



**A global simulation
of brown carbon**

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A global simulation of brown carbon: implications for photochemistry and direct radiative effect

D. S. Jo¹, R. J. Park¹, S. Lee¹, S.-W. Kim¹, and X. Zhang²

¹School of Earth and Environmental Science, Seoul National University, Seoul, 151-747, Republic of Korea

²Department of Civil and Environmental Engineering, University of California, Davis, CA, USA

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Correspondence to: R. J. Park (rjpark@snu.ac.kr)

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Abstract

Recent observations suggest that a certain fraction of organic carbon (OC) aerosol effectively absorbs solar radiation, which is also known as brown carbon (BrC) aerosol. Despite much observational evidence of its presence, very few global modeling studies have been conducted because of poor understanding of global BrC emissions. Here we present an explicit global simulation of BrC in a global 3-D chemical transport model (GEOS-Chem), including global BrC emission estimates from primary (5.7 and 4.3 TgCyr⁻¹ from biomass burning and biofuel) and secondary (5.7 TgCyr⁻¹ from aromatic oxidation) sources. We evaluate the model by comparing the results with observed absorption by OC in surface air in the United States, and with single scattering albedo observations at AERONET sites all over the globe. The model successfully reproduces the observed seasonal variations, but underestimates the magnitudes, especially in regions with high secondary source contributions. Our global simulations show that BrC accounts for 24 % of the global mean OC concentration, which is typically assumed to be scattering. We find that the global direct radiative effect of BrC is nearly zero at the top of the atmosphere, and consequently decreases the direct radiative cooling effect of OC by 17 %. In addition, the BrC absorption leads to a general reduction of NO₂ photolysis rates, whose maximum decreases occur in Asia up to -9 % (-19 %) on an annual (spring) mean basis. The resulting decreases of annual (spring) mean surface ozone concentrations are up to -6 % (-14 %) in Asia, indicating a non-negligible effect of BrC on photochemistry in this region.

1 Introduction

Carbonaceous aerosols (CAs) are one of the poorly understood aerosols (Goldstein and Galbally, 2007; Park et al., 2003) and are divided into black carbon (BC) and organic carbon (OC) aerosols. These two types of CAs are emitted together mainly by combustion processes (except for secondary organic carbon, SOC). In the literature,

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BC is considered as light-absorbing and OC as light-scattering aerosols. Therefore, the climatic effect of CAs depends on the relative contributions of BC to CAs. For example, the net climatic effect of biomass burning is estimated to be negligible, whereas diesel use causes climate warming although the first source is larger than the latter for CAs (Forster et al., 2007).

Many field observations and chamber studies recently showed that a certain fraction of OC could absorb solar radiation, especially for shortwave wavelengths (< 400 nm) (Alexander et al., 2008; Hecobian et al., 2010; Kirchstetter and Thatcher, 2012; Kirchstetter et al., 2004; Yang et al., 2009). This light-absorbing OC fraction is referred to as brown carbon (BrC) aerosol (Andreae and Gelencser, 2006). If BrC is prevalent, and its climate effect is significant, then previous estimates of the climate effect of CAs need to be revised.

Recent studies showed that the solar absorption of BrC is not negligible, and is even comparable to that of BC (Alexander et al., 2008; Chung et al., 2012; Kirchstetter and Thatcher, 2012). Using residential wood smoke samples, Kirchstetter and Thatcher (2012) calculated that BrC absorption accounts for 14 % of total solar absorption by CA, and even contributes 49 % of solar absorption of CA at wavelengths below 400 nm. Chung et al. (2012) found that OC contributes about 45 % of CA absorption at 520 nm by analyzing observations at the Gosan site in South Korea. Using aerosol optical property observations at Aerosol Robotic Network (AERONET) sites, Bahadur et al. (2012) estimated that BrC absorption at 440 nm is about 40 % of BC absorption at the same wavelength, whereas at 675 nm it is less than 10 % of BC absorption.

Several efforts have also been made to examine the chemical and physical properties of BrC. Some studies showed that humic-like substances (HULIS) were related to BrC (Hoffer et al., 2006; Kim and Paulson, 2013; Lukács et al., 2007) based on the high absorption Ångström exponent (AAE) of HULIS in the range of 6–7, indicating that the specific absorption increases substantially towards the shorter wavelengths (Hoffer et al., 2006), although the source of HULIS has not clearly been revealed yet (Graber and Rudich, 2006). Alexander et al. (2008) observed individual

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BrC spheres in East Asian outflows, and showed that the characteristics of BrC spheres (AAE of 1.5) were different from those of HULIS. Recently, SOC produced from aromatic species has been found to absorb solar radiation, especially in high NO_x conditions (Jaoui et al., 2008; Liu et al., 2012; Nakayama et al., 2010, 2013; Zhong and Jang, 2011).

Even though the chemical composition of BrC is not clearly understood yet, observations strongly indicate possible important sources of BrC. Using the positive matrix factorization analysis of absorption at 365 nm over the southeastern United States in 2007, Hecobian et al. (2010) showed that biomass burning was the most dominant source of BrC (55 %), followed by SOC (26–34 %). Many other studies have also suggested biomass burning as the most important BrC source (Chakrabarty et al., 2010; Clarke et al., 2007; Favez et al., 2009; Hoffer et al., 2006; Kirchstetter and Thatcher, 2012; Kirchstetter et al., 2004; McMeeking, 2008). Several studies recently proposed SOC as an additional BrC source, especially when it is aged in the atmosphere (Bones et al., 2010; Jaoui et al., 2008; Laskin et al., 2010; Nakayama et al., 2010, 2013; Nguyen et al., 2012; Updyke et al., 2012; Zhang et al., 2011; Zhong and Jang, 2011).

Despite the ample observational studies, very few modeling studies have been conducted to simulate global and regional distributions of BrC and to further quantify its radiative effect. Jacobson (2001) first assumed 10 % of OC as a solar-absorbing aerosol in a model, and this assumption resulted in an increase of the global direct radiative forcing (DRF) by $0.03\text{--}0.05\text{ W m}^{-2}$. Park et al. (2010) estimated BrC concentrations in East Asia using the mass ratio of BrC to BC, and the resulting annual DRF of BrC over East Asia was 0.05 W m^{-2} . Feng et al. (2013) simulated global BrC concentrations by considering 92 % of OC from biomass burning and biofuel use as BrC, and estimated 0.11 W m^{-2} for the global DRF of BrC. All the previous studies assumed a constant ratio of BrC to OC or BC globally. However, the assumed ratios could differ depending on sources and burning conditions, even from the same source.

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In this study, we estimate global primary BrC emissions from open burning and biofuel use based on a reported relationship between AAE and modified combustion efficiency (MCE) (McMeeking, 2008). In addition to the primary source above, we also consider SOC produced from aromatic oxidation as a secondary source of BrC (Hecobian et al., 2010; Jaoui et al., 2008; Nakayama et al., 2010, 2013; Zhong and Jang, 2011). Based on these sources, a global distribution of BrC concentrations is explicitly simulated for the entire year of 2007 using a global 3-D chemical transport model (GEOS-Chem). We evaluate the model by comparing its results with observations in the United States and all over the globe. Using the best estimate of annual mean BrC concentrations, we examine the global direct radiative effect (DRE) of BrC and its effect on photochemistry.

2 BrC emissions

In this section, we discuss our method to estimate primary and secondary sources of BrC, and provide explicit global BrC emissions. The primary and secondary sources include biomass burning and biofuel use, and the production from aromatic volatile organic compounds (VOCs), respectively. Estimated global emissions are used as input for GEOS-Chem below to explicitly simulate spatial and temporal distributions of BrC concentrations.

2.1 Primary sources

Biomass burning is the largest source of CA aerosols globally (Bond et al., 2004). OC is primarily emitted during the smoldering (low-temperature burning) phase of combustion (Chakrabarty et al., 2010; Schnaiter et al., 2006), whereas BC is preferentially emitted from the flaming (high-temperature burning) phase. Therefore, BrC is also emitted largely during the smoldering phase of burning. Here, we use the relationship between

the burning efficiency and the observed aerosol light absorption to estimate the BrC emission from biomass burning.

Previous studies have suggested MCE defined in Eq. (1) below to provide quantitative information of burning efficiencies that can be categorized into flaming vs. smoldering combustion (Kaufman et al., 1998; Ward et al., 1992; Ward and Hao, 1991).

$$\text{MCE} = \frac{\Delta C_{\text{CO}_2}}{\Delta C_{\text{CO}_2} + \Delta C_{\text{CO}}}, \quad (1)$$

where ΔC is the change in species concentration in fire off-gas relative to clean air (molecules m^{-3}). For example, Reid et al. (2005) used a MCE value of 0.9 to differentiate between flaming (MCE > 0.9) and smoldering combustion (MCE < 0.9).

McMeeking (2008) further found a linear relationship between the observed attenuation Ångström exponents and the calculated MCE values from a number of biomass burning samples, as shown in Eq. (2).

$$\text{Å} = -17.34 \times \text{MCE} + 18.20, \quad (2)$$

where Å is the AAE of biomass burning samples.

The coefficient of determination (R^2) of the relationship in Eq. (2) is 0.39, so the associated uncertainty appears to be significant. However, the negative relationship between AAE and MCE in Eq. (2) is robust as identified by previous studies (Kirchstetter and Thatcher, 2012; McMeeking, 2008). For example, absorption of aerosols from biomass burning can be contributed by either BC or BrC, or both. As discussed above, the absorption of carbonaceous aerosols are mainly caused by BC at high MCE conditions (> 0.9); in contrast, the BC/CA ratio is almost zero at low MCE conditions (< 0.8) (McMeeking, 2008). Using Eq. (2), we calculate AAE values of 0.86 and 4.3 at MCE values of 1.0 and 0.8, respectively, and each calculated AAE is in good agreement with the observed BC (0.86) and BrC AAE (5.0) from biomass burning samples measured by Kirchstetter and Thatcher (2012).

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In addition, we are able to obtain the BrC/BC absorption ratio using AAE. In the Appendix, we present a detailed description of our method for estimating the relationship between the BrC/BC absorption ratio and AAE. Figure 1 shows the estimated BrC/BC absorption ratio at 550 nm as a function of MCE. For high MCE conditions (> 0.95), the BrC contribution to the CA absorption is negligible, whereas it becomes significant for low MCE conditions (< 0.85).

We calculate the MCE of biomass burning based on the Fire Inventory from NCAR (FINN) (Wiedinmyer et al., 2011) with vegetation dependent emission factors of CO_2 and CO using Eq. (3) as follows:

$$\text{MCE} = \frac{\Delta C_{\text{CO}_2}}{\Delta C_{\text{CO}_2} + \Delta C_{\text{CO}}} = \frac{\text{EF}_{\text{CO}_2}/\text{MW}_{\text{CO}_2}}{\text{EF}_{\text{CO}_2}/\text{MW}_{\text{CO}_2} + \text{EF}_{\text{CO}}/\text{MW}_{\text{CO}}}, \quad (3)$$

where EF is the emission factor ($\text{g species kg dry matter}^{-1}$) and MW is the molecular weight ($\text{g species mole}^{-1}$).

Finally, mass absorption efficiency (MAE), which is used for converting light absorption to mass concentration, is needed to obtain the BrC/BC mass ratio from the BrC/BC absorption ratio. For the fresh BC MAE at 550 nm, we use the value of $7.5 \text{ m}^2 \text{ g}^{-1} \text{ C}$ recommended by Bond and Bergstrom (2006) (Nakayama et al., 2013; Park et al., 2010). For BrC, a large range of MAE values ($0.09\text{--}4.1 \text{ m}^2 \text{ g}^{-1}$ at $550 \pm 30 \text{ nm}$) has been reported (Alexander et al., 2008; Cheng et al., 2011; Chung et al., 2012; Clarke et al., 2007; Favez et al., 2009; Hecobian et al., 2010; Hoffer et al., 2006; Kirchstetter et al., 2004; McMeeking, 2008; Yang et al., 2009). The highest MAE ($3.6\text{--}4.1 \text{ m}^2 \text{ g}^{-1}$ at 550 nm) was observed by Alexander et al. (2008), who used transmission electron microscopy to identify the optical properties of individual BrC particles in the atmosphere. Generally, low MAEs were reported when analyzing water soluble organic carbon (WSOC) from water extracts (Cheng et al., 2011; Hecobian et al., 2010; Srinivas and Sarin, 2014), indicating that WSOC may include both BrC and colorless OC. Intermediate MAEs mostly came from optical measurements (Chung

et al., 2012; Favez et al., 2009; Yang et al., 2009). For the primary BrC MAE, we use $1.0 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 550 nm based on McMeeking (2008), who conducted a number of MAE measurements of biomass burning samples (~ 30 unique fuels tested in ~ 230 burns) using both filter-based and optical-based methods. In brief, we use BC MAE of $7.5 \text{ m}^2 \text{ g}^{-1} \text{ C}$ and BrC MAE of $1.0 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 550 nm.

Using the results in Fig. 1 with Eq. (3), we calculate the EF (mass) ratio of BrC to BC (or OC) as summarized in Table 1. The EF ratio of BrC to OC differs for each vegetation type (0.12–0.95). Among different vegetation types, cropland burning shows the highest BrC to OC mass ratio, driven by the low MCE and the highest ratio of BC to OC EF. Because we calculate the BrC to OC EF ratio by multiplying the BrC to BC EF ratio by the BC to OC ratio, the high BC to OC ratio can lead to a high BrC to OC ratio. Although Table 1 shows the highest BrC/OC ratio from cropland burning, its contribution to the global BrC emission is small because the OC emission from the cropland is the lowest (Wiedinmyer et al., 2011). Instead, the tropical forest burning is the highest, and the resulting total BrC emission from biomass burning is 5.7 Tg C yr^{-1} , which contributes about 25 % of total OC emission from biomass burning ($22.7 \text{ Tg C yr}^{-1}$) (Wiedinmyer et al., 2011).

Our method of estimating BrC emissions from biofuel use is similar to that of estimating emissions from biomass burning. We first estimate OC biofuel emissions from each biofuel category, including wood burning, with the information given by previous studies (Bond et al., 2007, 2004; Fernandes et al., 2007). Because there is no clear evidence that BrC is emitted by dung, charcoal, and the industrial sector, here we consider only fuelwood and agricultural residue as BrC sources. Fuelwood burning is the largest contributor to biofuel BrC emission. Our estimate of BrC/OC mass ratio is 0.663 from biofuel use. Overall results are summarized in Table S1 in the Supplement. Resulting BrC emission from biofuel use is 4.3 Tg C yr^{-1} , which is comparable to BrC emission from biomass burning.

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2.2 Secondary source

We consider SOC as a source of BrC in the model based on the observed optical characteristic of SOC, depending on its chemical formation, as follows: (1) anthropogenic (aromatic) SOCs tend to absorb solar radiation more efficiently than biogenic SOCs (Jacobson, 1999; Nakayama et al., 2010; Zhong and Jang, 2011; Zhong et al., 2012), (2) the solar absorption efficiency increases as SOCs undergo atmospheric aging processes (Bones et al., 2010; Lambe et al., 2013; Laskin et al., 2010; Updyke et al., 2012), (3) SOCs formed in inorganic seeds have a darker color than others (Jaoui et al., 2008; Nakayama et al., 2013; Zhong and Jang, 2011; Zhong et al., 2012); moreover, SOCs become darker when they undergo aging in the presence of nitrogen-containing inorganic gases and aerosols (Bones et al., 2010; Laskin et al., 2010; Liu et al., 2012).

Among those factors, the first two are more important than the last. For example, the absorbance of aged biogenic SOCs produced in inorganic seeds is much lower than that of fresh anthropogenic SOCs under no-seed conditions (Zhong and Jang, 2011). Furthermore, Lambe et al. (2013) suggested that the effect of NO_x on SOC light absorption is small under typical ranges of VOC/NO_x . Therefore, here we consider the first two factors for BrC simulations in the model. We assume anthropogenic (aromatic) SOCs with high atmospheric aging as BrC in the model. Atmospheric aging is calculated using the volatility basis set (VBS) approach with six bins in the model (Jo et al., 2013), where SOC concentrations of the first two bins are considered as BrC. Note that BrC from anthropogenic SOC has different optical properties (i.e, MAE, imaginary refractive index) compared with BrC from wood burning. Therefore, we apply different optical parameters for the model evaluation (Sect. 4) such as $5.3 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for primary BrC and $1.5 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for secondary BrC at 365 nm (note that the MAE of primary BrC at 550 nm is $1.0 \text{ m}^2 \text{ g}^{-1} \text{ C}$ as discussed in Sect. 2.1). The estimated annual amount of secondary BrC sources is 5.7 Tg C yr^{-1} , which contributes 36 % of total BrC sources.

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3 Model description

3.1 General

We use the GEOS-Chem (version 9.1.2) global 3-D chemical transport model (Bey et al., 2001) to simulate BrC for 2007. The model is driven by Modern Era Retrospective-analysis for Research and Applications (MERRA) assimilated meteorological data from the Global Modeling and Assimilation Office Goddard Earth Observing System (Rienecker et al., 2011). The data include winds, precipitation, temperature, boundary layer height, and other meteorological variables at $0.5^\circ \times 0.667^\circ$ horizontal resolutions, but are degraded to $2^\circ \times 2.5^\circ$ for computational efficiency.

We conduct a fully coupled oxidant–aerosol simulation, including SO_4^{2-} - NO_3^- - NH_4^+ , soil dust, and sea salt aerosols. The simulation of carbonaceous aerosols in the GEOS-Chem is based on Park et al. (2003, 2006). The model carries BC and primary organic carbon (POC), with a hydrophobic and hydrophilic fraction for each. We assume that 80% of BC and 50% of POC is emitted as hydrophobic (the rest is hydrophilic), then hydrophobic aerosols become hydrophilic with an e-folding time of 1.15 days (Cooke et al., 1999). For the SOC simulation, we use the VBS approach based on Jo et al. (2013). All SOC is considered as hydrophilic, and more details are described in previous SOC studies (Chung and Seinfeld, 2002; Henze and Seinfeld, 2006; Henze et al., 2008; Jo et al., 2013; Liao et al., 2007). Note that we consider only the carbon mass of OC including BrC as discussed below, to avoid uncertainties involved in converting organic carbon to organic matter concentrations, which is typically done by multiplying a constant ratio (e.g, 1.4–2.1) (Aiken et al., 2008; Turpin and Lim, 2001).

3.2 Emissions

We use fossil fuel and biofuel emissions of CAs for 2000 with no monthly variations from Bond et al. (2007). However, domestic wood burning for heating has strong seasonal dependency, so we additionally use the Monitoring Atmospheric Composition

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& Climate/City Zen (MACCity) emission inventory (Diehl et al., 2012; Granier et al., 2011) to obtain seasonal variations of global biofuel emissions and to scale up for 2007. For this, we divide the whole globe into regions with similar seasonality according to the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP) (Lamarque et al., 2010), which is the basis of the MACCity inventory. We apply the annual trend of each ACCMIP region to scale up the emission for 2007. The emissions for each region and trends are listed in Tables S2 and S3.

We use biomass burning emissions from FINN version 1.0 (Wiedinmyer et al., 2011), which provides global daily estimates of trace gases and aerosols at 1 km horizontal resolution for 2002–2012 (<http://bai.acd.ucar.edu/Data/fire/>). However, the FINN version 1.0 inventory does not include aromatic VOCs (benzene, toluene, and xylene), the emissions of which are estimated by multiplying dry burned matter by emission factors from Akagi et al. (2011) and Andreae and Merlet (2001).

4 Model Evaluation

We conduct a model evaluation using the observed light absorption of WSOC measured by Hecobian et al. (2010) and Zhang et al. (2011, 2013) in the United States. The model evaluation allows us not only to validate simulated BrC concentrations but also to examine each source contribution to BrC in the United States. We also use the global single scattering albedo (SSA) observations from the AERONET to evaluate the effect of including BrC on light absorption by aerosols over the globe.

4.1 United States

Prior to evaluating BrC simulations, we first focus on BC and OC aerosols in the model to examine the general model performance in simulating carbonaceous aerosol concentrations in the United States. We use BC and OC observations from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network for 2007

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(Malm et al., 1994). Most sites were situated in rural regions, measuring background concentrations of BC and OC. The data were available every three days; more than 20 000 samples were used for our comparison. For comparison with the model results, we computed the observed monthly mean concentrations of BC and OC averaged on the $2^\circ \times 2.5^\circ$ model grid.

Figure 2 shows scatterplot comparisons of the observed and simulated monthly mean BC and OC concentrations in the United States. The model slightly underestimates both BC and OC over the United States, consistent with similar comparisons in Huang et al. (2013). The simulated annual mean BC concentration is $0.22 \mu\text{gCm}^{-3}$, which is 12 % lower than the observed mean value ($0.25 \mu\text{gCm}^{-3}$). However, the bias in the model is larger for OC by 30 % (1.16 and $0.81 \mu\text{gCm}^{-3}$ for observed and simulated OC concentrations), which is additionally due to the underestimation of secondary OC in the model (Jo et al., 2013). This low bias for secondary OC can be reflected in the simulated BrC concentrations, which is discussed later in this section.

We use the light absorption observations of WSOC measured using a UV-Vis spectrophotometer and Long-Path absorption Cell by Hecobian et al. (2010), and compare them with the light absorption by BrC in the model. Absorption coefficients of WSOC at 365 nm were measured at 15 sites in the southeastern United States in 2007. Among them, eight sites are in urban areas, and the others are in rural regions. Detailed descriptions of the measurements are available in Hecobian et al. (2010).

Because light absorption observations are measured only for water soluble fractions of OC, and do not include water insoluble components, we separate BrC in the model into water soluble and water insoluble components. The model divides OC (or BrC) into hydrophilic and hydrophobic components. For the comparison, we do not use the simulated hydrophilic fraction, but instead use an observed WSOC/OC ratio because the assumed division of hydrophobic and hydrophilic fractions of OC and their conversion can be applicable in a global sense, but in a regional sense, it may cause a significant discrepancy. For example, the observed water soluble fraction of the total

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OC is generally low (on the order of 25 %) in the Los Angeles basin (Zhang et al., 2013), on the other hand, the model simulates a high water-soluble fraction of the total OC (63–74 %) in this region. For this reason, we decide to use the observed WSOC/OC ratio for the evaluations. In the southeastern United States, the observed WSOC/OC ratio is about 0.58 (Weber et al., 2007; Zhang et al., 2013), which is also used to estimate the water soluble BrC concentrations from the total BrC concentrations in the model.

Because the model simulates a mass concentration of BrC, a conversion from the mass concentration to light absorption is carried out by multiplying MAE values. For BrC from wood burning, we use the MAE value of $5.3 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 365 nm measured by McMeeking (2008) in order to retain the consistency between our emission estimates and the evaluation. For BrC from SOC, we select the MAE of $1.5 \text{ m}^2 \text{ g}^{-1} \text{ C}$ at 365 nm calculated by Nakayama et al. (2010) (see Fig. 4 in their paper).

Figure 3a shows monthly mean simulated and observed light absorption coefficients of BrC at 365 nm averaged over all sites in the southeastern United States for 2007. Black circles and colored bars indicate the observed and simulated BrC absorption at 365 nm, respectively, and different colors in the bar show contributions from different sources. In winter months (November through March), the observed light absorptions were generally high and reached a peak in March. These high absorptions were highly correlated with levoglucosan, which is a marker for biomass burning (Hecobian et al., 2010). During the summer, the observed light absorptions decrease substantially.

The model captures the observed seasonal variation with high absorption in the winter, having a peak in March and low absorption in the summer (R of 0.93), but is generally too high relative to the observations (by 46 % on an annual mean basis). However, we find that the annual mean OC of the model in this region is $1.81 \mu\text{g m}^{-3}$, which is 35 % lower than the IMPROVE OC ($2.79 \mu\text{g m}^{-3}$). Furthermore, during the months when large discrepancies occur (March, September, and October), the simulated OC ($2.79 \mu\text{g m}^{-3}$) is similar to the observed OC ($2.63 \mu\text{g m}^{-3}$).

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Although our model overestimates BrC absorption, the BrC source contribution of the model is similar to the observed source contribution. Hecobian et al. (2010) showed that biomass burning was the main contributor for the winter season, whereas the SOC contribution increased during the summer season. The simulated seasonal variation is consistent with the observation, as shown in Fig. 3a. The annual mass contribution of SOC to BrC is 34 %, which is in good agreement with the observed contribution of 32 % (Hecobian et al., 2010).

There are two possible causes for the overestimation of light absorption by BrC in the model, including a too high value of MAE ($5.3 \text{ m}^2 \text{ g}^{-1} \text{ C}$) for primary BrC, and a too high estimated BrC/OC ratio from biomass burning. An easy fix for the high bias in the model is to use a lower MAE value for primary BrC from biomass burning. Favez et al. (2009) used field observations to estimate $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for the MAE of BrC from agricultural waste burning. When we use this value for the comparison, as shown in Fig. 3b, the bias is significantly reduced (from 46 to -6 %). Based on these results, the MAE values of $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for BrC from primary sources are used in our model below as our best estimates. We, however, acknowledge that our estimates are very sensitive to both MAE and AAE values of BrC, which have wide ranges of observations (factor of ~ 2). Extensive studies would be needed to reduce uncertainties with BrC MAE and AAE values for different source types and observation methods.

In addition to the observation by Hecobian et al. (2010), we use the light absorption observations by Zhang et al. (2011, 2013). Measurements were carried out in Atlanta, GA ($33.778427^\circ \text{ N}$, $84.396181^\circ \text{ W}$), Pasadena, CA ($34.140528^\circ \text{ N}$, $118.122455^\circ \text{ W}$), and Riverside, CA (33.97185° N , $117.32266^\circ \text{ W}$) for a month or less. As discussed above, we apply the observed WSOC/OC ratio to the model BrC concentrations: 26 % for the Los Angeles basin (Pasadena and Riverside) (Zhang et al., 2013) and 58 % for Atlanta (Weber et al., 2007; Zhang et al., 2013).

Figure 4 shows the daily mean observed and simulated light absorption coefficients for Atlanta, Pasadena, and Riverside for 2010. The upper panel shows the comparison of the observed vs. simulated light absorption for Atlanta. The highest observed daily

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absorption occurs on 24 August but the model fails to reproduce it. Furthermore, the model generally overestimates the observed absorption by 33%, and the large discrepancies mainly occur in September. This large discrepancy in September is similar to the result shown in Fig. 3 for 2007.

The middle and lower panels show the comparisons for the Los Angeles basin sites in May and June. The observed mean light absorptions at these sites (0.81 and 0.98 Mm^{-1} for Pasadena and Riverside, respectively) are higher than the observed mean light absorption (0.56 Mm^{-1}) for Atlanta. However, the model underestimates the observations by 40% (Pasadena) and 50% (Riverside). Zhang et al. (2013) showed that the main sources of BrC at these sites were SOC from anthropogenic emissions. The model also shows a high contribution (83%) of the secondary source to the total BrC mass concentrations, but the magnitudes are generally lower than the observations, and this low bias is likely related to underestimation of the simulated SOC concentrations using the 1-D VBS (Jo et al., 2013).

We find from the model evaluation over the United States that the model generally captures the observed mean absorption and its seasonal variability in the region where primary sources are dominant. On the other hand, the model underestimates the observed mean absorption in the region with the dominant secondary sources. The low bias is partly explained by the SOC underestimation in the model. However, the underestimations of BrC from SOC (40–50%) are higher than those of SOC (18%), indicating the importance of additional secondary BrC sources that we did not include in the model.

A MAE value for secondary BrC could be another possible reason for the bias in the model. Although chamber studies suggested weak absorbing characteristics of BrC from SOC (Nakayama et al., 2010, 2013; Zhong and Jang, 2011), some field observations speculated the existence of strongly-absorbing BrC from SOC (Alexander et al., 2008; Chung et al., 2012). Extensive observations of optical characteristics of BrC depending on the formation mechanisms would be needed to reduce the associated uncertainties and to improve the model.

4.2 Evaluation against global AERONET observations

No global observation of BrC is available yet. Here we use the observed single scattering albedo (SSA) at AERONET sites to evaluate the model by focusing on the effect of BrC on the simulated aerosol absorption. We also use observed aerosol optical depth (AOD) to evaluate the model capability to simulate aerosol mass concentrations.

For comparisons of AOD and SSA between the model and observations, we use FlexAOD (<http://pumpkin.aquila.infn.it/flexaod/>), which calculates AOD and SSA using simulated aerosol mass concentrations from GEOS-Chem with the Mie algorithm (Mischenko et al., 2002).

For optical properties of BrC, we use imaginary refractive indices of BrC from McMeeking (2008) for wood burning sources, and from Nakayama et al. (2010) for SOC sources. We further adjust imaginary refractive indices from McMeeking (2008) according to the lower MAE value of $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for primary BrC, which produced our best model in Sect. 4.1. Detailed description of the values used in AOD and SSA calculation are provided in Sect. 6, where we discuss the DRE of BrC.

Figure 5 shows comparisons of monthly mean simulated vs. observed AOD at 500 nm, and SSA at 440 nm for 2007. We find that the model captures the observed AOD quite well with a regression slope of 0.86 and a R of 0.88. However, the model tends to overestimate the observed SSA, implying that the simulated aerosol concentrations appear to have too large a fraction of scattering aerosols. We find that the inclusion of BrC in the model reduces the high bias of simulated SSA by 33 and 23 % (lower left and lower right panel of Fig. 5), indicating a considerable contribution of BrC to aerosol absorption. Although the statistics suggest a greater improvement with the high MAE value in terms of the bias, simulated SSA values that are too low apart from the regression line (discrepancy > 0.1) are at sites in Africa, with heavy biomass burning influences. This result also supports our choice of the MAE value of $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for primary BrC.

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Despite a decrease of simulated SSA with BrC, the model is still too high relative to the observations. The overestimation might be partly caused by the underestimation of BC emissions from biomass burning (Bond et al., 2013). This is also supported by the fact that the discrepancy gets larger for biomass burning regions, where a difference between the model and AERONET SSA is 40 % higher than that in regions with high anthropogenic emissions. Emission factors of BC used in this study are 0.2–0.69 g kg⁻¹ (Wiedinmyer et al., 2011), which are lower than the value of 1 g kg⁻¹ used by Chin et al. (2009), who found no significant bias in their model compared with the AERONET SSA.

In addition to the biomass burning emission of BC, the anthropogenic emission of BC could also contribute to the simulated SSA bias. Cohen and Wang (2014) showed that a global top-down emission of BC is twice as large as the bottom-up estimates of BC based on the Kalman Filter approach. They suggested that BC emissions in East Asia, Southeast Asia, and Eastern Europe are significantly underestimated in current bottom-up inventories. This issue is critically important, and possibly has an important implication for climate. However, an investigation of BC emissions for the SSA discrepancy above is beyond the scope of our work, and will be conducted in future studies.

Light absorption enhancement of aged BC could also be one of the reasons for the overestimation in the model. We use the same optical parameters for all BC in the model. However, Bond et al. (2006) suggested that absorption by aged BC is about 1.5 times greater than that of fresh BC. Aged BC is assumed to be an internal mixture with other aerosols, and has higher absorption relative to fresh BC. Based on these results, we additionally consider the absorption enhancement of hydrophilic BC in the model, and find that the overestimation is additionally reduced by about 20 % (not shown).

5 Global budgets

5.1 Annual surface concentration

Figure 6 shows annual mean concentrations of BrC and each source contribution in surface air for 2007. Values are high in regions where biomass burning (Southeast Asia and South America) and biofuel (East Asia and Northeast India) sources are dominant. These primary sources account for 83% of BrC concentrations in surface air. On the other hand, secondary sources are relatively minor in the surface, but their contribution increases in the free troposphere, as discussed in Sect. 5.2.

Figure 7 shows BrC to BC and OC ratios in surface air in the model. Previous modeling studies employed constant ratios of BrC to BC or OC to obtain spatial distributions of BrC concentrations. Our results, however, show substantial spatial variation of the ratios. The BrC to BC ratio is highest over the eastern North Pacific and the North Atlantic. This high ratio over the ocean reflects a secondary chemical production, which contributes to BrC but not to BC. Over the continents, the ratio is generally higher in heavy biomass burning regions (South America and Africa) than in industrialized regions (East Asia, Europe, and the eastern United States) because more BrC than BC is emitted from biomass burning.

Similarly, the BrC to OC ratio is also high over the oceans because of secondary BrC, the concentrations of which increase with atmospheric aging. Over the continents, the ratio is smaller reflecting relatively fresh emissions of OC from anthropogenic sources that do not directly contribute to BrC. We find that the BrC to OC ratio is relatively high in regions with large biofuel use (North India and Central Asia). Although China is one of the largest emission source regions for BrC (Fig. 6), both BrC to BC and BrC to OC ratios are relatively low because of high concentrations of BC and OC. Our global mean BrC to BC and BrC to OC ratios are 1.7 and 0.29, respectively and are lower than the ratio of Feng et al. (2013), but higher than the ratio used in Park et al. (2010).

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5.2 Tropospheric budget of BrC

Table 2 summarizes the global tropospheric budgets of BrC, along with BC and OC. The global BrC source is 15.7 TgCyr^{-1} , which accounts for 33% of OC sources. Although the biofuel emission (6.5 TgCyr^{-1}) is three times lower than the biomass burning emission (22.7 TgCyr^{-1}) for OC, the biofuel emission (4.3 TgCyr^{-1}) becomes significant for BrC, contributing about 43% of primary sources. The secondary source of BrC is 5.7 TgCyr^{-1} , and is comparable to the biomass burning emission (5.7 TgCyr^{-1}).

Wet deposition is the main removal process for BrC, and accounts for 85% of total removal processes. The remaining loss is due to dry deposition. The contribution of wet deposition to total deposition of BrC is similar to that of OC (82%), because we treat BrC scavenging similarly to that of OC. Because secondary BrC is produced all over the troposphere (not only at the surface) and is hydrophilic, most secondary BrC is removed by wet deposition processes (92%).

The global burden of BrC shows the highest contribution from secondary BrC (40%) compared to primary contributions from biomass burning (36%) and biofuel (24%). This result is opposite to the source contributions in surface air shown in Fig. 6. The contribution of secondary BrC to the atmospheric burden is twice as high as the contribution of secondary BrC to the surface concentration (17%), reflecting a relatively large production of BrC in the free troposphere as well as relatively limited export of primary BrC from the surface to the free troposphere.

Our BrC lifetime is 5.7 days, which is lower than that of OC (7.9 days) because of different contributions of the secondary sources for BrC and OC. The latter species includes a larger fraction of secondary species (52%), the lifetime of which is usually longer than that of POC especially for not aged biogenic SOC (Jo et al., 2013). No significant difference between the lifetimes of BrC and BC exists because BrC, which is more hydrophilic than BC, is more prone to wet scavenging than BC.

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6 Direct radiative effect of BrC

We use imaginary refractive indices of BrC as a function of wavelength for radiative transfer calculations to account for the wavelength dependency of the BrC absorption. Imaginary refractive indices in the literature have a wide range of values, even from the same sources, such as wood burning (Chakrabarty et al., 2010; Kirchstetter et al., 2004; McMeeking, 2008). In order to maintain the consistency with BrC emission estimates from primary sources, we use the imaginary refractive indices reported by McMeeking (2008), which are 0.18, 0.14, and 0.10 at 370, 405, and 532 nm, respectively. For primary BrC, we decrease these values by 40 % in order to maintain consistency with the MAE value of $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for our best estimates. The values are interpolated with the AAE at every 50 nm wavelength interval for the radiative transfer calculations. For secondary BrC, values from Nakayama et al. (2010) are used with 0.047 and 0.007 at 355 and 532 nm, respectively, based on the measurements for secondary organic aerosols from toluene.

We calculate AOD, SSA, and asymmetry parameters using FlexAOD, which is described in Sect. 4.2. Note that we calculate DRE rather than DRF. DRE is the instantaneous radiative impact of all atmospheric particles on the Earth's energy balance, and DRF is the change in DRE from pre-industrial to present-day (Heald et al., 2014). We use the Rapid Radiative Transfer Model for GCMs (RRTMG) (Iacono et al., 2008) for DRE calculations. Wavelengths used for the calculation are 300, 304, 393, 533, 702, 1010, 1270, 1462, 1784, 2046, 2325, 2788, 3462, and 8021 nm. MERRA reanalysis data are used for albedo and other meteorological variables.

Figure 8a and b shows the clear sky DRE values of primary and secondary BrC concentrations. Because the imaginary refractive indices of BrC are between those of strongly absorbing BC and scattering OC, the global mean DRE of BrC is close to zero, as shown in Fig. 8a and b.

Although the DRE of BrC at the top of the atmosphere is nearly zero, the increased DRE after considering BrC absorption (usually considered as scattering

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OC) is 0.12 W m^{-2} , as shown in Fig. 8c. The DRE of OC without BrC absorption is -0.69 W m^{-2} (Fig. 8d), and this value is increased to -0.57 W m^{-2} after considering BrC absorption. Consequently, the cooling effect of OC is reduced by 17%.

Despite the negligible effect of BrC on DRE or DRF, its significance manifests for OC DRF estimates, which have been conducted based on the assumption of scattering OC. For example, AeroCom phase II simulations calculated -0.03 W m^{-2} as the global mean DRF of POC from fossil fuel and biofuel, and -0.06 W m^{-2} for that of SOC (Myhre et al., 2013). Because the biofuel emission is about twice as large as the fossil fuel emission (Bond et al., 2007), and two-thirds of OC from biofuel is BrC, at least one-third of the POC from fossil fuel and biofuel is BrC. Therefore, one-third of DRF (-0.01 W m^{-2}) of POC in AeroCom is related to BrC, whose DRF is close to zero. For SOC, because the pre-industrial biogenic SOC concentration is similar to present-day conditions, almost all DRF of SOC is from anthropogenic SOC. Based on previous SOC studies (Henze et al., 2008; Jo et al., 2013; Murphy and Pandis, 2010), approximately one-third of anthropogenic SOC is highly aged, and can thus be assumed to be BrC in this simple estimation. As a result, one-third of DRF (-0.02 W m^{-2}) of SOC in AeroCom is related to BrC. The total DRF of BrC that was assumed to be scattering OC in the AeroCom study is -0.03 W m^{-2} . Because DRF of BrC is almost negligible, the negative DRF of OC (-0.09 W m^{-2}) in AeroCom could likely be overestimated by 33%. We think, however, the warming effect of BrC on the negative DRF or DRE of OC would be a low-end value because our best model likely underestimates BrC concentrations especially from the secondary source.

7 Effect on ozone photochemistry

BrC absorption, particularly at UV wavelengths, has an important implication for ozone photochemistry. Here we examine the effect of BrC absorption on photochemistry by updating photolysis rate calculations in GEOS-Chem following Martin et al. (2003). Table 3 shows the calculated extinction efficiency and SSA at $0.4 \mu\text{m}$, of important

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aerosols that affect UV extinction, and thus photolysis rate calculations, in the model. Values of OC, BC, and inorganic aerosols are from GEOS-Chem, in which we update aerosol optical properties by adding those of BrC. We include optical properties of primary and secondary BrC separately because they differ substantially. For example, SSA values of primary BrC are smaller than those of secondary BrC, and thus have a greater impact on UV radiation. Compared with other aerosols, SSA values of BrC are generally lower than those of OC and inorganic aerosols, but higher than those of BC.

Martin et al. (2003) showed that the effects of aerosols on photolysis rates increased CO by 5–15 ppbv in the remote Northern Hemisphere (annual mean concentrations less than 140 ppbv). This increase resulted in an improved the model agreement with observations, but there was a still gap between the model and the observations. In our simulation with BrC, CO concentration is further increased by 0.3–2.2 ppbv in remote Northern Hemisphere regions (annual mean concentrations less than 140 ppbv in the model). On the other hand, OH concentrations are decreased by 0–11 % in the boundary layer over the Northern Hemisphere (maximum decreases occur in regions with high BrC concentrations, shown in Fig. 6). The change of OH owing to BrC is about one-third of the OH change according to the overall aerosol effects from Martin et al. (2003). Therefore, the inclusion of BrC significantly affects tropospheric chemistry, especially for regions with heavy biomass burning and biofuel emissions.

Finally, we quantify the effects of BrC on global NO₂ photolysis rates and ozone concentrations at the surface. Figure 9 shows changes in annual NO₂ photolysis rates and O₃ concentrations in surface air owing to BrC absorption. Although BrC absorption is included, there are no significant changes (less than 1 %) of the global mean NO₂ photolysis rate and O₃ concentration in surface air. However, the effect of BrC appears to be important for regions with high BrC concentrations. We find a maximum decrease of the annual mean NO₂ photolysis rate by 9 % in surface air over Asia where the resulting reduction of O₃ concentration is up to –2 ppbv (6 % of annual mean surface O₃ concentration). We also find that the BrC effect has a strong seasonal variation

such that it is maximized in the spring when surface O₃ concentration is decreased up to -14 % in Asia because of high BrC concentration (55 μgC m⁻³).

8 Conclusions

OC has been considered to be a scattering aerosol, but emerging evidence has shown that some OC can efficiently absorb solar radiation. This absorbing OC is called BrC. With increasing recognition of its importance, especially for solar absorption at UV and short visible wavelengths, quantification of its spatial and temporal distribution is much needed for the study of climate and air quality issues. Here we conducted an explicit global BrC simulation for the full year of 2007 using a global 3-D chemical transport model (GEOS-Chem), and examined its implication for climate and O₃ photochemistry.

We first estimated primary BrC emissions from biomass burning and biofuel use based on the relationship between AAE and MCE. Our estimates of primary BrC emissions are 5.7 and 4.3 TgC yr⁻¹ from biomass burning and biofuel use, respectively. The secondary BrC source is estimated to be 5.7 TgC yr⁻¹ from the aromatic oxidation.

With explicit BrC emissions, a coupled oxidant-aerosol simulation was conducted for 2007 to obtain the spatial and temporal distributions of BrC concentrations. We first evaluated the model by comparing the simulated vs. observed BrC absorption in the United States and found that the model successfully reproduced the observed seasonal variation, but was biased high in the southeastern United States, whereas the model significantly underestimated secondary BrC over the Los Angeles basin. The choice of a lower MAE value for primary BrC decreased the high bias in the model, and provided our best results, which were used to examine the effect of BrC on climate and O₃ photochemistry.

Our budget analysis showed that BrC from primary sources are dominant (83 %) in surface air, but BrC from secondary sources becomes important with increasing altitudes. For example, BrC from secondary sources accounts for the 40 % of the tropospheric BrC burden, which is higher than its 17 % contribution to surface BrC

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concentrations. Our global mean value of the BrC to BC ratio is 2.3 for the whole atmosphere, and 1.7 for the surface, which significantly differs from the values used in previous studies.

Using our best results, we estimated the DRE of BrC to be close to zero at the top of the atmosphere because the imaginary refractive indices of BrC are in the midpoint between those of BC and OC. Despite a negligible contribution to DRE, the inclusion of BrC absorption in the model offsets the negative radiative effect of OC by 0.12 W m^{-2} (17%).

Finally, we included BrC absorption in photolysis rate calculations in the model. We found that the NO_2 photolysis rate is decreased up to 9%, especially for Asia, where BrC concentration is high. Resulting annual surface O_3 concentrations are decreased up to -2 ppbv (6%). This effect is more important in the spring, when a typical O_3 maximum occurs in Asia, where the effect of BrC decreases the surface O_3 concentration by up to -14 %.

Many chemical transport models and air quality models have included the effect of aerosols on photolysis rate calculations, but have not considered the BrC effect. Based on our analysis, BrC absorption could have a significant direct impact on regional air quality by being involved in O_3 photochemical formation. Its significance, however, can be expanded to the globe by its effect on the atmospheric oxidation capacity, which has an indirect but important implication for global air quality and climate.

Appendix A:

A1 Relationship between BrC/BC absorption ratio and AAE

In this section we describe a procedure for obtaining the relationship between the BrC/BC absorption ratio and AAE. Assuming no internal mixing and dust influence, total absorption at a certain wavelength (λ) can be expressed as:

$$\alpha_{\lambda, \text{CA}} = \alpha_{\lambda, \text{BrC}} + \alpha_{\lambda, \text{BC}} \quad (\text{A1})$$

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Rewriting Eq. (A1) using AAE:

$$\alpha_{\lambda_0,CA} \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{CA}} = \alpha_{\lambda_0,BrC} \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \alpha_{\lambda_0,BC} \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BC}} \quad (\text{A2})$$

Dividing each side of Eq. (4) by $\alpha_{\lambda_0,BC}$:

$$(1 + F) \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{CA}} = F \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BC}} \quad (\text{A3})$$

where F is the BrC/BC absorption ratio at λ_0 .

We can solve Eq. (A3) analytically, and the procedure is described in Appendix A2. We do not use the analytical relationship because it uses only three wavelengths for the calculations. The Ångström relationship is based on empirical fitting. AAE varies in different wavelength regions, even if we use the same samples. For example, Chung et al. (2012) showed that CA AAE is about 1.2 when the first four wavelengths (370, 470, 520, 590 nm) are used while the CA AAE is 1.35 with the last four wavelengths (590, 660, 880, 950 nm). This discrepancy is much increased in the case of BrC AAE. Liu et al. (2014) showed that BrC AAE varies by approximately 20%, depending on wavelength pairs. Furthermore, if we calculate AAE of BrC using the mass absorption efficiency (MAE) of Kirchstetter et al. (2004), AAE of BrC in all wavelengths (from 350 to 650 nm, 7 values) is fitted to 5.9 with a R^2 of 0.96. However, AAEs of BrC using just two wavelengths yield 4.1 and 8.0 for the 350–400 nm and 550–600 nm region, respectively.

Therefore, we calculate the relationship between MCE and F by regression using multiple wavelengths: [300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900 nm]. If we rewrite Eq. (A3) for the regression form,

$$\dot{A}_{CA} \log(\lambda) + C = -\log \left[F \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda}{\lambda_0} \right)^{-\dot{A}_{BC}} \right] \quad (\text{A4})$$

where the residual term C is

$$C = \dot{A}_{CA} \log(\lambda_0) - \log(1 + F) \quad (\text{A5})$$

The left side of Eq. (A4) has the shape of $Ax + B$. Therefore, by linear regression analysis, we can obtain \dot{A}_{CA} (the slope of the regression) as varying F on the right side.

5 We choose an \dot{A}_{BrC} value of 5.0 and an \dot{A}_{BC} value of 0.86, following Kirchstetter and Thatcher (2012), who estimated mean \dot{A}_{BrC} using several wood samples (87 samples).

We assign a λ_0 value of 550 nm. The coefficient of determination (R^2) is greater than 0.98 in all the regression analyses. The calculated relationship between MCE and F is plotted in Fig. 1. As expected, emissions of BrC are increased when MCE is decreased.

10 **A2 Analytical derivation of Eq. (A3)**

Here we describe the procedure to obtain the analytical relationship between MCE and F . First, substituting λ_1 and λ_2 in Eq. (A3),

$$(1 + F) \left(\frac{\lambda_1}{\lambda_0} \right)^{-\dot{A}_{CA}} = F \left(\frac{\lambda_1}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda_1}{\lambda_0} \right)^{-\dot{A}_{BC}} \quad (\text{A6})$$

$$(1 + F) \left(\frac{\lambda_2}{\lambda_0} \right)^{-\dot{A}_{CA}} = F \left(\frac{\lambda_2}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda_2}{\lambda_0} \right)^{-\dot{A}_{BC}} \quad (\text{A7})$$

15 Assuming AAE between λ_0 and λ_1 is equal to AAE between λ_0 and λ_2 , divide Eq. (A6) by Eq. (A7), and rearrange terms:

$$\left(\frac{\lambda_1}{\lambda_2} \right)^{-\dot{A}_{CA}} = \frac{F \left(\frac{\lambda_1}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda_1}{\lambda_0} \right)^{-\dot{A}_{BC}}}{F \left(\frac{\lambda_2}{\lambda_0} \right)^{-\dot{A}_{BrC}} + \left(\frac{\lambda_2}{\lambda_0} \right)^{-\dot{A}_{BC}}} \quad (\text{A8})$$

Taking the logarithm of both sides:

$$\mathring{A}_{CA} = -\log \left(\frac{F \left(\frac{\lambda_1}{\lambda_0} \right)^{-\mathring{A}_{BrC}} + \left(\frac{\lambda_1}{\lambda_0} \right)^{-\mathring{A}_{BC}}}{F \left(\frac{\lambda_2}{\lambda_0} \right)^{-\mathring{A}_{BrC}} + \left(\frac{\lambda_2}{\lambda_0} \right)^{-\mathring{A}_{BC}}} \right) / \log \left(\frac{\lambda_1}{\lambda_2} \right) \quad (\text{A9})$$

Substituting Eq. (2) into Eq. (A9) gives:

$$\text{MCE} = \left[18.2 + \log \left(\frac{F \left(\frac{\lambda_1}{\lambda_0} \right)^{-\mathring{A}_{BrC}} + \left(\frac{\lambda_1}{\lambda_0} \right)^{-\mathring{A}_{BC}}}{F \left(\frac{\lambda_2}{\lambda_0} \right)^{-\mathring{A}_{BrC}} + \left(\frac{\lambda_2}{\lambda_0} \right)^{-\mathring{A}_{BC}}} \right) / \log \left(\frac{\lambda_1}{\lambda_2} \right) \right] / 17.34 \quad (\text{A10})$$

5 After assigning \mathring{A}_{BrC} , \mathring{A}_{BC} , and the corresponding three wavelengths (λ_0 , λ_1 and λ_2) in Eq. (A10), we obtain the relationship between MCE and F analytically.

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Table 1. Emission factors (EFs) and calculated parameters used for primary BrC emission estimates. Biomass burning emission is classified for six vegetation types based on the FINN inventory. Here BrC/BC (or OC) is the mass ratio of BrC to BC (or OC) emitted from biomass burning and biofuel use.

Source Type	CO ₂ EF [g kg ⁻¹]	CO EF [g kg ⁻¹]	MCE	BrC/BC	OC EF [g kg ⁻¹]	BC EF [g kg ⁻¹]	BrC/OC
Biomass burning							
Boreal Forest	1514	118	0.891	5.265	7.8	0.20	0.135
Cropland	1537	111	0.898	4.523	3.3	0.69	0.946
Savanna/Grassland	1692	59	0.948	1.328	2.6	0.37	0.189
Temperate Forest	1630	102	0.910	3.465	9.2	0.56	0.211
Tropical Forest	1643	92	0.919	2.820	4.7	0.52	0.312
Woody Savannah/Shrubland	1716	68	0.941	1.620	6.6	0.50	0.123
Biofuel*							0.663

*Detailed information is given in Table S1.

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**Table 2.** Global tropospheric budgets of BrC compared to those of OC and BC.

Unit: [GgC]		BrC	OC	BC	BrC/OC	BrC/BC
Sources	Biomass burning	5679				
	Biofuel	4334				
	Aromatic SOC	5690				
	Total	15703	46929	6847	0.33	2.29
Wet deposition	Biomass burning	4666				
	Biofuel	3444				
	Aromatic SOC	5244				
	Total	13354	38681	5458	0.35	2.45
Dry deposition	Biomass burning	1012				
	Biofuel	891				
	Aromatic SOC	445				
	Total	2348	8272	1397	0.28	1.68
Burden	Biomass burning	87				
	Biofuel	59				
	Aromatic SOC	98				
	Total	244	1021	107	0.24	2.28
Lifetime [days]	Biomass burning	5.6				
	Biofuel	5.0				
	Aromatic SOC	6.3				
	Total	5.7	7.9	5.7		

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Table 3. Extinction efficiencies and SSAs of selected aerosols at 0.4 μm used for calculating photolysis rates in GEOS-Chem. SNA indicates inorganic salt comprised of sulfate, nitrate and ammonium aerosols.

0.4 μm	RH	BrC (Primary)	BrC (Secondary)	OC	BC	SNA
Extinction efficiency	0%	1.3806	1.2922	1.3933	0.6229	1.2147
	50%	1.6316	1.5645	1.4967	0.6229	1.6566
	70%	1.7300	1.6781	1.5815	0.6229	1.8440
	90%	1.7883	1.7474	1.8485	0.4607	2.2568
	99%	2.3250	2.4390	2.5870	0.4181	2.9655
Single scattering albedo	0%	0.6771	0.8683	0.9735	0.1935	1.0000
	50%	0.6604	0.8584	0.9841	0.1935	1.0000
	70%	0.6538	0.8540	0.9873	0.1935	1.0000
	90%	0.6444	0.8480	0.9927	0.3004	1.0000
	99%	0.6396	0.8372	0.9977	0.5233	1.0000

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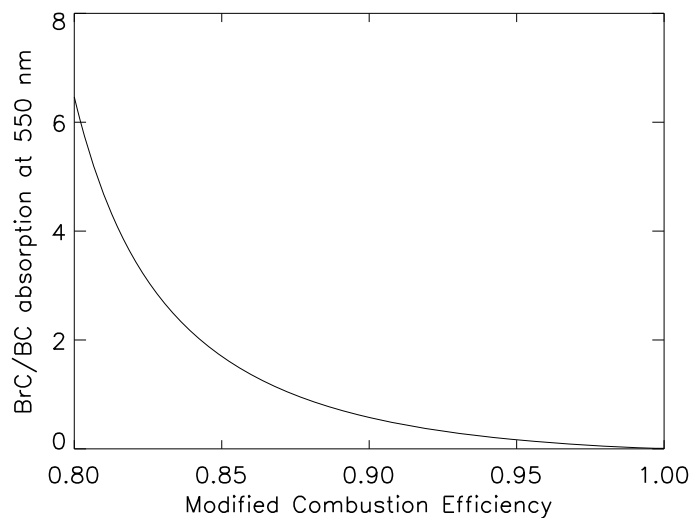


Figure 1. Estimated absorption ratios of BrC to BC at 550 nm as a function of MCE. We assume that the CA absorption is only contributed by BC and BrC absorption.

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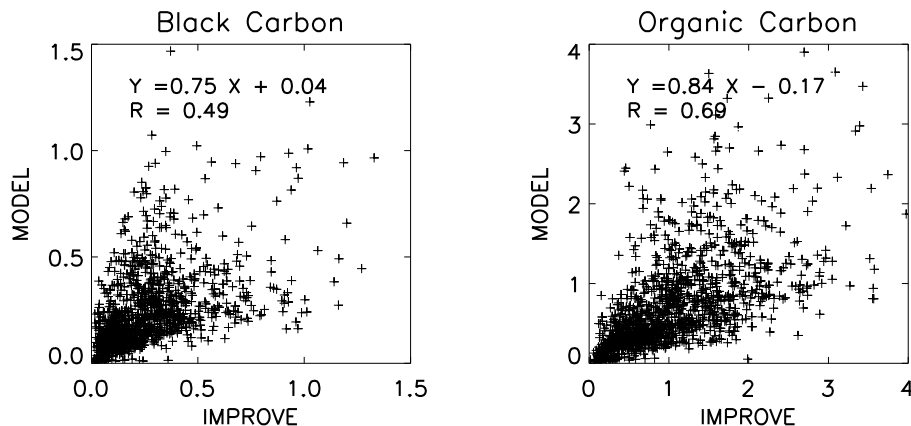


Figure 2. Scatterplot of simulated vs. observed BC concentrations (left) and OC concentrations (right). Unit is $\mu\text{g C m}^{-3}$. Values are monthly means for 2007. Regression equations and correlations are shown inset. Regression is computed with reduced major axis (RMA) method.

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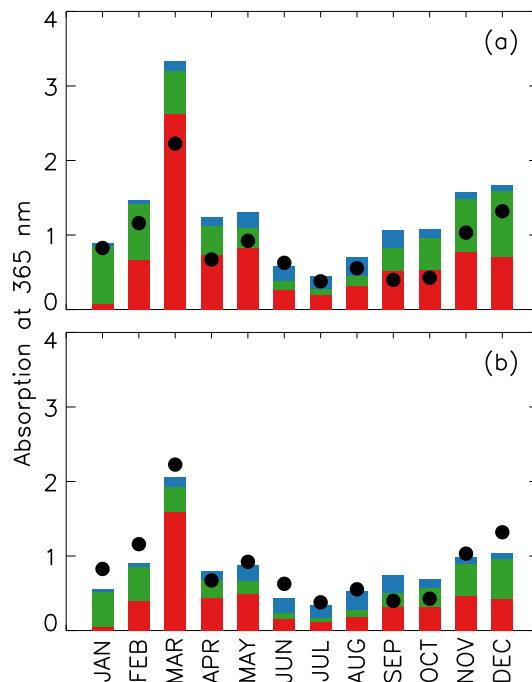


Figure 3. Simulated vs. observed monthly mean light absorption at 365 nm by water soluble BrC over the southeastern US in 2007. Unit is Mm^{-1} . Black circles denote observations, and bar graphs indicate model results for each source: biomass burning (red), biofuel (green), and SOA (blue). Upper and lower panels show the comparisons using different MAE values of **(a)** 5.3 and **(b)** $3.2 \text{ m}^2 \text{ g}^{-1} \text{ C}$ for primary BrC used in the model.

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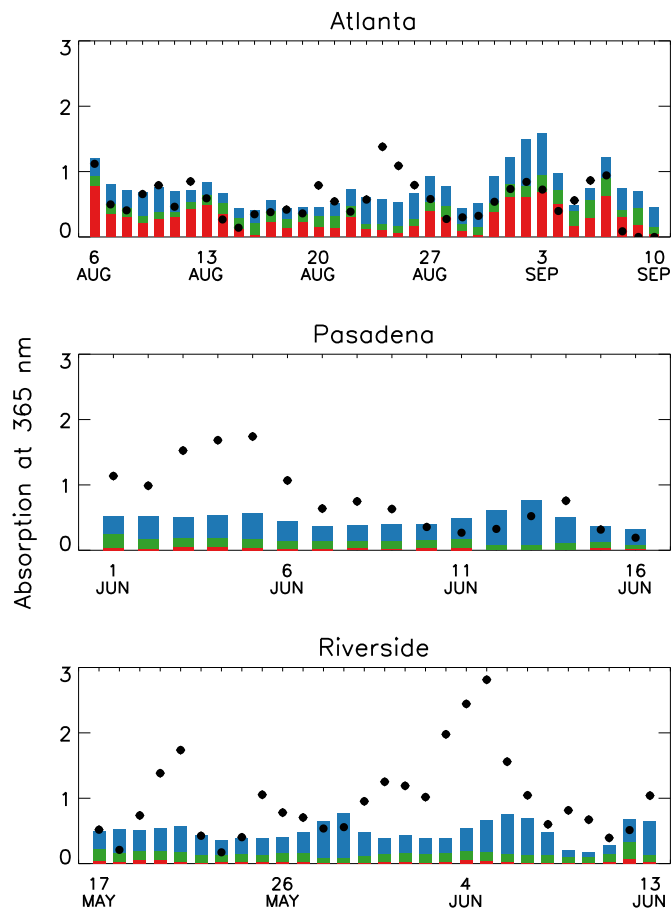


Figure 4. Simulated vs. observed daily mean light absorption at 365 nm by water soluble BrC over the US in 2010. Unit is Mm^{-1} . Black circles denote observations and bar graphs indicate model results for each source – biomass burning (red), biofuel (green), and SOA (blue).



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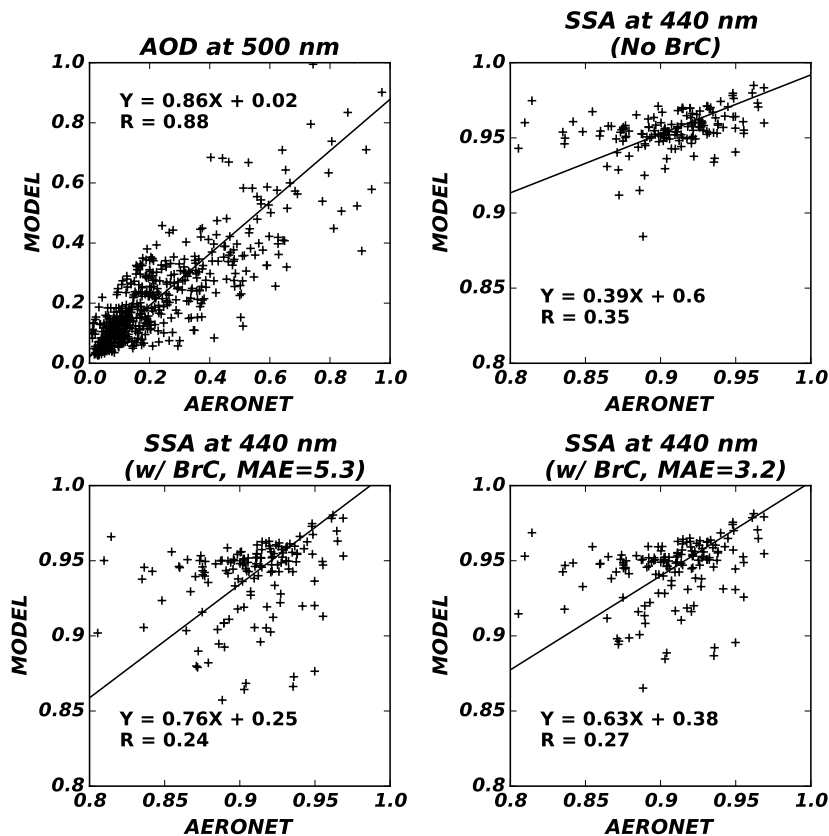


Figure 5. Scatterplots of simulated vs. observed AOD at 500 nm (upper left), SSA at 440 nm without BrC (upper right), SSA at 440 nm with BrC when MAE of primary BrC is 5.3 (lower left), and SSA at 440 nm with BrC when MAE of primary BrC is 3.2 (lower right) for 2007. Reduced major axis regression is shown along with the regression equation and R . Each point indicates monthly averaged AOD or SSA when the number of observation is greater than 10 days.



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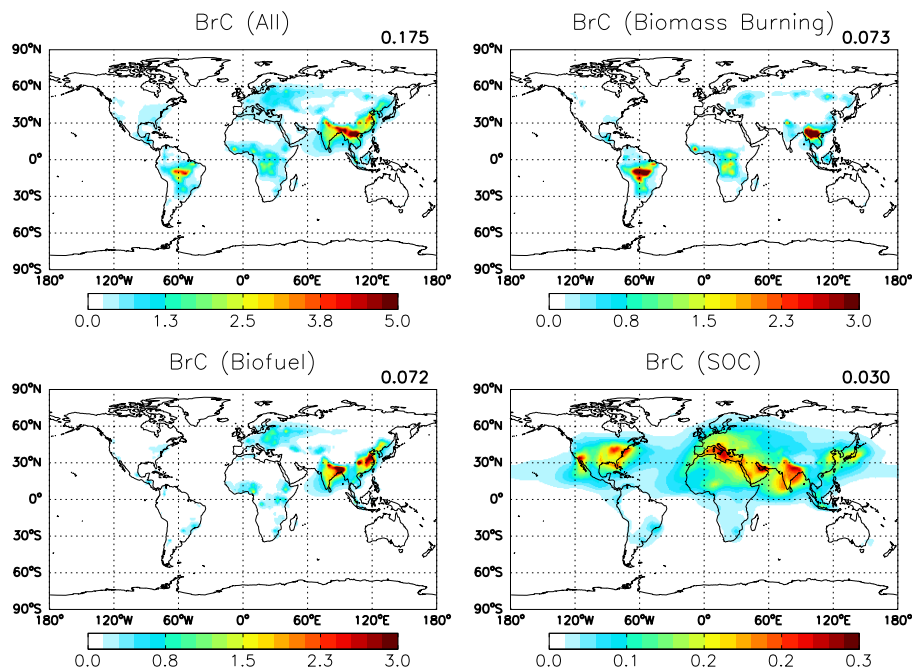


Figure 6. Annual surface map of total BrC (top left) and BrC from three source categories: biomass burning (top right), biofuel (bottom left), and SOC (bottom right). Mean values are presented in the upper right corner of each panel. Unit is $\mu\text{g C m}^{-3}$.

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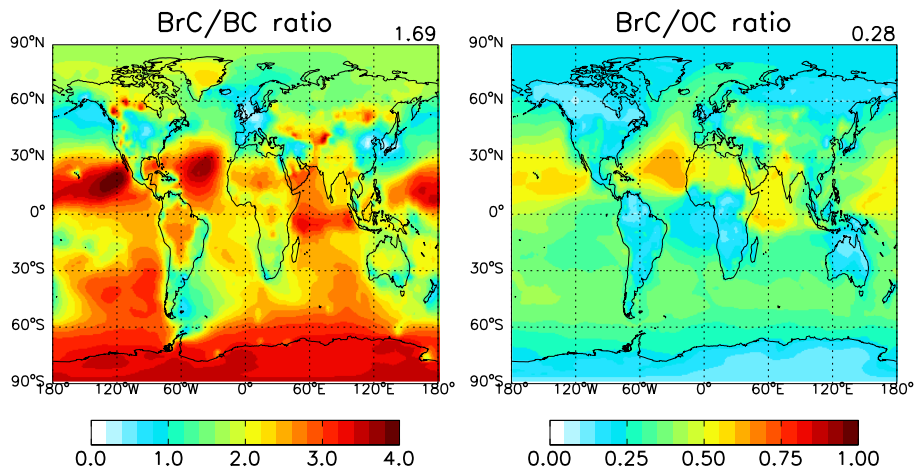


Figure 7. Annual mean ratios of BrC to BC (left) and OC (right) in surface air. Global mean values are presented in the upper right corner of each panel.

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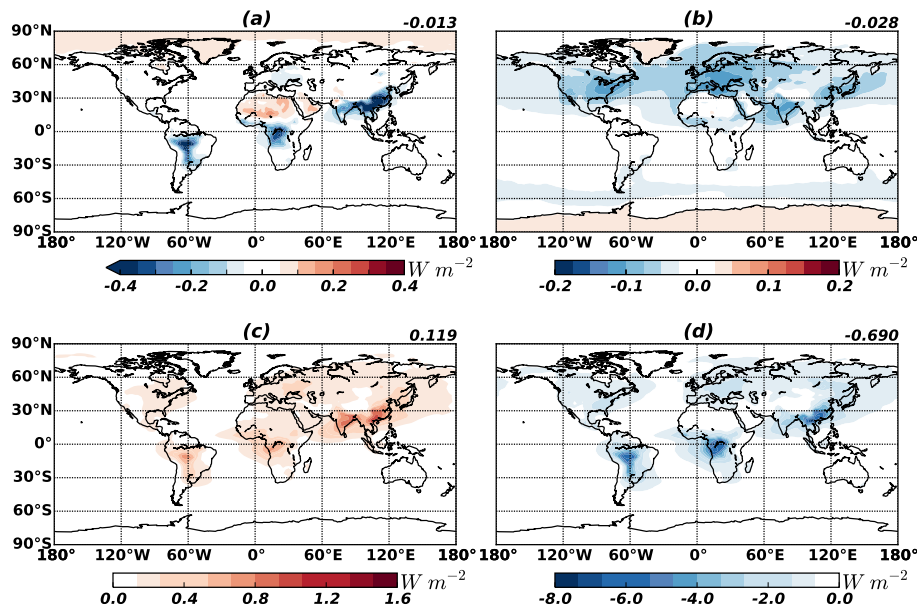


Figure 8. DRE of BrC at the top of the atmosphere. Upper panels are for radiative effect of BrC from primary sources **(a)** and from secondary sources **(b)**. The DRE difference between BrC assumed to be scattering OC and BrC is shown in **(c)**. Radiative effect of total OC (BrC is assumed to be scattering OC) is represented in **(d)**. The 70°S – 70°N averages are shown in the upper right corner of each panel.

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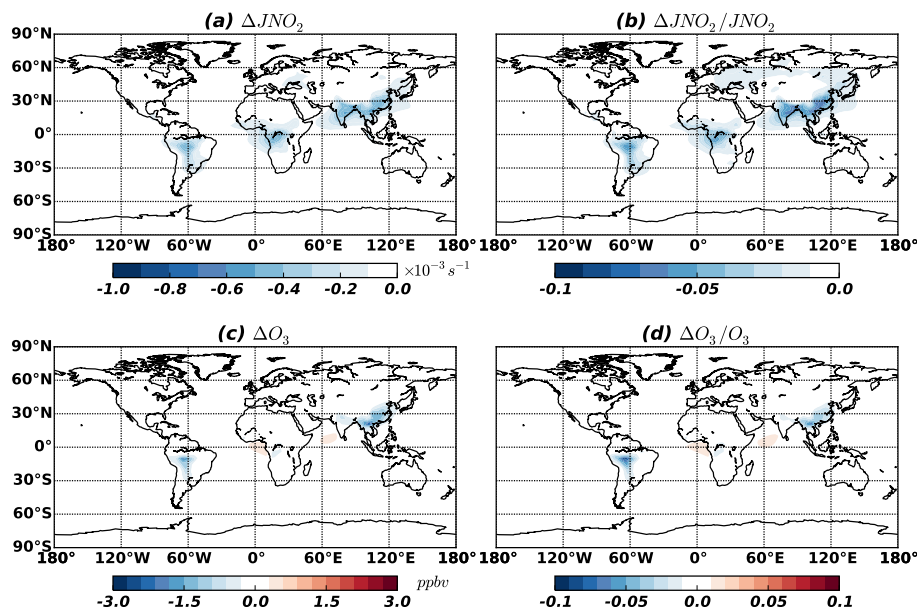


Figure 9. Changes in annual NO_2 photolysis rate (a, b) and O_3 concentration (c, d) at the surface due to BrC absorption.

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