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Nationwide summer peaks of OC/EC ratios in the contiguous United States

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ABSTRACT

The ratios of observed organic carbon (OC) to elemental carbon (EC) from the rural sites of the IMPROVE network are analyzed for the 5-year period from 2000 to 2004. Among these years, nationwide OC/EC peaks are observed most consistently in the summer of 2002. Several potential factors are analyzed, including biomass burning, secondary organic aerosols (SOA) formation from biogenic sources and in-cloud processing, long-range transport from East Asia, and meteorological conditions over the U.S. We find that biomass burning and SOA formation make the most significant contributions using the global GEOS-Chem model simulations. The effect of model estimated in-cloud SOA formation is significant compared to the estimate of (non-cloud) biogenic SOA. The impacts of Canadian and western U.S. fires are larger than fires in Russia or Mexico in summer. The dry meteorological condition of the summer of 2002 tends to promote higher OC/EC ratios by inducing larger fire emissions, SOA formation, and a longer OC lifetime.

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1. Introduction

Organic carbon (OC) and elemental carbon (EC) aerosols are large contributors to fine particulate matters (PM2.5) in the atmosphere (Turpin et al., 2000; Kanakidou et al., 2005). Biomass burning has large spatial and temporal variations leading to potentially large inter-annual variability of OC, EC, and PM2.5 (Park et al., 2007). Most biomass burning occurs in the tropics. At the northern mid and high latitudes, boreal forest fires in Russia and Canada are the largest (Giglio et al., 2006; Van der Werf et al., 2006).

Other than direct emissions of EC and OC from biomass burning, large amounts of secondary organic aerosol (SOA) can be produced during atmospheric oxidation processes (Kroll and Seinfeld, 2008, and references therein). OC can also form through the oxidation of biogenic volatile organic compounds (VOCs), such as isoprene (C_5H_8), monoterpenes ($C_{10}H_{16}$), and sesquiterpenes ($C_{15}H_{24}$). Biogenic emissions are positively correlated to light intensity and temperature (Guenther et al., 2006) and therefore are higher in summer. In the areas with large forest coverage such as the southeastern U.S., they could contribute to the summertime OC maximum (e.g., Zheng et al., 2002) and thus OC/EC peaks. Another important SOA formation pathway is aqueous-phase reactions of some VOCs such as glyoxal (CHOCHO) and methylglyoxal ($CH_3C(O)CHO$) in cloud and fog (e.g., Blando and Turpin, 2000). For example, recent lab and field studies (Loeffler et al., 2006; Volkamer et al., 2006) suggested glyoxal as an important SOA precursor in the aqueous environment of cloud and fog. Half glyoxal and 80% of methylglyoxal are estimated to emit from biogenic sources (Fu et al., 2008), which are higher in summer. They potentially contribute to the observed summer OC/EC peaks.

The ratio of particulate OC to EC is an important index that reflects source type and source strength (e.g., Blando and Turpin, 2000). Many case studies using OC/EC ratios have been reported (e.g.. Lim et al., 2003; Yu et al., 2004; Liu et al., 2006). A comprehensive study of OC/EC is needed because OC/EC ratios differ largely in regions and seasons. In this study, we examine the 5-year OC and EC data collected from a national network, the Interagency Monitoring of Protected Visual Environments (IMPROVE) network.

Generally OC and EC have large spatial and temporal variations. In contrast, consistent patterns of OC/EC ratio can be more easily found partly because the ratio of two chemicals tends to be less sensitive to atmospheric processing (e.g., McKeen and Liu, 1993; Wang and Zeng, 2004). The OC/EC emission ratios from biomass burning are usually higher than fossil fuel sources (e.g., Liu et al., 2006; Marmur et al., 2009). SOA formation increases only OC concentrations and hence OC/EC ratios. We compare in Fig. 1 the OC/EC ratios from biomass burning (Andreae and Merlet, 2001), anthropogenic coal combustion, gas and oil combustions, and

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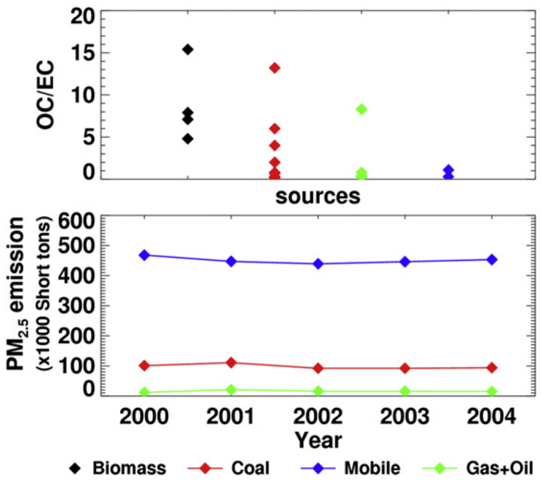

Fig. 1. (Top panel) OC/EC ratios from biomass burning (black) (Andreae and Merlet, 2001), coal combustion (red), gas and oil combustions (green), and mobile emissions (blue) (Bond et al., 2004). OC/EC ratios are calculated based on the emission factors from different sources. (Bottom panel) Annual $PM_{2.5}$ emissions in the United States from coal combustion, gas and oil, and mobile sources from the US EPA national emission inventory (NEI) in 2000–2004.

mobile sources (Bond et al., 2004). Although coal, gas, and oil combustions may occasionally have comparable OC/EC emission ratios to biomass burning, these emissions are much less than mobile sources, which have very low OC/EC ratios (<2.5). More significantly, fossil fuel sources have overall small seasonal variations. Fig. 1 shows that they have small inter-annual variation too. Therefore, the variations of the OC/EC ratios are more sensitive indicators for biomass burning and SOA than OC or EC alone.

Observed OC/EC ratios over the contiguous United States from 2000 to 2004 are analyzed in this study. A consistent distribution of high OC/EC ratios is found over the entire contiguous United States in the summer of 2002. We investigate a number of potential reasons, including biomass burning, biogenic SOA production, SOA production from large-scale cloud processing, and inter-continental transport from Asia. Given the modeling uncertainties in the biomass burning emissions particularly with respect to prescribed burning in the South (e.g., Zeng et al., submitted for publication), biogenic SOA formation (e.g., Henze and Seinfeld, 2006), in-cloud SOA formation (e.g., Fu et al., 2008), and the simulated inter-annual variations of meteorological fields, we do not attempt in this work to apply the GEOS-Chem model to simulate the observed inter-annual variations of OC/EC ratios. Instead, we focus the modeling effort on understanding the observations of consistently high OC/EC ratios across the United States in the summer of 2002.

2. Seasonal patterns of OC/EC ratio from 2000 to 2004

OC and EC measurements of 2000–2004 from the IMPROVE network are analyzed. IMPROVE sites are mostly located in the class I areas, covering national parks and wildness areas defined by the Clean Air Act in 1977, with small local emissions. These measurements generally represent the background conditions. Consistent quality assurance and control standards are applied (Chow et al., 2001) using the same measurement protocol, thermal optical reflectance (TOR). It is an excellent dataset to investigate the spatial distribution of PM2.5 composition. 24-h fine particle mass samples are collected every 3 days and analyzed. It provides enough temporal resolution to estimate the monthly and seasonal variations of OC/EC ratios. The observation data can be obtained online at http://vista.cira.colostate.edu/improve/Data/IMPROVE/improve_data.htm.

Traditionally, source apportionment methods can be used and essential key ratio indictors can be derived (e.g., Liu et al., 2005, 2006). However, since we will apply the model to analyze the reasons for the consistent OC/EC ratios we discovered, a simple key ratio indicator is more appropriate. Here, we compare OC/EC ratio to OC or EC as a function of sulfate. Although sulfate is exclusively from anthropogenic sources, its sources do not necessarily collocate with OC and EC sources such as vehicles. We find in Fig. 2 that both high OC and low OC data points tend to have low sulfate concentrations, all of which could be from non-anthropogenic sources such as biomass burning or biogenic SOA. Long-range transport of fire emitted OC and EC, for example, do not have a large impact on the absolute levels of OC due to dilution but can significantly alter the OC/EC ratio in remote regions. The distribution of EC and OC/EC ratio as a function of sulfate follows a similar pattern. As discussed in the previous section, fossil fuel sources do not affect the seasonal or inter-annual variations of OC/EC ratios nearly as much as biomass burning or SOC. We therefore choose the ratio of OC/EC as the key parameter in this analysis and investigate its seasonal variations.

We examine the OC/EC ratios over the contiguous United States by grouping the 174 sites over 6 regions (Fig. 3), i.e. West, Northern Plains, Southern Plains, Midwest, Northeast, and Southeast. The division into 6 U.S. regions is primarily based on the definition of the 10 US Environmental Protection Agency (EPA) regions (http://www.epa.gov/tribalportal/whereyoulive/regions.htm) by combining the regions and states with similar variation patterns of OC/EC ratios. The West region has 60 sites; other regions have ~20 sites. Monthly mean OC/EC ratios are then calculated for the 6 regions. Note that there are 12 IMPROVE urban sites ($<10\%$ of the whole dataset). We did not include these urban sites in our analysis.

OC/EC ratios are generally lower in winter and higher in spring and summer (Fig. 4). The Northern Plains is the only region with consistent occurrence of a summer maximum in the 5 years. The highest summer peak of >10 occurred in the Northern Plains, comparing to ~6 in the Midwest and Northeast. The least seasonal variation of OC/EC ratios is in the Midwest. In winter, the OC/EC ratio is more consistent across these regions from a low of 3 in the Midwest and the Northeast to a high of 4 in the Southeast. During the 5-year period, 2002 is the year with the most consistent summer (June, July, and August) peaks across all 6 regions (Fig. 4). In the West, the Midwest, and the Northeast, the OC/EC peaks in summer 2002 were especially striking compared to other years. Fig. 4 clearly demonstrates the highest summer increases of OC/EC ratios in 2002 in most regions.

3. Methods

We investigate five factors that can potentially contribute to the abnormally consistent OC/EC peaks in summer 2002. We apply a global chemical transport model, GEOS-Chem, to explore the individual contributions from biomass burning and biogenic SOA formation. Cloud processed SOA formation from glyoxal and methylglyoxal and inter-continental transport from East Asia are also assessed by GEOS-Chem model. The inter-annual variations of the meteorological conditions are discussed qualitatively as another important factor.

GEOS-Chem model is a global 3-D model of atmospheric composition driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling Assimilation Office (GMAO) (Bey et al., 2001). We use it to study the variations of OC/EC ratios in the U.S. in 2002. GEOS-4 meteorological products are used. The model has a resolution of 2° × 2.5° in horizontal and 30 layers in vertical. Anthropogenic emissions of OC and EC over the U.S. from the EPA NEI 99

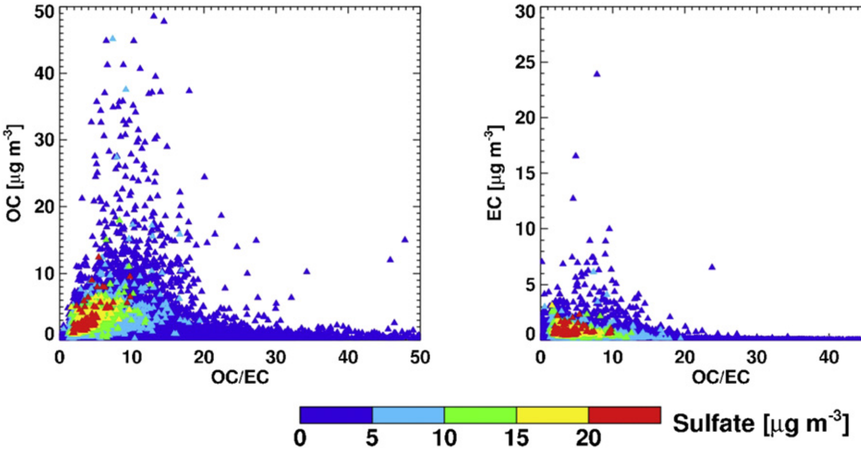

Fig. 2. The distributions of OC and OC/EC ratios (left panel), and EC and OC/EC ratios (right panel) as a function of sulfate measured by the IMPROVE network 2000–2004.

inventory (http://www.epa.gov/ttnchie1/net/1999inventory.html) and those for the rest of the world (Bond et al., 2007) have been included in the base and all sensitivity simulations. Carbonaceous aerosol simulation in GEOS-Chem generally follows the previous study by Henze and Seinfeld (2006). Biomass burning is a major source for EC and OC. We use in GEOS-Chem model the fire emissions of EC and OC for 2002 from the Global Fire Emissions Database (GFED) version 2 dataset (Randerson et al., 2006) (ftp://ftp.daac.ornl.gov/data/global_vegetation/fire_emissions_v2.1/data/). It was compiled using the burned area from MODIS satellite data (Giglio et al., 2006) and the Carnegie-Ames-Stanford Approach (CASA) biogeochemical model (Field et al., 1995). The emission ratios of OC/EC are 7.0 (=3.2:0.46), 8.3 (=5.2:0.63), and 16.3 (=9.1:0.56) over savanna, tropical forest, and extratropical forest (Andreae and Merlet, 2001), respectively. We aggregate the original 1° × 1° EC and OC emissions into the 2° × 2.5° grids of GEOS-Chem.

In the base run, the SOA production is calculated from the oxidation of terpenes and isoprene (Henze and Seinfeld, 2006). To study the contribution of biogenic SOA, we evaluate the inter-annual variations of biogenic emissions of terpenes and isoprene by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) emission model (Guenther et al., 2006) in GEOS-Chem. MEGAN model was adopted into GEOS-Chem model with some modifications to only estimate the biogenic gaseous emissions of isoprene, monoterpenes, and methyl butenol. The spatial resolution is reduced from 1 × 1 km^2 to GEOS-Chem model grids. In this study, a full year base run in 2002 is done with biomass burning OC and EC emissions and SOA formation. Another 1-year sensitivity run with no biomass burning emissions is conducted to study the overall impact of biomass burning.

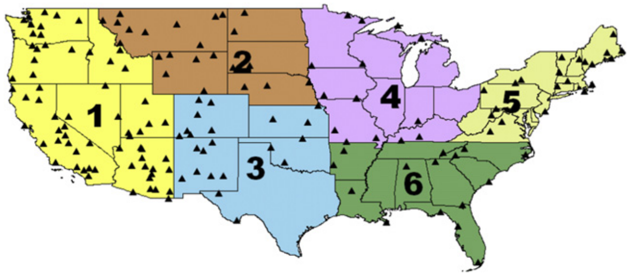

Fig. 3. Contiguous U.S. is divided into 6 regions: 1. West, 2. Northern Plains, 3. Southern Plains, 4. Midwest, 5. Northeast, and 6. Southeast. Black triangles represent the locations of the IMPVOE sites.

Several sensitivity runs from May to August 2002 with one-month spin-up in May are designed to study the importance of each individual factor in summer season (June, July, and August). After considering the amount and geographical region of biomass burning, we define 5 source regions: eastern Russia, western Canada (west of 110°W), eastern Canada (east of 110°W), the United States, and northern Mexico (north of 20°N). We first estimate the net effect of biomass burning by comparing the standard simulation to a sensitivity simulation without biomass burning emissions. The impacts of biomass burning from 5 individual source regions are then investigated by comparing the base simulation and the sensitivity simulation with biomass burning in the selected region removed. The difference between the base run and each sensitivity run therefore represents the contribution of biomass burning emissions from that region to observed OC/EC ratios in the U.S. Another sensitivity run without biogenic SOA production in 2002 is also conducted to assess the impact of biogenic SOA.

Aqueous uptakes of glyoxal and methylglyoxal in cloud can lead to irreversible SOA production (Fu et al., 2008), which has been found in a number of field studies (Volkamer et al., 2006; Yu et al., 2005; Zhang et al., 2005). Quantitative assessment using GEOS-Chem model follows the previous study by Fu et al. (2008), except changing the horizontal resolution from 4° × 5° to 2° × 2.5° to be consistent with other model runs in this work. The largest source of glyoxal and methylglyoxal is isoprene (>50%), followed by biomass burning (Fu et al., 2008). The in-cloud SOA contribution is assessed by comparing the sensitivity simulation to the base run results.

We also evaluate the impact of aerosol emissions from the eastern part of China (east of 105°E), one of the most important source regions with its rapid industrialization in the last two decades. The inter-continental transport of particulate matter from China can potentially contribute to the PM variations in the U.S. In the sensitivity run, carbonaceous aerosol emissions over East China are turned off. The results are then compared to the base model simulation.

In the following discussion, we first examine the contributions of biomass burning emissions in detail. We then discuss the potential roles of biogenic SOA, in-cloud SOA production, and inter-continental transport from Asia. The 5-year meteorological conditions are analyzed at the end.

4. Model simulations and analysis

We note first the spatial resolution of the global model (2° × 2.5°) is too coarse to simulate the details of episodic OC/EC

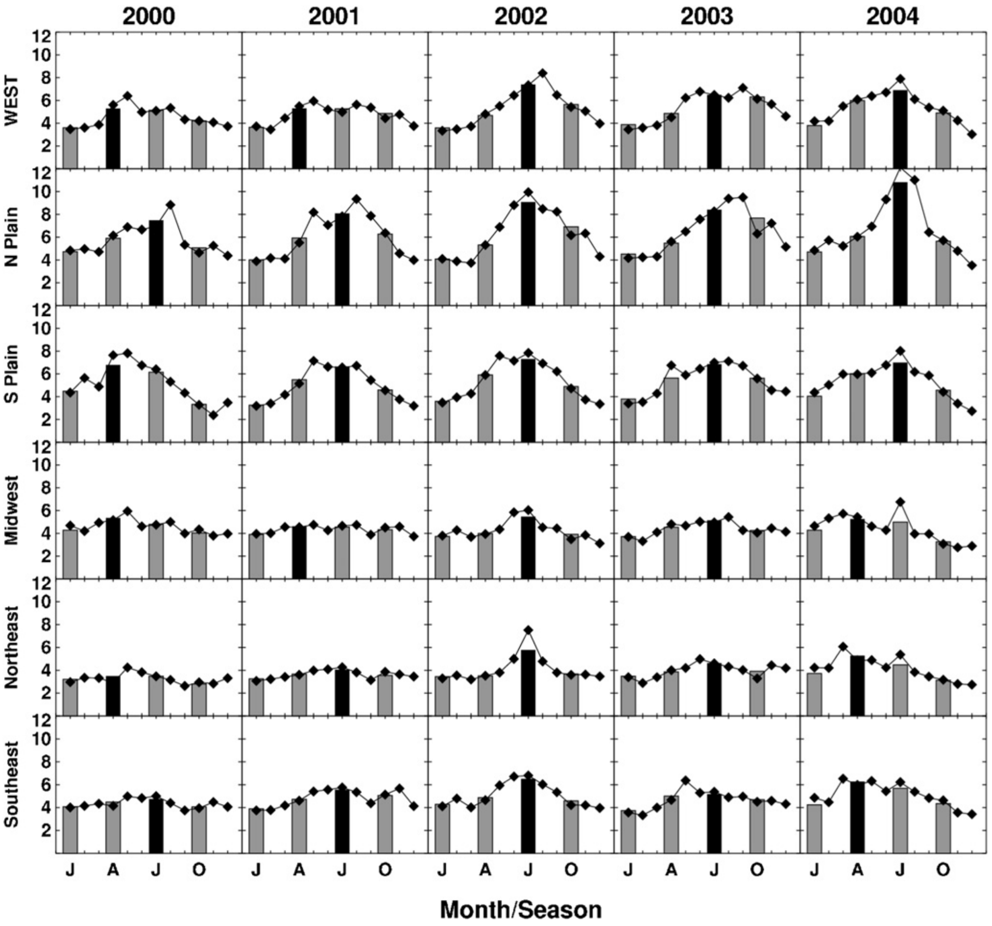

Fig. 4. Monthly (lines) and seasonal (bars) OC/EC ratios at the IMPROVE observation sites over the 6 regions from 2000 to 2004. Note that seasonal values for winter, spring, summer, and fall are shown by bars at the locations for January, April, July, and October. The highest seasonal OC/EC ratio values are shown by black bars.

enhancements at a surface site. Therefore, monthly statistics are used in this work. Higher-resolution regional models are needed to simulate the surface episodes. We choose a global model because long-range and even inter-continental transport of biomass burning could be important factors affecting the observed OC/EC ratios. The GEOS-Chem model performance in the simulations of OC, EC, and OC/EC ratios are evaluated in Table 1. The model tends to overpredict concentrations of OC and EC by 60% and 150%, respectively. The overprediction is partly due to the emission reductions from 1999 to 2002. The OC/EC ratio is underpredicted by about 30%, close to the US EPA (2005) recommended criteria for gaseous species. More detailed evaluations are shown in the supplementary materials. Fig. S1 (supplementary materials) shows that the variation patterns are generally consistent between the simulated and observed OC, EC, and OC/EC ratios. Half of the observed variations are explained by model simulations ($r > 0.7$). Figs. S2 and S3 (supplementary materials) show than regional-scale enhancements by biomass burning and SOC formation are simulated by the model. Although the large model uncertainties prevent us from detailed discussion of carbonaceous aerosol sources, the overall model performance of the OC/EC simulation is adequate for analyzing the factors contributing to high OC/EC ratios observed in the summer of 2002. To take advantage of the trend consistency and to reduce the effects of model biases, we use the deviations of OC/EC ratios from the mean values in the following discussion. The relative source contributions are compared in the model analysis.

Fossil fuel emissions including coal, gas, and oil combustions and mobile emissions are important sources of OC and EC. The inter-annual variations of these emissions are small in the 5-year period (Fig. 1) (http://www.epa.gov/ttn/chief/trends/). Moreover, fossil fuel combustion sources have generally smaller OC/EC ratios than biomass burning emissions (Fig. 1) (Bond et al., 2004, 2007). The simulated average OC/EC ratios from fossil fuel sources over the

Table 1
GEOS-Chem model performance on the simulations of OM, EC, and OC/EC over the contiguous U.S.

Tracer	Mean observation ($\mu g\ m^{-3}$)	Mean simulation ($\mu g\ m^{-3}$)	Mean bias ($\mu g\ m^{-3}$)	Mean error ($\mu g\ m^{-3}$)	Normalized mean bias (%)	Normalized mean error (%)
OM[a]	1.83	2.90	1.07	1.20	58	65
EC	0.26	0.66	0.39	0.39	150	151
OC/EC[b]	5.08	3.35	−1.73	1.79	−34	35

[a] OM = 1.4*OC.
[b] OC/EC is unitless.

U.S. are $\sim$2 with almost no seasonal variation (Fig. 6). Therefore, fossil fuel sources are unlikely the cause of the summer OC/EC peaks in 2002.

4.1. *Biomass burning*

Global distributions of biomass burning emissions in 2000–2004 are derived based on the satellite remote sensing based dataset, GFED v2 (Randerson et al., 2006) (Fig. 5). In contiguous U.S., the annual biomass burning emission is not the highest in 2002, although the largest monthly biomass burning emission is found in summer 2002 among the 5 years (not shown). The boreal forest fire emissions in Canada increased from 2000 to 2004. In eastern Canada, fire burning dropped in 2004. There are large inter-annual variations in the spatial distribution of the boreal forest fires in North America (not shown). In 2002, most of the summer burning occurred in Alberta, Ontario, and Quebec close to the U.S. and Canadian border and very few burnings were found in Alaska. While in 2004, most of the boreal forest burnings were in Alaska and the Northwest Territories of Canada, which are far away from the contiguous U.S. Therefore, the geographical extent of the boreal burning impact on U.S. OC/EC ratios is likely larger in 2002 than 2004. The boreal fire emissions in Russian Siberia had the highest peak in 2003 followed by 2002. Eastern China has the least amount of biomass burning among the 6 regions. As shown below, the largest emissions from Siberia have little impact on U.S., China is thus not investigated as a separate source region for biomass burning impact. The fossil fuel and industrial sources in China are far more important than biomass burning. We therefore study the total anthropogenic impact of OC and EC emissions from China. Mexico is examined as a separate source region due to its proximity to the U.S. Uncertainties exist in the fire emission inventory mainly due to uncertainties in fuel loading, combustion completeness, burned area, and emission factors. To reduce the impact from the uncertainties from model simulations and observations, we focus our discussion on the peaks in summer season with relatively high OC and EC concentrations and OC/EC ratios.

The GEOS-Chem simulations of monthly averaged OC/EC ratios are shown with the observations in Fig. 6. We compare the monthly deviations from the simulated annual means, respectively, in 6 regions (Fig. 3). In the West, Midwest, and Northeast, GEOS-Chem captures well the observed peaks. In the Northern Plains, Southern Plains, and the Southeast, there is one-month phase difference between the observed and simulated OC/EC peaks. It may reflect the uncertainties in the emission inventory. The biomass burning induced increase in OC/EC ratio is the largest in the West ($\sim$4) and is the smallest in the Southeast ($\sim$0.5). Moderate enhancements are found in the Northern Plains, Midwest, and Northeast. Without biomass burning emissions, GOES-Chem simulates lower OC/EC ratios than the observations in summer over most regions.

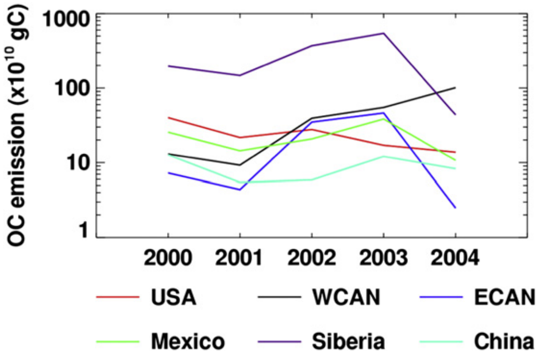

Fig. 5. GFED v2 dataset based OC emissions from biomass burning in 2000–2004 over the contiguous U.S. (red), western Canada (west of 110°W, black), eastern Canada (east of 110°W, dark blue), northern Mexico (north of 20°N, green), Russian Siberia (purple), and eastern China (east of 105°N, sky blue).

The summertime contributions of biomass burning from specific source regions are shown in Fig. 7. Long-range transport from biomass burning emissions in eastern Russia does not have a large impact. Local and nearby sources are more important. In the West, biomass burning from the U.S. is the main contributor to the OC/EC peak. Inter-annual variations of OC concentrations are found to be highly correlated with fire emissions in the West (Spracklen et al., 2007), while EC is less correlated with fire emissions. Local fire emission from the Biscuit Fire, a large wildfire event with 500,000 acres burnt in summer 2002 in the Siskiyou National Forest in the northwestern California and southwestern Oregon, is the main contributor to the increase, resulting in the largest OC/EC anomaly (Fig. 7) among the 6 regions. Source apportionment study in the Yosemite National Park in summer 2002 (Engling et al., 2006) attributed the observations of up to 18 μg m^{-3} organic matter to biomass burning during this period.

In the Northern Plains, fire emissions from the U.S. and western Canada are equally important to explain the second largest summer peak of OC/EC ratios. In the northern states, the impact from Canadian fires can be significant. In the Midwest, the OC/EC anomalies are from biomass burning emissions from both western and eastern Canada. The biomass burning emissions from eastern Canada and the U.S. play equally important roles in the Northeast. Emissions from Canadian forest fires can be transported even further south of Baltimore (Wotawa and Trainer, 2000; Sapkota et al., 2005). Local emissions of biomass burning are more important in the Southern Plains.

In the Southeast, simulated local fire emission has very limited contribution to the summertime OC/EC peak (Fig. 7). Although the OC/EC ratio in the GFED2 emission inventory is high at 16.3 for fire emissions, the model simulates a bigger role of SOA production in the Southeast and the Southern Plains. However, the biomass burning source in these regions may be severely underestimated because burning in the region is dominated by prescribed burning (e.g., Zeng et al., 2008), the signal of which in satellite measurements is weaker than wildfires. For example, the GFED biomass burning emissions in spring in the Southeast are much lower than a more detailed regional inventory described by Zeng et al. (2008). Furthermore, our analysis using MODIS monitored fire activities (Giglio et al., 2003) find a large number of summertime fire counts in these regions (Zeng et al., submitted for publication). We are currently estimating this potentially large summer burning source, but it is too complex to include in this work. What should be noted is that the large summer MODIS fire counts are only observed in 2002 during the period of 2000–2004 and that the GFED inventory may significantly underestimate the emissions of prescribed burning in the region in the summer of 2002.

Fine particle potassium (K) is another good indicator of biomass burning (e.g. Chow, 1995; Echalar et al., 1995). The K emissions from biomass burning generally have much larger temporal fluctuation than from soil and biofuel sources and largely contribute to the annual/seasonal variations (Park et al., 2007). We analyze the non-soil component of elemental K observations from IMPROVE network from 2000 to 2004 (Fig. S4, supplementary materials). Soil element K is estimated from measured Fe at the IMPROVE sites based on (K) = 0.6(Fe) (Malm et al., 1994). To target the data affected by biomass burning, we filtered out the data with EC concentrations $<$1 μg m^{-3}. Better correlations are found between that the observed OC/EC ratios and non-soil elemental K in the summers of 2002 and 2004 ($r > 0.6$), reflecting the larger impacts from biomass burning in these years. We note, however, that the correlation analysis is more sensitive to large fire events and less

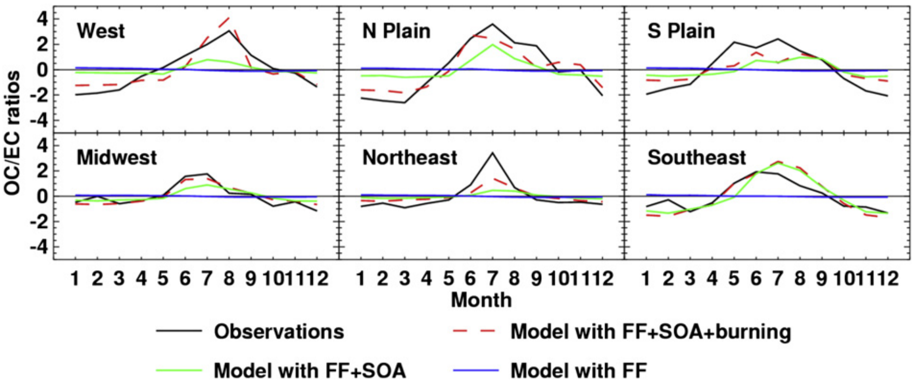

Fig. 6. Observed (black solid line) and GEOS-Chem simulated monthly OC/EC ratios with fossil fuel emissions (FF, blue solid line), fossil fuel emissions and SOA formation (green solid line), and all emissions (red dash line) in 2002 over the 6 U.S. regions (Fig. 3). The observed and simulated annual means of OC/EC ratios are removed respectively. Only the anomalies from yearly averages are shown.

sensitive to the geographical extension of fire impacts. Nevertheless, it provides additional observational evidence for large fire impacts in 2002.

4.2. *Biogenic SOA*

SOA contributions from biogenic emissions in summer 2002 are simulated in GEOS-Chem (Fig. 8). In-cloud SOA formation from biogenic emissions is discussed in the next section and is not included in the contribution of biogenic SOA in this paper. Since biogenic VOCs are emitted largely from terrestrial plant foliage (Guenther et al., 2006), they peak in the summer. The relative role of biogenic SOA is the largest in the Southeast and the smallest in the West. The Southeast is the only region where simulated biogenic SOA contribution is larger than biomass burning, although as indicated previously, the biomass burning contribution in the region for 2002 may have been underestimated in the model.

The quantitative estimate of the changes of biogenic SOA production in the 5 years is more complicated because of the large uncertainties in the emission inventories and particularly in the oxidation pathways and yields (Kroll and Seinfeld, 2008). We therefore explore its variations in two aspects, the emissions and the photochemical oxidation.

The biogenic emissions of isoprene and monoterpene in summer from 2000 to 2004 are estimated in GEOS-Chem (Fig. 9) using the MEGAN emission model (Guenther et al., 2006). The GEOS-4 meteorological dataset is used to drive the MEGAN model. Chemical and dynamic processes are turned off in this simulation. The emissions of these two species have similar variations. The largest biogenic emissions are found in the Southeast, and the smallest is in the Northern Plains. Among all the 5 years, emissions in 2000 are the largest in 4 out of 6 regions (Fig. 9). The estimated biogenic emissions in 2002 are moderate and not higher than the other years.

Ground level ozone is analyzed as an indicator of photochemical activity. Historic surface ozone data collected by EPA, state, local, and tribal air pollution control agencies from thousands of monitoring stations are available from the US EPA Air Quality System (http://www.epa.gov/ttn/airs/airsaqs/). Only the O_3 data from the 771 non-urban monitoring sites are analyzed. There are 63, 42, 96, 253, 187, and 130 non-urban sites in Region 1–6 (Fig. 3), respectively. Four regions (the West, Northern Plains, Southern Plains, and Northeast) have the highest daily 8-h O_3 maximum in summer 2002 (Fig. S5, supplementary materials). In the Midwest, ozone in 2002 is the 2nd highest after 2000. High ozone generally reflects a fast oxidation environment, which is more favorable for SOA production. Therefore, more biogenic SOA formation is possible in the four regions in 2002, although biomass burning could also contribute to the observed ozone peaks in 2002 over those regions. While in the Southeast with the most biogenic SOA contribution in the model, ozone concentration in 2002 is the 3rd highest among the five years.

4.3. *In-cloud SOA formation*

In-cloud SOA formation is studied through the aqueous uptakes of 2 major dicarbonyls, glyoxal and methylglyoxal, in GEOS-Chem model (Fig. 8). It gives an upper-limit estimate of cloud formed SOA since 90% of the uptake is assumed to occur in cloud (Fu et al., 2008). The estimated average surface concentration of SOA from the dicarbonyls in summer over contiguous U.S. is 0.15 $\mu g\ m^{-3}$. It accounts for ~60% of the (non-cloud) biogenic SOA and ~40% of the total estimated SOA by GEOS-Chem over the U.S. It has a similar spatial distribution pattern as biogenic SOA since ~80% of the dicarbonyl SOA is biogenic (the other fraction is anthropogenic) (Fu et al., 2008). After including in-cloud SOA, the SOA contribution is much larger than biomass burning in the Southeast and they are comparable over the Southern Plains, Midwest, and Northeast.

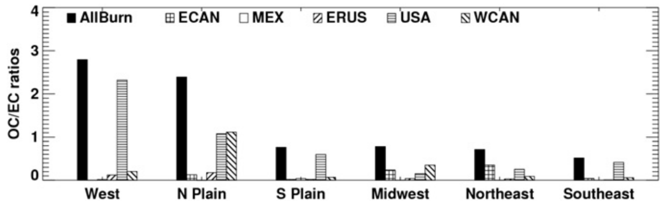

Fig. 7. Simulated mean contributions to OC/EC ratios over the 6 U.S. regions (Fig. 3) in summer (June, July, and August) 2002 by total biomass burning (AllBurn), and the biomass burning emissions from eastern Canada (ECAN), Mexico (MEX), eastern Russia (ERUS), the United States (USA), and western Canada (WCAN), respectively.

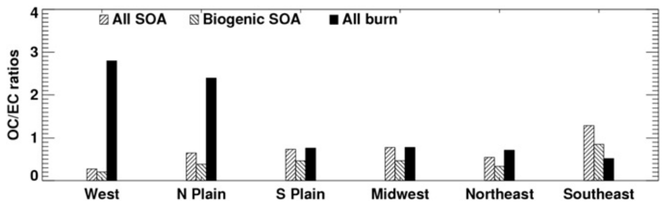

Fig. 8. Simulated mean contributions to OC/EC ratios over the 6 U.S. regions (Fig. 3) in summer (June, July, and August) 2002 by total (biogenic and in-cloud) SOA (denoted by "All SOA"), biogenic SOA, and the respective contributions of all biomass burning (denoted by "All burn").

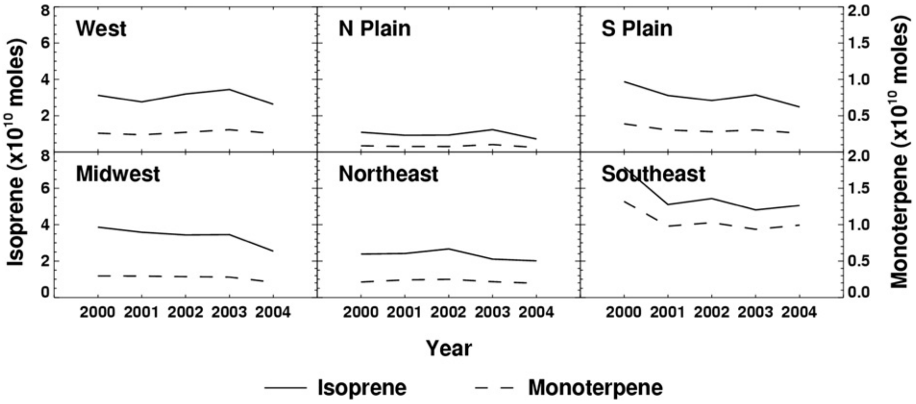

Fig. 9. Regional means of summertime biogenic emissions of isoprene and monoterpene during 2000–2004 in the 6 U.S. regions.

Since the biogenic emissions based on MEGAN model do not show a peak in 2002 (Fig. 9) and model estimated in-cloud SOA is largely from the biogenic VOCs (Fu et al., 2008), we analyze the meteorological conditions to assess qualitatively if in-cloud formation of SOA from carbonyl-containing organics (Blando and Turpin, 2000) could peak in 2002. The hypothesis here is that a large presence of cloud would facilitate the formation of SOA. The satellite observed daily cloud coverages in summer by MODIS (Level-3, MOD08, 1° × 1°) are compared from 2000 to 2004 (available at http://ladsweb.nascom.nasa.gov/data/search.html). No significant difference in-cloud coverage is found over the 6 regions in the 5 years. Cloud fractions in 2002 are generally at mid range among the 5 years (Fig. S6, supplementary materials), implying moderate in-cloud SOA producing environment in summer 2002. The only maximum in year 2002 appears in the Southern Plains, favorable for building 45% compared to 41% for 5-year mean. However, it is not so different from 2003 (44%) or 2004 (45%). Among the 6 regions, larger mean cloud fractions are found in the Northeast (53%) and Southeast (54%) in 2002, which are still lower than the largest cloud fractions (62%) observed in 2003. In fact, the OC/EC ratios in the Northeast and Southeast are relatively low in 2003 (Fig. 4).

4.4. *Inter-continental transport from Asia*

Inter-continental transport from Asia to the North America has impacts on some episodic enhancements of ground level trace gases and aerosols in the West (e.g., Jaffe et al., 1999). It is generally stronger in spring as a result of enhanced vertical transport in Asia and stronger westerlies over the Pacific. We apply the GEOS-Chem model to simulate the impact of the total emissions over East China (east of 105°E), where most of the pollutant emissions are located, in summer 2002. The average contributions of the eastern China emissions to the fine particulate OC and EC over U.S. are <0.1 μg m^{-3}. It translates to $<1\%$ change of OC/EC ratios over the U.S.

To further investigate its inter-annual variation, the westerlies (U wind) from the NCAR/NCEP Reanalysis Project (NNRP) at 300 mb are used to represent the magnitude of transpacific transport (http://dss.ucar.edu/datasets/ds090.0/). Other factors, such as emission strength and distribution, the updraft and downdraft of pollutants, can affect the overall impact of inter-continental transported air pollutants, we simplify the discussion of the meteorological effect by choosing one of the most important factors in this section. We compare the summertime mean westerlies over the northern Pacific Ocean (defined between 150°E–140°W and 30–50°N). The mean westerly speed in summer 2002 is 15.8 m s^{-1}, which is 2–3 m s^{-1} faster than the other 4 years. However, it is only half of the westerly speed in spring when the largest transpacific Asian outflow was observed (e.g., Nam et al., 2009). Model studies (Park et al., 2003; Heald et al., 2006) suggested a negligible contribution of Asian outflow to OC concentrations in the U.S. According to another field study (Lim et al., 2003), OC/EC ratio in Asian outflow shows a decreasing trend along the transport due to a longer residence time of EC. Although a model study (Heald et al., 2005) reported that GEOS-Chem failed to simulate enhanced OC concentrations in Asian plumes in the free troposphere, recent aircraft measurement (Dunlea et al., 2009) during INTEX-B campaign in later spring over the Eastern Pacific Ocean did not find higher OC concentrations in Asian plume in the free troposphere than at the surface. Fast aerosol scavenging in the boundary layer may reduce the impact of Asian outflow on the surface aerosol concentrations, although the OC/EC impact of Asian outflow is debatable over the western U.S. In summary, the contribution from Asian outflows to the surface OC in contiguous U.S. has large variations and does not seem to be a major reason for the nationwide increase of OC/EC ratios in 2002.

4.5. *Meteorological conditions over the U.S.*

Generally, dry meteorological conditions tend to lead to more ozone production, higher surface temperature (hence more biogenic emissions), and more SOA because of more active oxidizing environment, a longer OC lifetime (e.g., Lim et al., 2003), and more local burning. Therefore, dry conditions tend to promote higher OC/EC ratios. We analyze the temperature and precipitation data from the National Centers for Environmental Prediction (NCEP) Automated Data Processing (ADP) global surface observation dataset (http://dss.ucar.edu/datasets/ds464.0/). The mean temperature has <1 K variation in each region. And the temperature in 2002 is in the middle among the five years in all regions (not shown). However, 2002 is the year with the least rainy days in four regions, the West, Southern Plains, Midwest, and Northeast (Fig. S7, supplementary materials). The biggest variation is in the Northeast with 3 less rainy days per month in summer 2002. The Southeast has the 2nd least rainy days in 2002 after 2000. The relatively drier environment is a positive factor that enhances the photochemical processing time scale. It can increase secondary aerosol production with relatively abundant biogenic emissions in 2002. Even though less aerosol removal due to less precipitation is favorable for building up higher OC and EC concentrations, it may not be as effective for inducing higher OC/EC ratios if OC and EC have the same washout efficiencies.

5. Conclusions

A consistent nationwide peak of OC/EC ratio was found in the summer of 2002 during the 5-year period of 2000–2004. Contributions from several potential factors to this observed feature are investigated. Transpacific transport does not appear to be a significant factor. We assess the impacts of biomass burning using the global GEOS-Chem model. Over most regions, significant fire contributions are found. Canadian fire emissions have large impacts on the northern states close to Canada. The wildfires in Oregon and California in 2002 caused the OC/EC spikes in the western United States. Impacts of fire emissions over Russia and Mexico are relatively small during this season.

SOA formation is also found to make important contributions; the estimated impact of in-cloud SOA is significant compared to (non-cloud) biogenic SOA. Model estimated (biogenic and in-cloud) SOA contribution is much larger than biomass burning in the Southeast, and the two contributions are comparable in the Southern Plains, Midwest, and Northeast, although the MODIS fire count measurements from 2000 to 2004 showed large burnings only in the summer of 2002 in the Southeast. The dry meteorological condition in summer 2002 tends to promote higher OC/EC ratios by inducing larger fire emissions, SOA formation, and a longer OC lifetime.

Satellite observations indicate that biomass burning is highly variable (in spatial distribution as well as magnitude) in summer from year to year and could be an important factor that differentiates 2002 from the other 4 years, although quantitative modeling analysis is not conducted because of the large uncertainties in fire emission estimates (particularly with respect to prescribed burning in the South) and the simulations of SOA and inter-annual variations of meteorological fields. Specific measurements targeting fire emissions and SOA formation are needed in the U.S. monitoring networks to quantify their impacts and provide quantitative observational constraints on modeling simulations and analysis.

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2010.10.038.

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