius; $\sum_i r_i$ is the sum of all particle radius in each grid box. Combining Eqs. (3) and (4), we have

$$k_{CC} = \beta \cdot [OH] \text{(where } \beta = \frac{k_1 M[SO_2]}{\sum_i 4\pi R\delta_c r_i}\text{)}, \quad (5)$$

Taking coagulation effect into account, Eq. (5) becomes

$$k_{CC} = \beta \cdot [OH] + \alpha, \quad (6)$$

where β and α are assumed to be constant, with values 4.6×10^{-12} cm^3 $molecule^{-1}$ s^{-1} and 5.8×10^{-7} s^{-1}. With globally average concentration of OH is about 10^6 molecules cm^{-3}, β is

derived by assuming an e-folding aging time of 2.5 days; α is estimated by assuming e-folding lifetime for coagulation is 20 days.

With Eq. (6), we obtain

$$\tau_{CC} = \frac{1}{\beta \cdot [OH] + \alpha}, \quad (7)$$

where τ_{CC} is the e-folding conversion lifetime from condensation-coagulation scheme."

Section 3.2-"3.2 Impacts of the condensation-coagulation aging mechanism on model simulations of carbonaceous aerosol

The τ values by condensation-coagulation aging scheme strongly depend on the global distributions of OH concentrations. Due to the low surface concentrations of OH in the Arctic and Antarctic, compared with the oxidation aging scheme, hot spots for τ values shift from tropical regions to both Poles (Fig. 8), which is consistent with the findings by Liu et al. (2011). However, both aging schemes have long τ values at the Amazon regions, South Asia and West Africa. Moreover, τ values at the northern midlatitude also significantly increase by more than a factor of 4, implying lower aging rates for primary carbonaceous aerosols from the anthropogenic emissions and more hydrophobic aerosols existing in the atmosphere. Figure 9 shows the vertical profile of τ values with highest ones located at the upper troposphere, indicating lowest OH concentrations there. Overall, this aging scheme leads to the global average burden (0.146 Tg) and lifetime (7.29 days) of BC increase by 25%, compared with the control simulation (Table 1). The global average burden of OC is 0.607 Tg, with lifetime 5.18 days, which increases by 13% by contrast with the control runs. As discussed in Section 3.1, the oxidation aging scheme increases the burdens and lifetimes of BC and OC, compared with the condensation-coagulation aging scheme, implying lower aging efficiency.

With the condensation-coagulation aging scheme, model simulated surface BC concentrations are shown in Figure 10. Compared with the control run, increases BC concentrations are observed over South America, South Africa, Southeastern Asia and high latitude of North Hemisphere, by up to 0.05 μg C m^{-3}. Ratio plot shows that this aging scheme increases the BC surface concentrations at both Poles by over a factor of 2. Similar impacts are found for model simulated OC concentrations in surface air, with largest increases by up to 0.25 μg C m^{-3} over South America, South Africa and South Asia (Figure 11). Ratio plot shows that OC surface concentrations at remote regions increase by a factor of 1.7.

Global vertical profiles of BC and OC are shown in Figure 12 and 13, respectively. It reflects that the concentrations of BC and OC at the Arctic regions are significantly strengthened, which means that the burdens of carbonaceous aerosols in the Arctic is larger than the control runs and the magnitude of the impact of anthropogenic emissions from lower latitude on the Arctic is larger, compared with the control runs. This is justified by global models, which always underestimate the carbonaceous aerosols against aircraft

campaigns as well as long-term surface observations (Chung and Seinfeld, 2002; Heald et al., 2011; Wang et al. 2011; Liu et al. 2011). Similar to the oxidation aging scheme, OC concentrations at the tropical regions are strengthened due to strong emissions of biomass burning as well as biogenic emissions there. Strongest perturbations to simulated BC and OC are found at the Arctic and Antarctic regions as well as upper troposphere by a factor of 2-4."

Specific comments

1. *P 28995; L 3-5 – Can you rewrite the sentence or just change to "include direct emissions from fossil fuel"?*

Response :

The sentence has been rewritten as "Major sources of carbonaceous aerosols include direct emissions from fossil fuel, biomass and biofuel burning as well as photochemical oxidation of volatile organic compounds (VOCs)."

2. *P 28995; L 16 – Instead of "around 1 day", can you provide the range of aging timescale used in references? Related to this, please add new column in Table 1 to provide the aging timescale assumed in each model.*

Response :

We have revised this to "which is usually around 1 day (day (with a range of 1-2.5 days; see literature in Table 1).

3. *P 28995; L 21-23 - Besides listing the control factors in the aging mechanism, I think, you should provide a brief description on the aging mechanism.*

Response :

We have added a brief description on the aging mechanism. "In Pöschl et al. (2001) study, the coating of soot particles by the oxidation of benzo(a)pyrene (BaP) with ozone leads to the particles conversion from hydrophobic to hydrophilic, while water vapor serves as an inhibitor by competitive adsorption."

4. *P 28995; L 26 – what's the value widely used in climate models?*

Response :

The value widely used in climate models is around 1 day. We have clarified this sentence as "Maria et al. (2004) reported observations that the average hydrophobic-to-hydrophilic conversion rate for organic aerosols was at least three times lower than the value widely used in climate models (τ ~ 1 day), which would potentially increase the burden of carbonaceous aerosols by 70% in climate models."

5. *P 28996; L 10-17 – Past verb tense might be correct one: "we used" and "we ran"*

Response :

The sentences have been changed to past verb tense.

6. *P 28998; L 9-12 – Please delete the sentence starting "Several studies: : :" as this doesn't provide any information.*

Response :

We have deleted the sentence.

7. *P 28998; L 16-20 – Did you compare the updated aging parameterization with the 1-day aging timescale? Please provide the exact setup of the sensitivity simulations.*

Response :

Point well taken. Now we have rewritten the paragraph as

"The changes in carbonaceous aerosols' lifetime could have significant implications for the long-range transport of carbonaceous aerosols. To examine the potential impacts of the updated aging schemes on the intercontinental transport of carbonaceous aerosols, we set up sensitivity model runs where emissions of carbonaceous aerosols outside of the Asian region are turned off in the model. For the purpose of this study, we define the Asian region spanning longitudes 63° E to 150° E and latitudes 10° N to 58° N, as shown in Figure 1. These sensitivity simulations allow us to evaluate and compare the continental outflow of carbonaceous aerosols from Asia with the old and updated aging schemes respectively."

8. *P 28999; L 2-4 – Is the 30% or 38% increase at HAVO and HALE really significant improvement? As it is mentioned, the model BC and OC are still severely underpredicted even*

with the updated aging parameterization, and this indicates other problems. Also missing marine OC source is not reasonable because this doesn't explain for the BC underprediction.

Response :

We have changed "significantly" to "considerably".

9. *P 29000; L 15-17 – What is "BC climate forcing"? Is this direct radiative forcing? Please be specific. The sentence suggests a linear relationship between BC burden and forcing (i.e. 31% increase in global burden leads to 31% increase in forcing). Is this really reasonable?*

Response :

We have removed that discussion in the text since that is beyond the scope of our study here.

10. *P 29001; L 25-26 – This sentence is a bit unclear. what do you mean by "on surface air"? Is this OC concentration in the lowermost layer? Please re-write this.*

Response :

Yes, the surface air is the lowermost layer in the model. We have rewritten the sentence as "Similar results are found for OC aerosols in the surface air (the lowermost model layer) (Fig. 26). The maximum difference between control and combined aging scheme simulation on surface air is approximately 0.16 μg C m^{-3}."

11. *Figure 2 – Please bring the long/lat information to the first sentence and use full name of HAVO and HALE in the legend.*

Response :

Point well taken. Since we have added several aging schemes for our sensitivity studies, we re-plot the observations from three remote sites for BC and OC from IMPROVE, including the Hawaii Volcanoes National Park (HAVO) (19.4˚N, 155.3˚W), the Haleakala National Park (HALE) (20.8˚N, 156.3˚W) and Denali National Park (DENALI) (63.7˚N, 149˚W).

References

N. Riemer, H. Vogel, B. Vogel, "Soot aging time scales in polluted regions during day and night", Atmospheric Chemistry and Physics 4, (2004), 1885-1893, SRef-ID: 1680-7324/acp/2004-4-1885.

Saathoff, H., et al. "Coating of soot and (NH4)2SO4 particles by ozonolysis products of ?-pinene." Journal of aerosol science 34.10, (2003), 1297-1321.

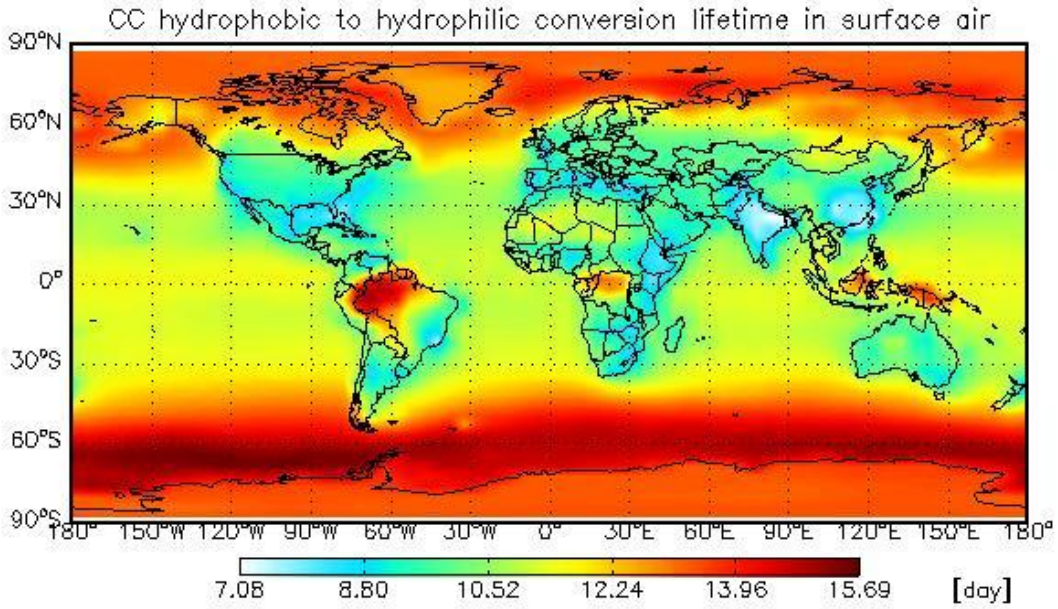

Fig. 8. Model calculated hydrophobic to hydrophilic conversion lifetime for carbonaceous aerosols in surface air by condensation-coagulation aging scheme. CC (hereinafter) represents condensation-coagulation aging scheme.

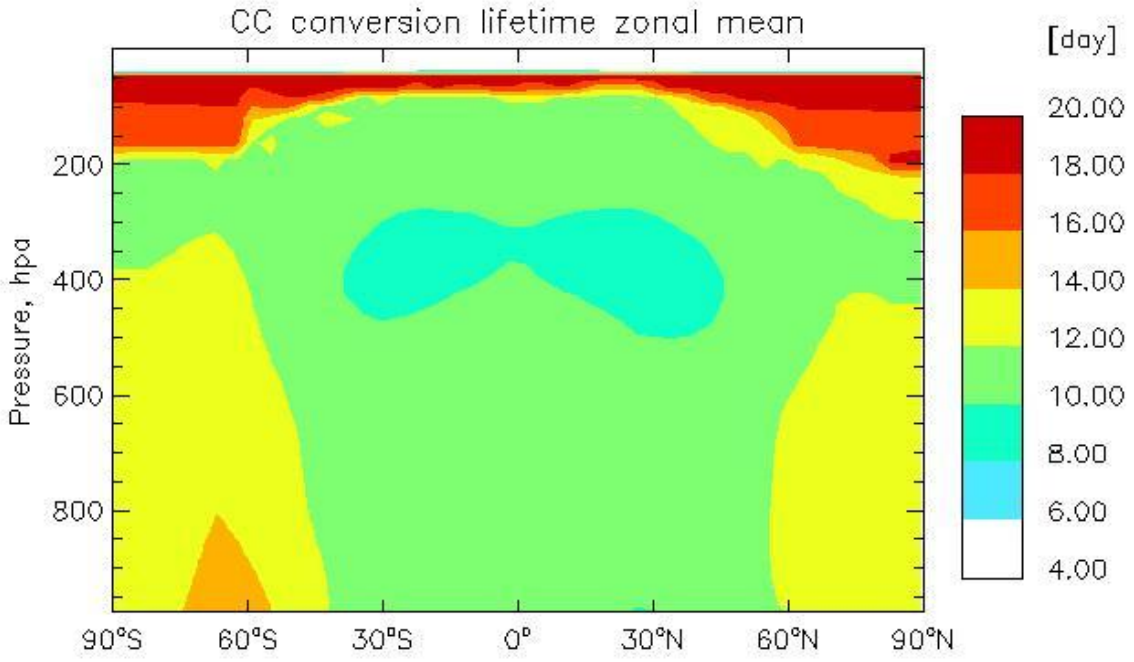

Fig. 9. Zonal mean plot for hydrophobic to hydrophilic conversion lifetime for carbonaceous aerosol by condensation-coagulation aging scheme.

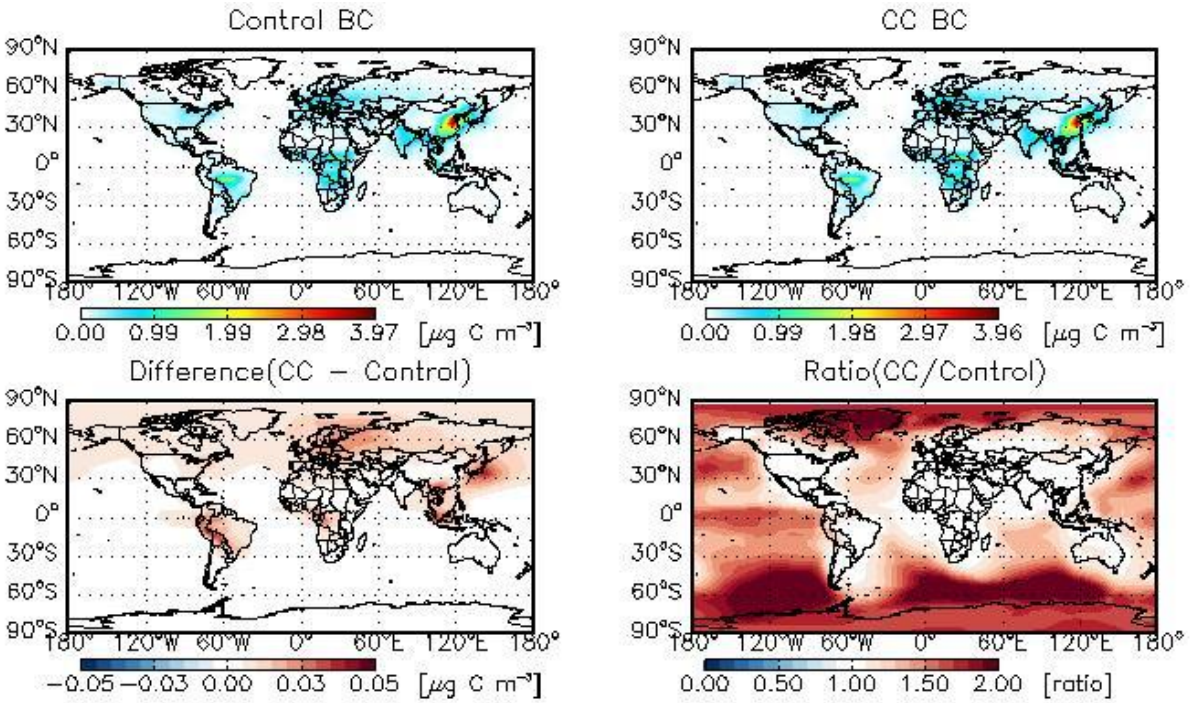

Fig. 10. Model simulated annual mean surface BC concentrations from the sensitivity run versus the control run. (Upper left) BC concentrations from the control run; (upper right) BC concentrations from the sensitivity run using the condensation-coagulation aging scheme; (lower left) differences between the sensitivity run and control run results; (lower right) ratio between sensitivity run and control run results.

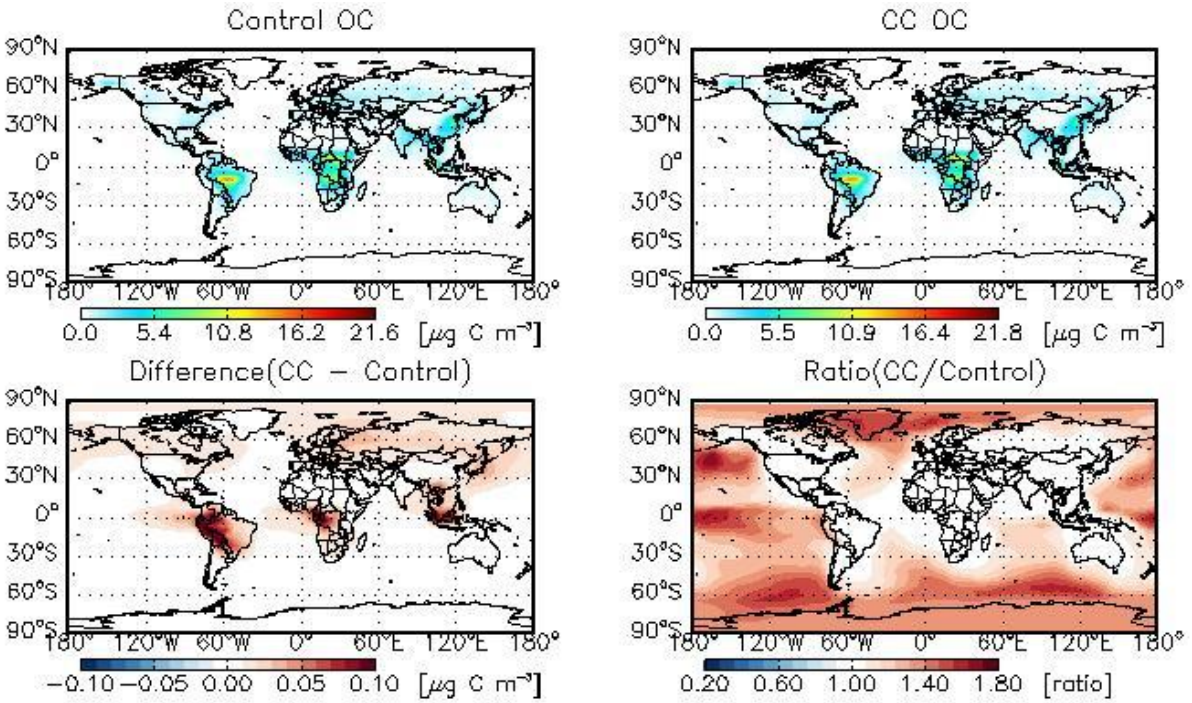

Fig. 11. Same as Figure 10 but for OC.

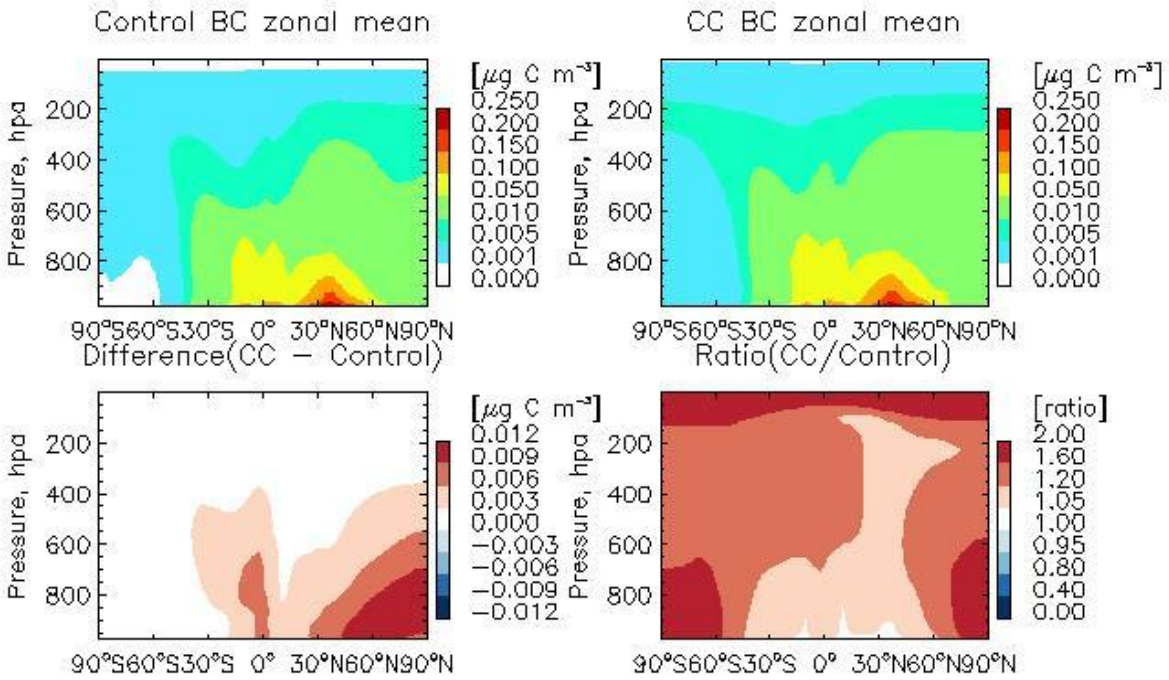

Fig. 12. Same as Figure 10 but for zonal mean.

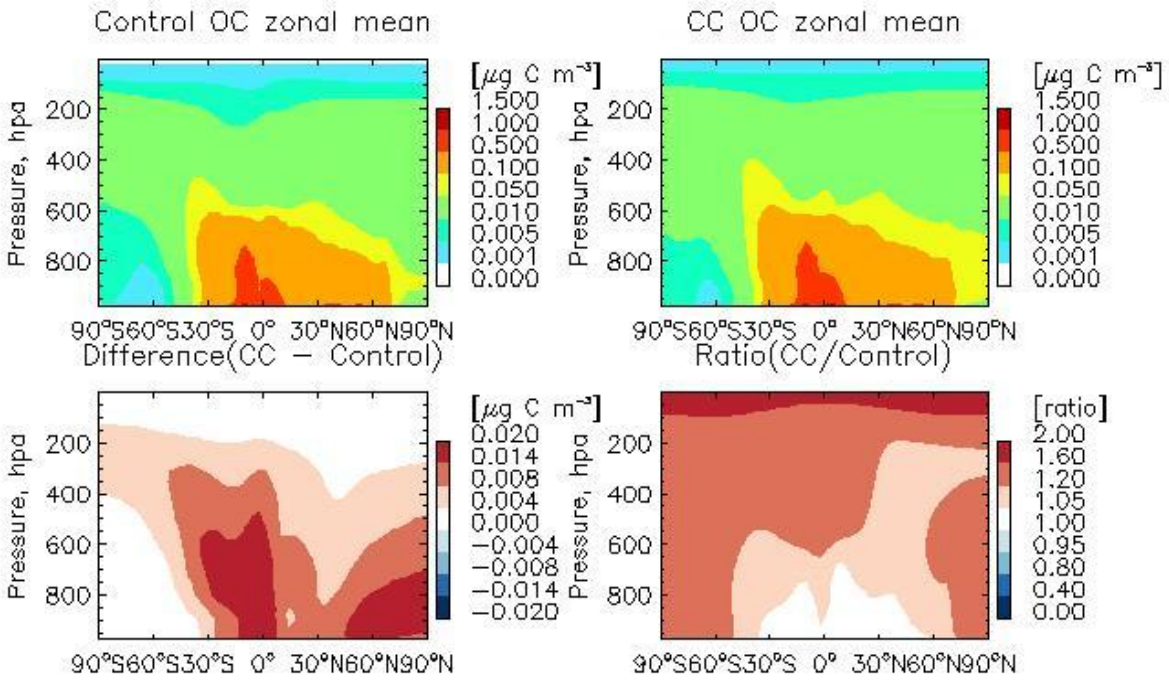

Fig. 13. Same as Figure 11 but for zonal mean.

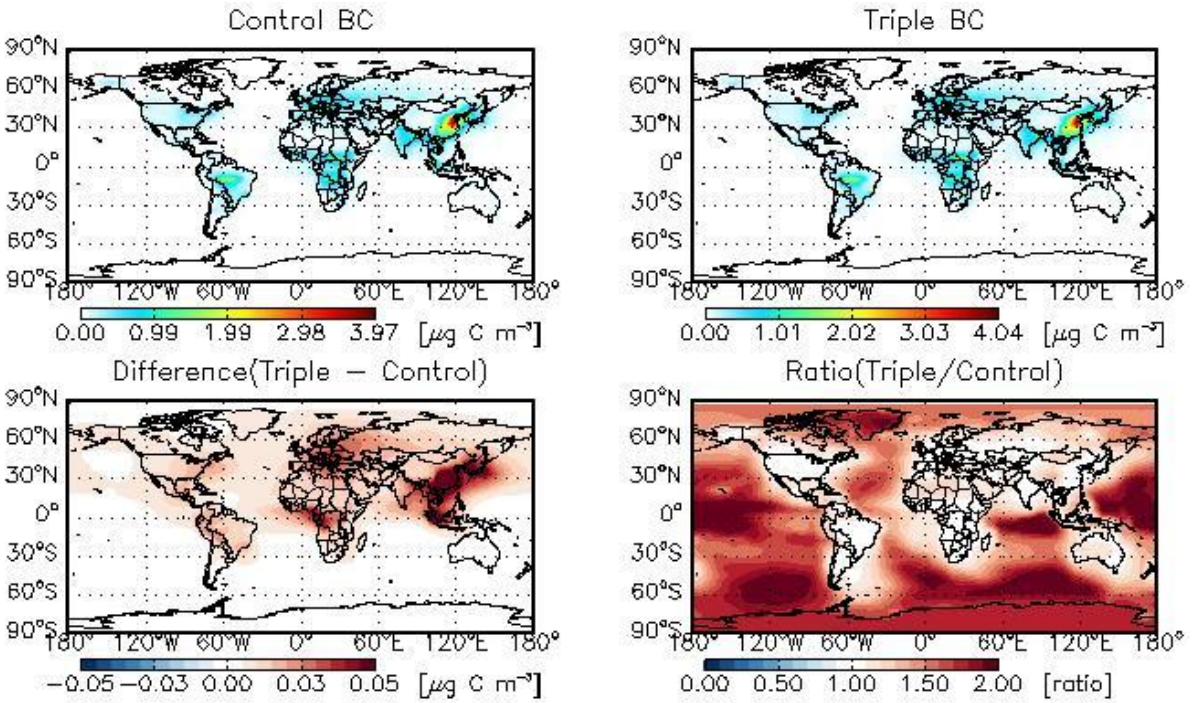

Fig. 18. Model simulated annual mean surface BC concentrations from the sensitivity run versus the control run. (Upper left) BC concentrations from the control run; (upper right) BC concentrations from the sensitivity run using the TRIPLE aging scheme; (lower left) differences between the sensitivity run and control run results; (lower right) ratio between sensitivity run and control run results.

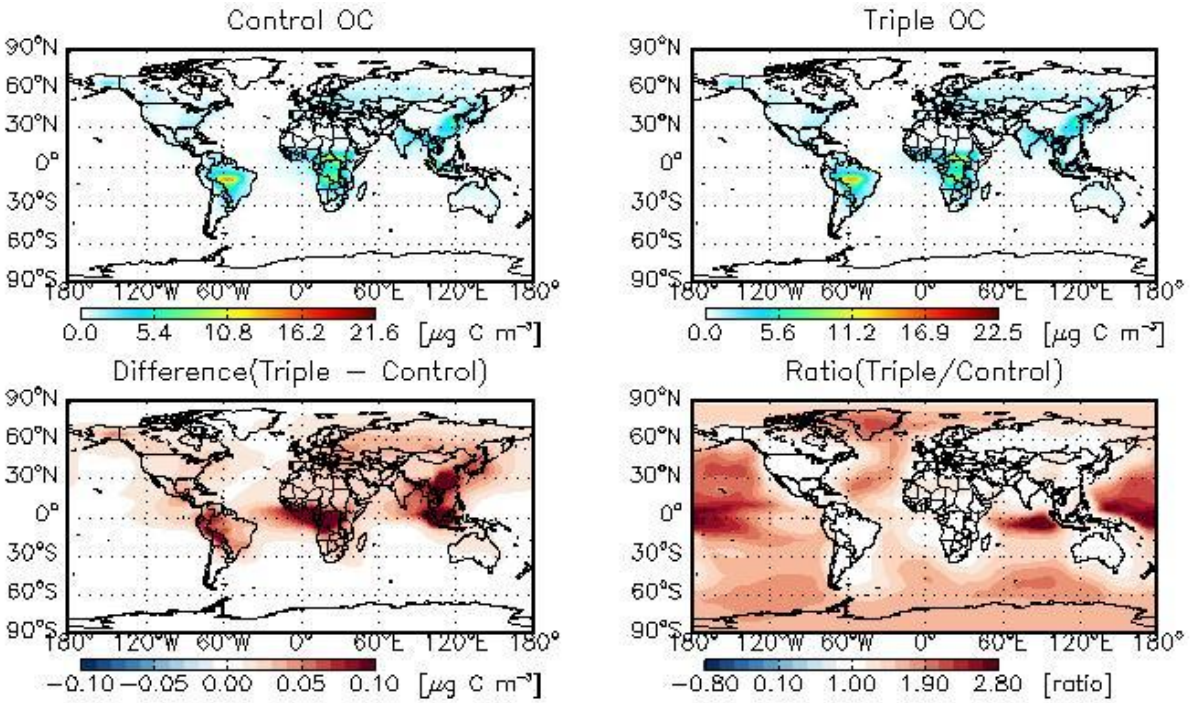

Fig. 19. Same as Figure 18 but for OC.

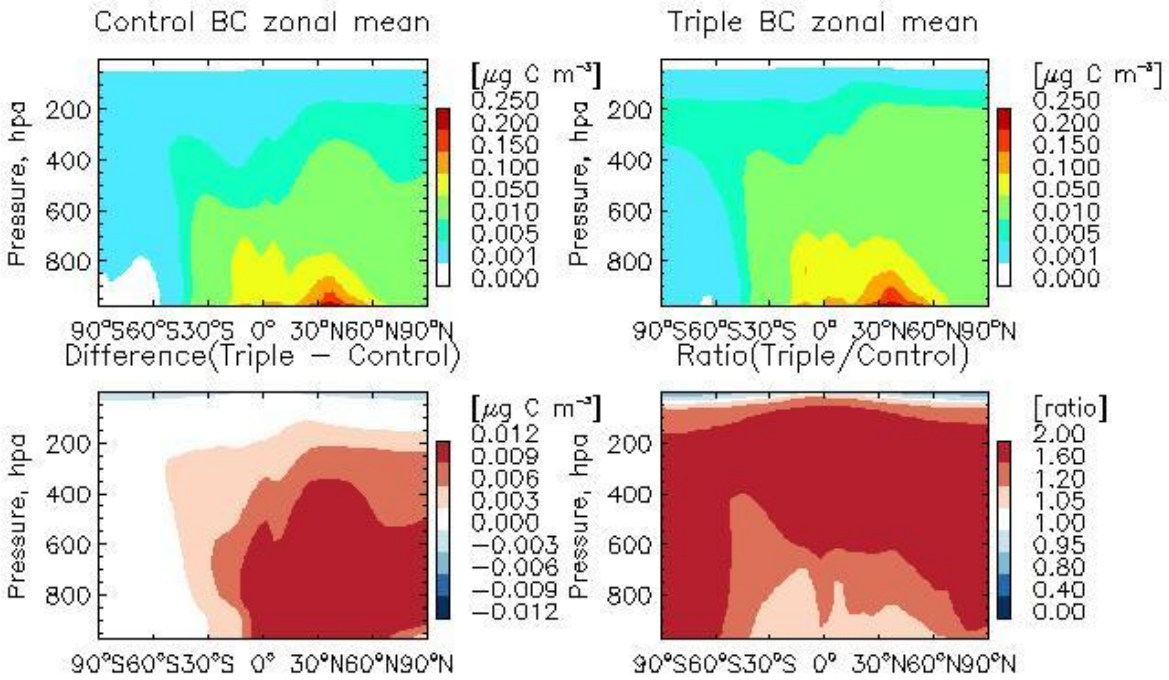

Fig. 20. Same as Figure 18 but for zonal mean.

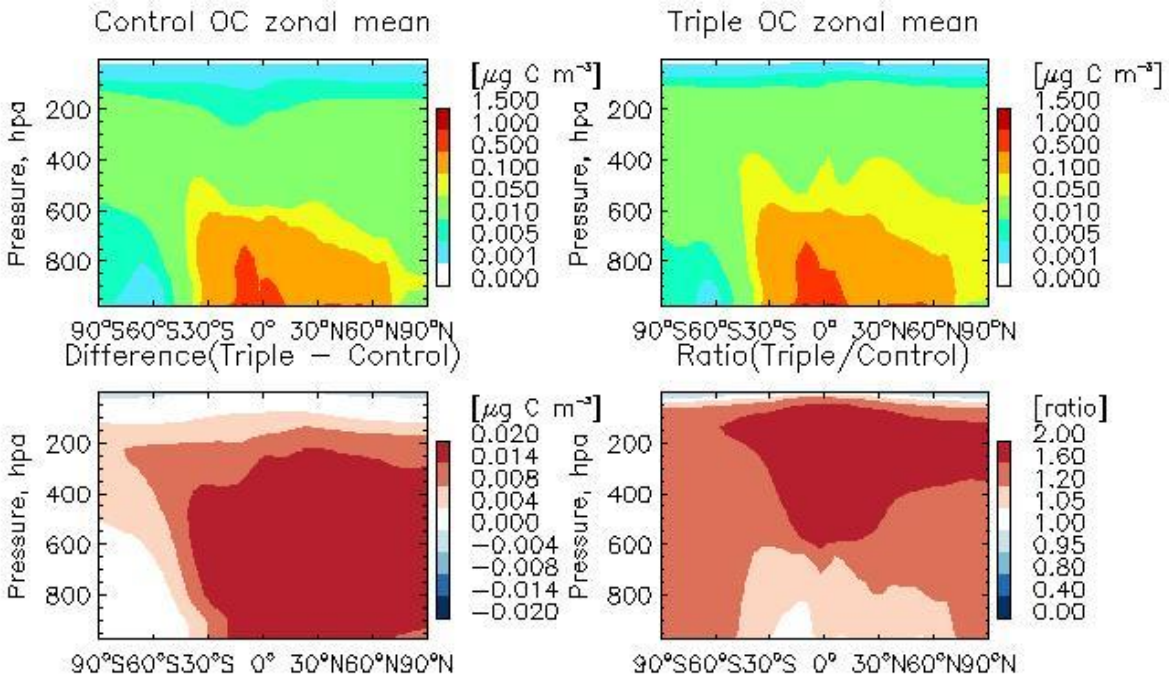

Fig. 21. Same as Figure 19 but for zonal mean.

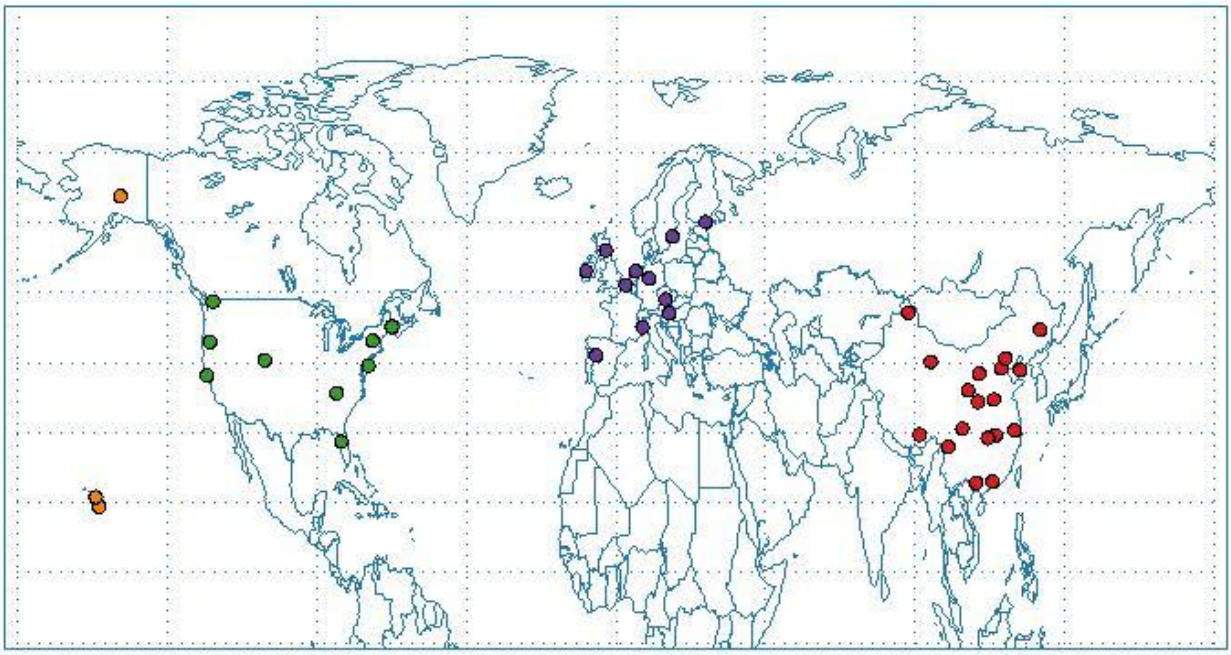

Fig. 22. Observational sites from CAWNET (red circles), EMEP (purple circles) and IMPROVE (green circles). Remote sites-HAVO, HALE and DENALI are from IMPROVE with orange circles.

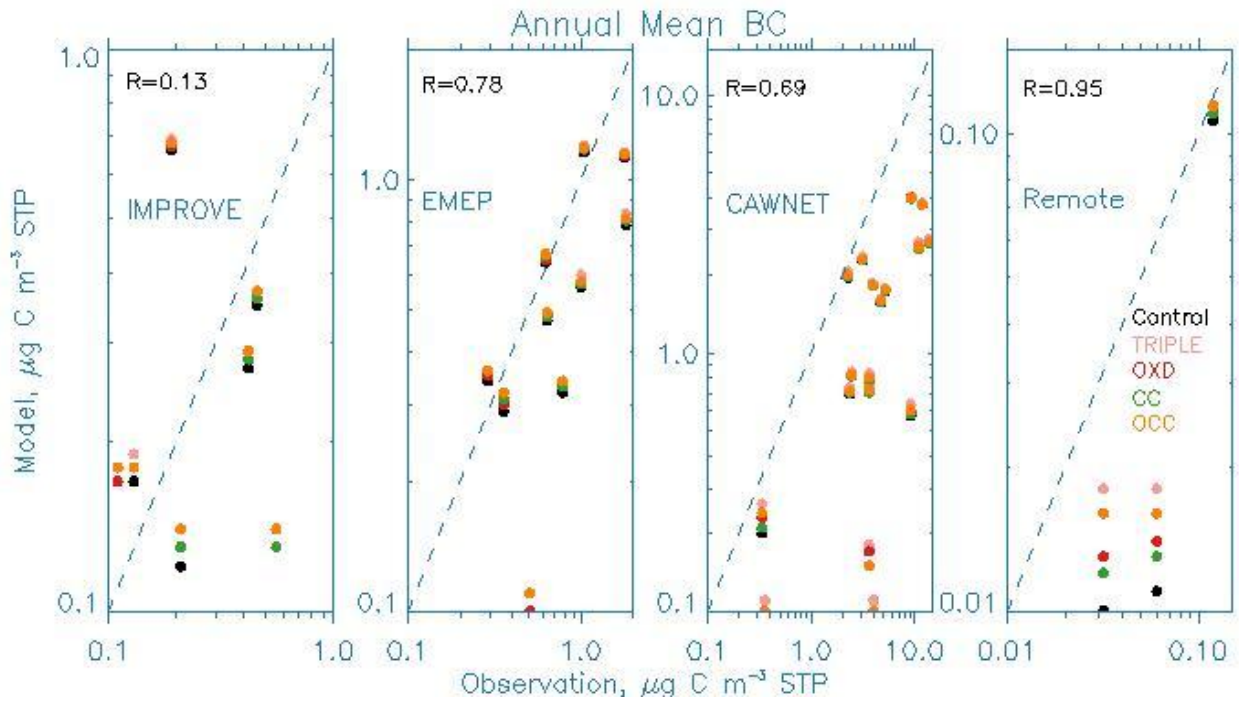

Fig. 23a. Scatter plots for annual mean BC between model simulation results and observations from IMPROVE, EMEP, CAWNET and remote sites. Black circles represent control simulation results, with TRIPLE, oxidation, condensation-coagulation and combined aging schemes are shown by purple, red, green and orange circles, respectively.

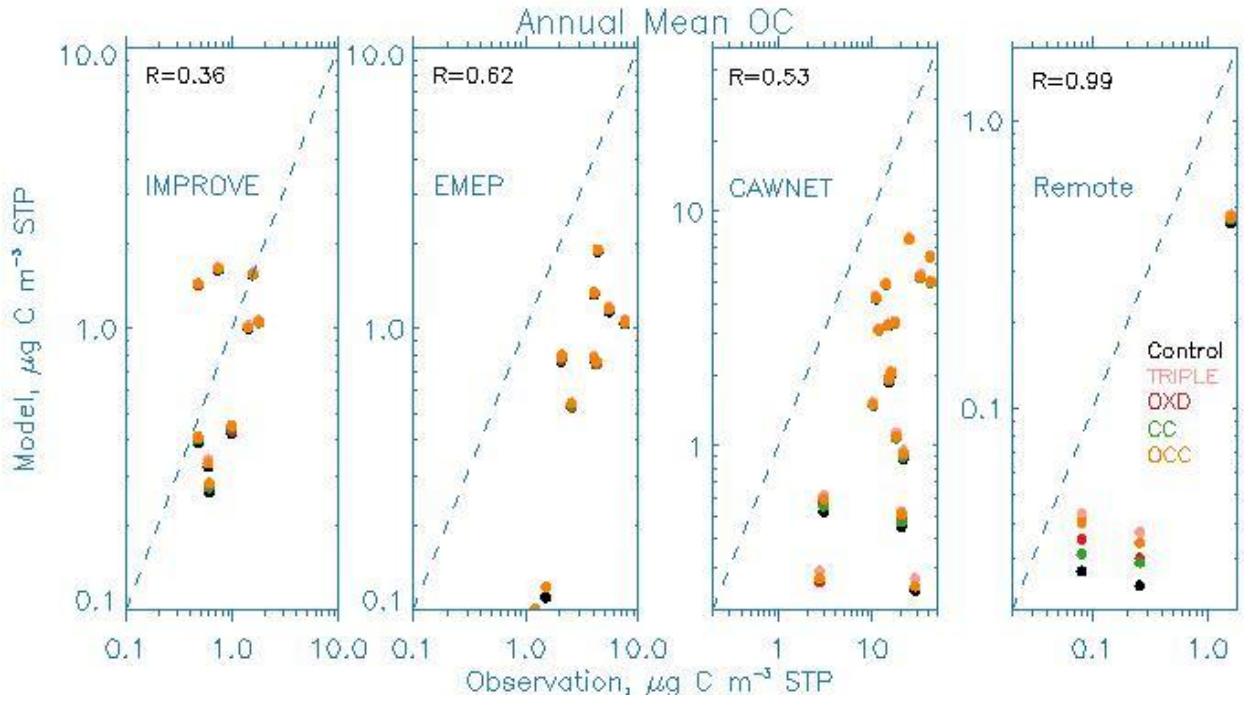

Fig. 23b. Same as Figure 23a but for OC.

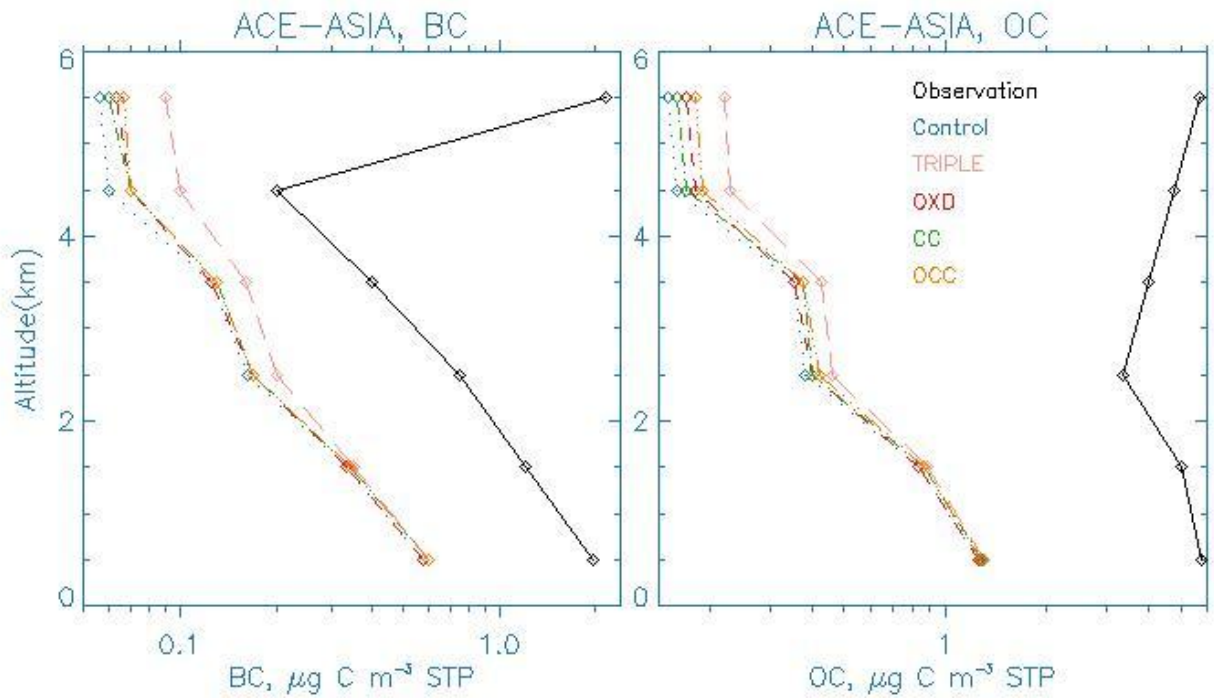

Fig. 24. Vertical profiles of BC (left) and OC (right) between model simulations from various aging schemes and NSF/NCAR C-130 aircraft campaign in ACE-Asia. Model and observational data are averaged over 1-km altitude bins. Simulation data is sampled along the track of C-130 during April 2001.