Understanding the contributions of anthropogenic and biogenic sources to CO enhancements and outflow observed over North America and the western Atlantic Ocean by TES and MOPITT

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ABSTRACT

We investigate the effects of anthropogenic and biogenic sources on tropospheric CO enhancements and outflow over North America and the Atlantic during July–August 2006, the 3rd warmest summer on record. The analysis is performed using the 3D Regional chEmical trAnsport Model (REAM), satellite data from TES on the Aura satellite, MOPITT on the Terra satellite and surface monitor data from the SEARCH network. The satellite measurements of CO provide insight into the location of regional CO enhancements along with the ability to resolve vertical features. Satellite and surface monitor data are used to compare with REAM, illustrating model's ability to reproduce observed CO concentrations. The REAM model used in this study features CO emissions reduced by 50% from the 1999 EPA NEI and biogenic VOC emissions scaled by EPA-observed isoprene concentrations (20% reduction). The REAM simulations show large variations in surface CO, lower tropospheric CO and column CO, which are also observed by the surface observations and satellite data. Over the US, during July–August 2006, the model estimates monthly CO production from anthropogenic sources (5.3 and 5.1 Tg CO) is generally larger than biogenic sources (4.3 and 3.5 Tg CO). However, the model shows that for very warm days, biogenic sources produce as much CO as anthropogenic sources, a result of increased biogenic production due to warmer temperatures. The satellite data show CO outflow occurs along the East Coast of the US and Canada in July and is more broadly distributed over the Atlantic in August. REAM results show the longitudinally exported CO enhancements from anthropogenic sources (3.3 and 3.9 Tg CO) are larger than biogenic sources (2.8 and 2.7 Tg CO) along the eastern boundary of REAM for July–August 2006. We show that when compared with the impacts of both sources on increasing tropospheric CO exports, the relative impacts in August are greater than in July because of preferable outflow transport.

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1. Introduction

The combustion of fossil fuel, the oxidation of methane and anthropogenic and biogenic hydrocarbons, and biomass burning are the primary sources of CO (e.g., Logan et al., 1981; Holloway et al., 2000). CO is both an air pollutant and an important precursor of tropospheric O_3. CO has been designated as one of the EPA's six criteria pollutants that adversely affect human health and biological ecosystems. CO can indirectly influence climate by affecting the concentration of greenhouse gases such as methane and O_3 in the troposphere (Daniel and Solomon, 1998).

The emission rates for fossil-fuel CO from the 1999 US EPA National Emission Inventory (referred to as "EPA99") have been shown to be high by as much as 50%, based on a study using EPA estimates of on-road vehicle emissions (Parrish, 2006) and a study of measurements of CO in urban regions (Warneke et al., 2006). Model studies of tropospheric CO have shown that decreasing fossil-fuel emissions have led to better model/data comparisons. Other studies using the GEOS-Chem model have shown those reductions in fossil-fuel emissions on the order of 30% when compared to in situ surface data (Millet et al., 2006b) or by as much as 60% comparing to aircraft measurements during 2004 ICARTT campaign (Hudman et al., 2008). The studies showed that comparisons between GEOS-Chem lead to improved agreement with in situ ground data over Nova Scotia and aircraft data over the eastern US. While the results of the studies differ regarding the

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magnitude by which EPA99 overestimates fossil-fuel CO emissions, they are broadly consistent in the degree to which model/data comparisons are improved. In this study, we chose to reduce the fossil-fuel CO emissions from EPA99 by 50% as suggested in the previous studies by Parrish (2006) and Warneke et al. (2006), which is within the range of reductions suggested in the GEOS-Chem studies. In addition, we scale biogenic VOC emissions by using *in situ* isoprene concentrations measured at EPA AIRS stations.

Biogenic Volatile Organic Compound (VOC) emissions are temperature (T) and solar radiation dependent, which leads to a T and light dependence on CO sources (Guenther et al., 1995). High temperatures enhance biogenic VOC emissions (Guenther et al., 1995) and their oxidation processes, which lead to the production of atmospheric tracers such as CO in addition to formaldehyde (Atkinson and Avey, 1998). In particular, the oxidation process of short-lived biogenic VOCs affects the distribution of CO over the US (Hudman et al., 2008). Hudman et al. (2008) showed in their modeling study that CO production from the fast oxidation processes was larger than anthropogenic CO sources over the US during the ICARTT campaign. The surface temperature during the summer of 2006 over the US was the 3rd warmest on record (http://lwf.ncdc.noaa.gov/oa/climate/research/cag3/cag3.html). The meteorological conditions during this time confirm a significant number of consecutive warm, sunny days, which lead to enhanced isoprene emissions (e.g., Sharkey et al., 1999) and understanding the resulting CO concentrations is a reason for performing this study.

Major pathways for North American pollution outflow into the free troposphere include cloud convection (Pickering et al., 1988) and the warm conveyor belt (Cooper et al., 2002). The large enhanced CO in the upper troposphere is quickly exported into the Atlantic by westerly winds (Choi et al., 2008a). Pollution exported from North America (NA) has been shown to impact air quality and/or radiative budget over Chebogue Point, the eastern US, or the Atlantic Ocean (Millet et al., 2006b; Hudman et al., 2007; Choi et al., 2009). Li et al. (2005) used GEOS-Chem to show interannual variability in North American anthropogenic and biomass burning CO fluxes during the month of July (1998–2002). The strong CO fluxes were shown over the northeastern US, the Canadian Maritime Provinces, and Newfoundland. In this study, we characterize regional convective outflow and investigate how the differences in dynamics between July and August affect the outflow of anthropogenic and biogenic produced CO.

Satellite observations of CO provide an additional measurement constraint to study the contribution of anthropogenic and biogenic emissions to CO production over NA and the Atlantic. We examine enhancements in tropospheric CO using measurements from two satellite instruments, the Tropospheric Emission Spectrometer (TES) and the Measurements Of Pollution In The Troposphere (MOPITT). We use satellite observations to confirm the location of CO plumes in the model and then use the model to study the contribution of different sources of CO and its outflow over NA.

We first evaluate the ability of REAM to simulate summertime temperature and CO at the surface by using ground-based measurements from the Southeastern Aerosol Research and Characterization Study (SEARCH) network for July–August 2006. We also estimate the CO sources over the US and examine the contributions of anthropogenic and biogenic sources calculated by REAM to the large CO enhancements observed over NA and the Atlantic by MOPITT and TES. Using REAM simulations, we investigate which sources are the primary driver for variations in CO enhancements on both a daily and monthly basis. Using satellite data to test the location and amount of CO from REAM, we examine the contributions of both sources to the CO exports from NA, and also characterize monthly changes in the CO outflow patterns from July to August.

2. Measurements

2.1. SEARCH network

The ground data test the model's ability to simulate surface CO and allow for identification of time periods of enhanced CO production. The SEARCH network provides hourly CO data from eight surface sites in the southeastern US (Hansen et al., 2003) with a detection limit of 10 ppbv (Choi et al., 2008a). CO observations at EPA monitoring sites are not useful for this study because of their high detection limits (0.5 ppmv) (Choi et al., 2008a). For our analysis, among eight sites, we use observations from four rural and suburban sites (Fig. 1): Oak Grove in Mississippi (OAK, 89°W, 32°N), Outlying Landing Field #8 in Florida (OLF, 87°W, 30°N), Yorkville in Georgia (YRK, 85°W, 34°N), and Centerville in Alabama (CTR, 87°W, 33°N). The focus on the southeastern US is due to large biogenic sources in the region.

2.2. TES and MOPITT

TES, a high-resolution Fourier transform spectrometer (Beer et al., 2001) launched onboard the Aura satellite, provides global, vertically-resolved measurements of CO. MOPITT is an instrument onboard the Terra satellite (Drummond and Mand, 1996) which measures CO on the global scale. The Aura satellite passes over the equator at approximately 01:40 and 13:40 h local time (LT) while the Terra satellite crosses the equator at 10:45 AM and 22:45 PM local time. The nadir footprint of TES and MOPITT are 5×8 km and 22×22 km. For July–August 2006, TES made special observations over NA, providing additional data over its routine observations.

Due to the inability of passive remote sensing (TES and MOPITT) to obtain measurements with the same vertical resolution as the model, the simulation results need to be processed with a vertical resolution and sensitivity representative of the satellite measurements using the averaging kernel (AK) from the satellite retrievals (Deeter et al., 2003; Emmons et al., 2004; Luo et al., 2007). We take the differing sensitivities of the satellite measurements into account when doing comparisons with the model.

The TES data are version 3, and only CO retrievals passing quality flag tests (Osterman et al., 2008) are used in the analysis. The MOPITT CO columns are version 3 data and only MOPITT retrievals with a contribution from the a priori profile of <50% are used in the analysis. MOPITT data with a mixing ratio <40 ppbv at 500 hPa, are filtered out of the analysis, as suggested in the MOPITT L3 Quality Statement (http://web.eos.ucar.edu/mopitt/). Consistency in the use of the satellite data is maintained by excluding TES profiles meeting the same criteria.

TES and MOPITT CO have been compared to each other (Luo et al., 2007; Ho et al., 2009) and in general see similar spatial and temporal CO patterns. TES tends to be biased slightly low when compared to MOPITT (Ho et al., 2009). TES CO profiles near Houston agree with the DACOM study within 10% in the lower and middle troposphere with TES being lower in the middle troposphere for March 2006 (Luo et al., 2007). MOPITT tends to be biased high in the lower troposphere (7–14% at 700 hPa) and upper troposphere (3% at 350 hPa) over NA when compared to *in situ* aircraft observations from the MOZAIC program and the COBRA study (Emmons et al., 2007). The use of TES and MOPITT data allows us to compare REAM to satellite data both in the local morning (MOPITT) and afternoon (TES).

3. Model

Previous studies of chemical transport over NA, Choi et al. (2005, 2008a, 2008b, 2009) have been performed using the REAM model.
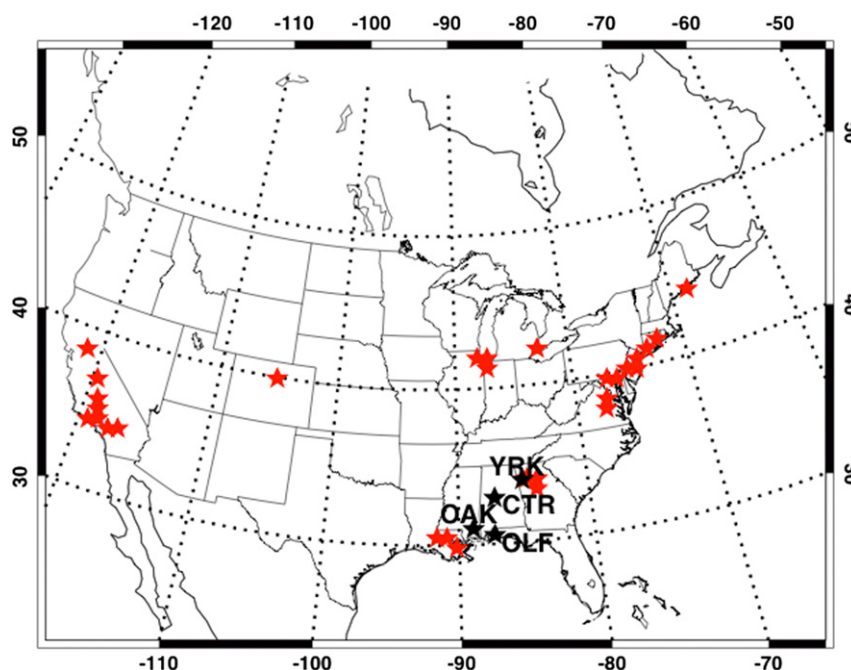
Fig. 1. The locations of 4 SEARCH rural and suburban sites measuring CO (black colored): Oak Grove site in Mississippi (OAK, 89°W, 32°N), the Outlying Landing Field #8 site in Florida (OLF, 87°W, 30°N), the Yorkville site in Georgia (YRK, 85°W, 34°N), and the Centerville site in Alabama (CTR, 87°W, 33°N), and 29 EPA AIRS sites measuring isoprene (red colored).

We use a similar model setup in this analysis, except for the changes in fossil-fuel CO emissions and biogenic VOC emissions. We use the MM5 dynamical model to provide the meteorological fields for REAM. The REAM model has 70 km horizontal resolution with 23 vertical layers reaching to 10 hPa. GEOS-Chem (version 7.2) results (Bey et al., 2001) are used to specify boundary conditions for chemical tracers. The regional model simulations were carried out in the last two weeks of June (for spin up), and used to determine the initial chemical conditions for the July–August simulation.

Emission algorithms for vegetation and soil are adopted from GEOS-Chem (Bey et al., 2001). Isoprene and monoterpene emissions are based on the GEIA inventory (Guenther et al., 1995) and the modifications described by Bey et al. (2001). The modified GEIA inventory in GEOS-Chem, which was adopted by REAM, has been evaluated using formaldehyde (Palmer et al., 2003; Millet et al., 2006a) and CO observations (Millet et al., 2006b; Hudman et al., 2008). The dependence of HCHO yields on NO_x concentration is described by Palmer et al. (2003) and Millet et al. (2006a), and the CO yields from VOC oxidation are calculated in REAM in a manner similar to those in GEOS-Chem (Duncan et al., 2007; Hudman et al., 2008). We use fire emissions from the Global Fire Emissions Database (GFED) version 2 (Van der Werf et al., 2006) sampled to an eight daytime time step using MODIS fire hot spots.

As mentioned previously, we reduce fossil-fuel CO emissions by 50% over the US from EPA99 (Parrish, 2006; Warneke et al., 2006) while we keep unchanged NMHC emissions inventory, which results in anthropogenic CO emissions (5.3 and 5.1 Tg CO) for July–August 2006 (Table 1). Among these, 1.3 and 1.1 Tg CO tracers are produced by the oxidation of anthropogenic VOCs over the US (Table 1). The anthropogenic source of CO in this study (referred to as "ANTS") is from fossil-fuel CO emissions and the oxidation of anthropogenic VOCs.

There is a sparse set of EPA AIRS monitoring sites measuring isoprene concentrations (Fig. 1) making it difficult to scale the biogenic emissions at each point or through interpolation for each grid. Thus, the emissions are evenly scaled using monthly isoprene

concentrations from the monitors during the daytime (12:00–18:00 PM) with corresponding model values for July 2006. We apply a uniform 20% reduction of biogenic emissions over the continent. The resulting monthly-averaged REAM isoprene daytime concentrations are well correlated with corresponding observed concentrations ($R = 0.83$) (Fig. 2). The biogenic source of CO in this work (referred to as "BIOS") comes from the oxidation of biogenic VOCs such as isoprene, monoterpene and alkenes. The model calculations suggest that BIOS produces 4.3 Tg CO in July and 3.5 Tg CO in August. These totals include 3.4 and 3.0 Tg CO from isoprene and 0.9 and 0.5 Tg CO from monoterpene and alkenes. CO sources affecting regional variations over the US are summarized in Table 1.

The CO emissions from wildfires over the US, primarily from the West, are roughly 0.6 Tg CO mon^{-1} (Table 1). Over Canada and northern Mexico, the emissions inventories of CO were prepared by the Sparse Matrix Operator Kernel Emissions (SMOKE) model by using VISTAS 2002 Emissions Inventory (Kaynak et al., 2008).

Table 1
Regional CO sources (Tg CO)[a] over the US for July–August 2006.

Source	July	August
Fossil fuel	4.0[b]	4.0[b]
Oxidation of anthropogenic VOCs	1.3	1.1
Oxidation of isoprene	3.4[c]	3.0[c]
Oxidation of monoterpene and alkenes	0.9[c]	0.5[c]
Biomass burning	0.6[d]	0.6[d]
Total	10.2	9.2

[a] The REAM model considers tropospheric CO from all other sources (including the oxidation of CH_4, acetone and methanol) and from boundary conditions, but Table 1 includes CO sources affecting regional CO variations.

[b] 50% fossil-fuel CO emissions from EPA99 are reduced, which is based on the on-road emissions and urban observation studies (Parrish, 2006; Warneke et al., 2006).

[c] Biogenic VOC emissions are uniformly reduced by 20%. Details are in the text. About 30% uncertainty of CO production from the oxidation of biogenic VOCs was estimated from that estimated by Hudman et al. (2008).

[d] Biomass burning CO emissions are from the GFED emissions inventory (Van der Werf et al., 2006).
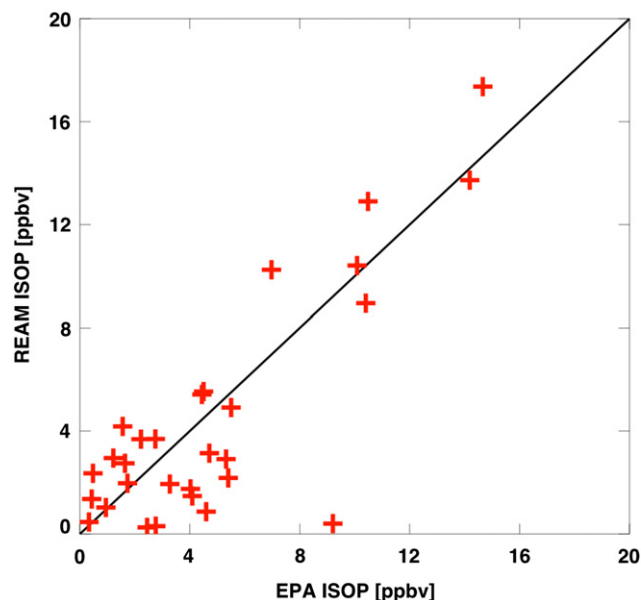
Fig. 2. The REAM-simulated (adjusted) and EPA sites-observed monthly mean isoprene concentrations for afternoon (12−18 PM) for July 2006. A correlation coefficient is 0.83. Biogenic VOC emissions in REAM are uniformly reduced by 20% based on the comparison of REAM-simulated and corresponding *in situ*-observed isoprene concentrations.

Choi et al. (2008a) provide more detail on the REAM setup and methodology for comparisons with surface, ozonesonde, aircraft, and satellite measurements.

In addition to the standard REAM run described above, the model is used in two "sensitivity" modes. The first is with ANTS turned off while all other sources are unchanged. The second is similar with only BIOS turned off. Turning off the different sources and examining the changes in the total CO concentration allow an analysis of the relative importance of each of these sources to the spatial distribution of CO and provide understanding of the flux of CO exports.

4. Results

The use of CO and temperature data from ground monitors in the Southeastern US provides information on the ability of REAM to simulate CO at the surface. The surface data also helps identify time periods with high CO concentrations for July−August 2006. The satellite data provide information on a continental scale for the distribution of CO, which can be used in conjunction with REAM to examine the transport of plumes and the relative importance of different sources.

4.1. Model evaluation using surface CO and temperature

We examine CO concentrations at the SEARCH sites, sampling both rural and suburban air. The data show that these sites have broadly similar temporal patterns (Fig. 3a) mainly due to the meteorology of the region. In order to illustrate the effects of meteorological changes on CO, we show the observed temperature measured at the sites over July and August (Fig. 3b). Temperature variations are a key driver for changes in biogenic VOC emissions, with higher temperatures leading to more emissions. The corresponding REAM model results show good agreement with the observations for both surface temperature and CO concentrations (Fig. 3a, b). Compared with OAK, OLF, and CTR, the larger multiday variations observed at YRK (Fig. 3a) are likely due to larger meteorological variations there (Fig. 3b).
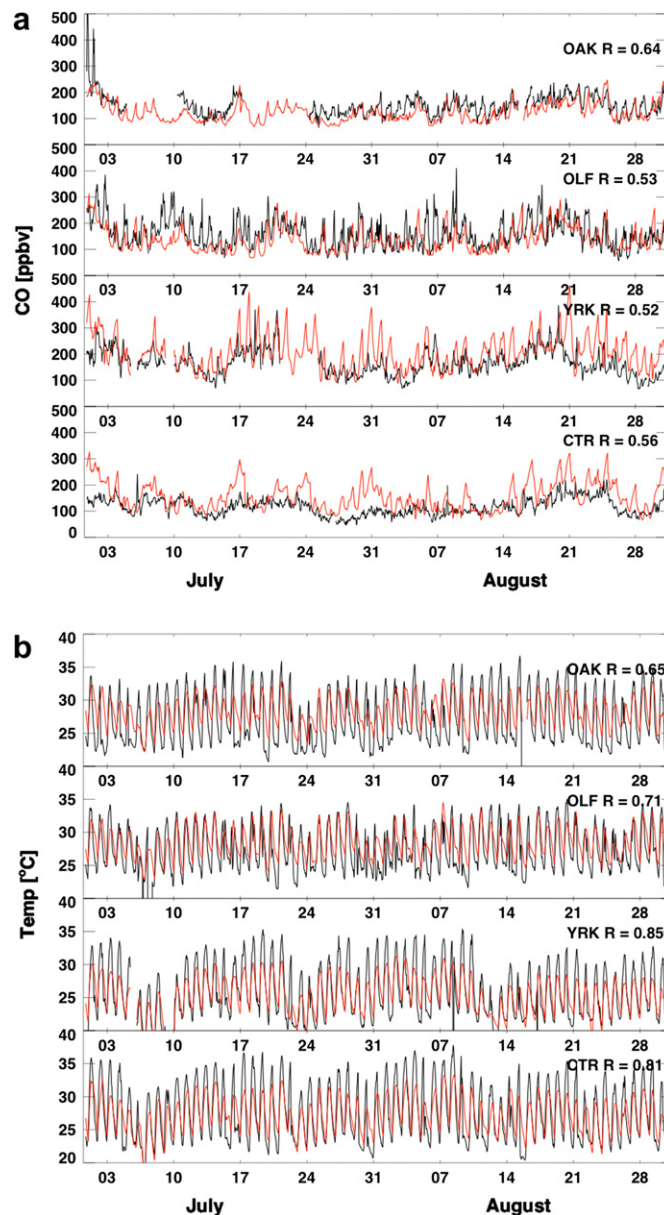

Fig. 3. (a) Observed and simulated hourly CO at OAK, OLR, YRK, and CTR (Fig. 1). Black lines represent the SEARCH measurements and red lines represent REAM results. (b) Observed and simulated hourly temperatures at OAK, OLF, YRK, and CTR (Fig. 1). Black lines represent the SEARCH measurements and red lines represent the MM5 model results.

The correlation coefficients in a scatter plot between the REAM calculation and SEARCH measurements of CO are within the range of 0.52−0.64. This comparison is slightly better than our previous springtime study (Choi et al., 2008a), in which the correlation coefficients ranged from 0.48 to 0.63. Whereas the REAM simulation overestimates observed CO concentrations at YRK and CTR by 23% and 35%, respectively, REAM underestimates CO concentrations at two other sites, OAK and OLF, by 14% and 12%, respectively, for reasons that remain unclear. It is likely that REAM has a low correlation coefficient at YRK because YRK is close to Atlanta and the model might not accurately separate YRK from the urban site.

The time series of surface data can also be used as a means of determining periods of elevated CO for July−August 2006. Based on the SEARCH data, we pick four periods of elevated CO: July 16−18,

July 19–21, August 16–18, and August 19–21 (Fig. 3a). We discuss an analysis of these periods of high CO in Section 4.2.1 and 4.2.2.

4.2. Contributions of both sources to tropospheric CO

The SEARCH measurements do not provide the horizontal and/or vertical coverage necessary to constrain the spatial distribution of CO. The satellite data from MOPITT and TES provide data for examining the vertical and spatial distribution of CO over NA and the Atlantic. We first compare REAM simulations of CO concentrations with those from MOPITT and TES during hot summer days, in order to examine the relative importance of BIOS and ANTS to the amount of tropospheric CO observed under those conditions. Second, data from two TES special observations are used to evaluate the REAM CO profiles. Third, the ability of REAM to simulate monthly mean MOPITT and TES observations
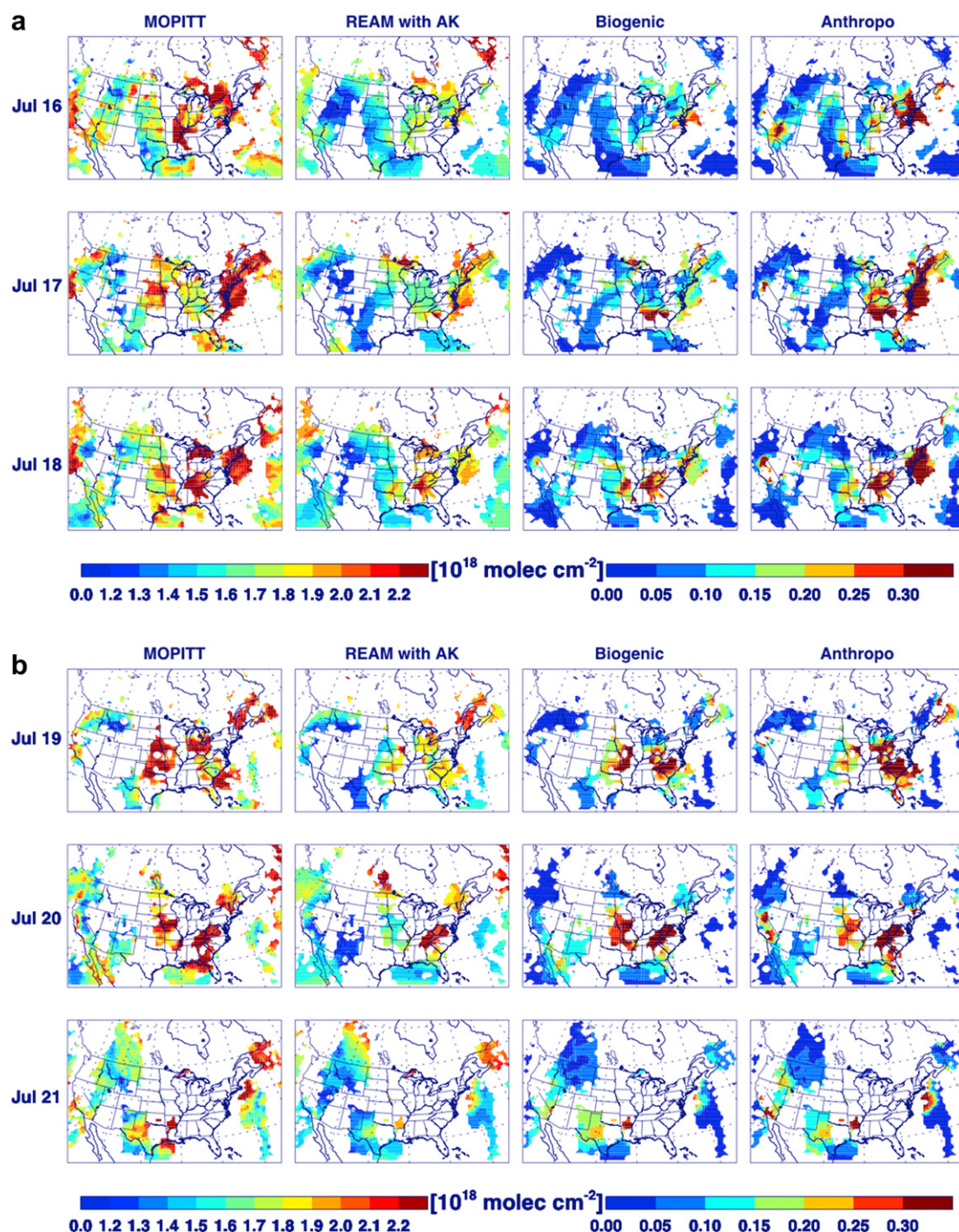

Fig. 4. (a) Daily mean CO columns for July 16–18, from MOPITT CO (the first column), REAM CO with *AK* (the second), and the contribution of BIOS (the third) or ANTS (the fourth) to CO columns. Only measurements with the a priori fraction of <50% and CO concentration at 500 hPa >40 ppbv are used. The corresponding model-simulated CO columns are sampled at the same time and locations as the MOPITT measurements. (b) Daily mean CO columns for July 19–21, from MOPITT CO (the first column), REAM CO with *AK* (the second), and the contribution of BIOS (the third) or ANTS (the fourth) to CO columns. Only measurements with the a priori fraction of <50% and CO concentration at 500 hPa >40 ppbv are used. The corresponding model-simulated CO columns are sampled at the same time and locations as the MOPITT measurements.
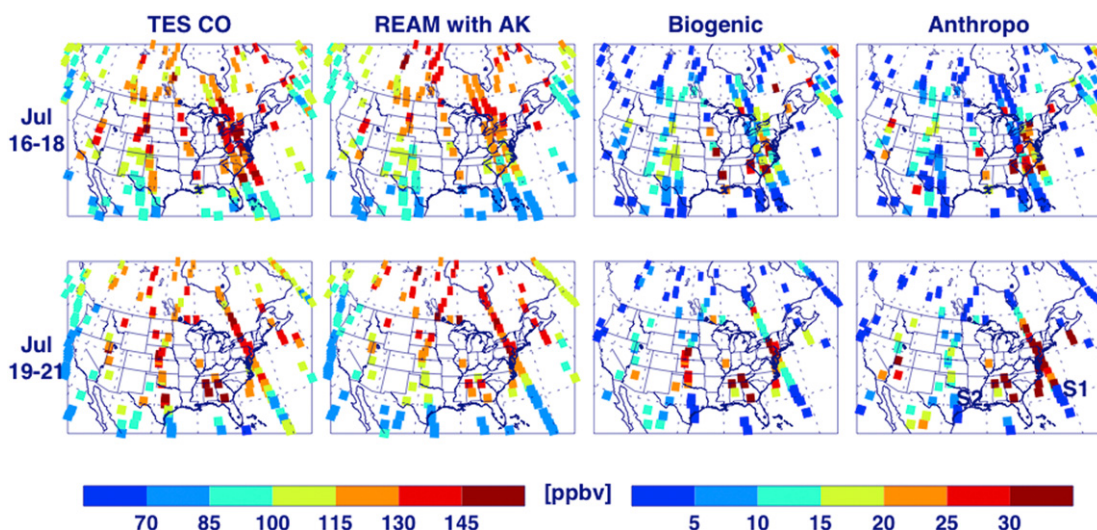
Fig. 5. Mean CO concentrations at 800 hPa for July 16–18 and July 19–21, from TES (the first column), REAM with *AK* (the second), and the contribution of BIOS (the third) or ANTS (the fourth) to 800 hPa CO. Only TES CO data with a degree of freedom of >1.0 and CO concentration at 500 hPa >40 ppbv are used. The corresponding model results are sampled at the same time and locations as the TES measurements.

allows for an understanding of contributions of both sources to the transport of CO.

4.2.1. High CO periods from MOPITT

Among the periods of high CO seen in SEARCH data, two of the periods, July 16–18 and July 19–21, illustrate the increased relative importance of BIOS over ANTS to observed tropospheric CO enhancements seen at the Yorkville site (Fig. 3a). We initially focus our analysis of the satellite data on these time periods.

We first test the model CO fields against MOPITT data. MOPITT provides vertical information about CO with excellent spatial coverage, but for this study we use a tropospheric column to check the geographic distribution of CO by REAM. Compared with MOPITT, the REAM (adjusted to MOPITT sensitivity, referred to as

with *AK*) CO columns are lower by 11.3–11.9% and 9.3–12.5% over NA and the Atlantic (Fig. 4a, b). Generally, when compared with MOPITT, REAM CO columns are low over the region. This tendency for the model to make the July/August mean values of the CO column lower is also seen in comparisons to monthly mean MOPITT observations (Fig. 7). This could be due to the high bias of the MOPITT CO over NA (Emmons et al., 2007) and possible underestimate of CO emissions by the 50% reduction in fossil-fuel CO emissions from EPA99 used in REAM. Even though the REAM simulations are less than the MOPITT CO observations, REAM accurately represents the peak of MOPITT CO columns over the southeastern US and some regions of the Atlantic (Fig. 4a, b).

Compared with REAM simulations (no adjustment to satellite sensitivity, referred to as without *AK*), the sensitivity tests indicate
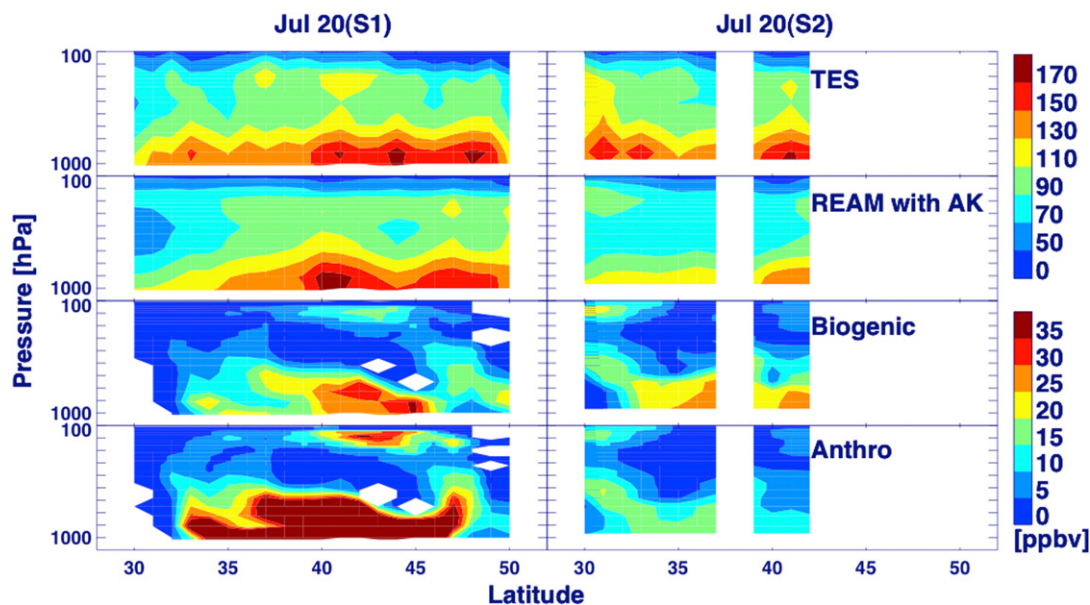

Fig. 6. A comparison of CO vertical profiles from TES and REAM using two special observations performed on July 20. The first row represents TES CO vertical profile. The second represents corresponding REAM-simulated CO vertical profile with *AK*, and the third and fourth rows represent increased CO concentration by BIOS or ANTS. Only TES data of degrees of freedom >1.0 and CO concentration at 500 hPa >40 ppbv are used. The S1 crosses over the northeastern US and the Atlantic and S2 crosses over the Midwestern US and Texas (Fig. 5).
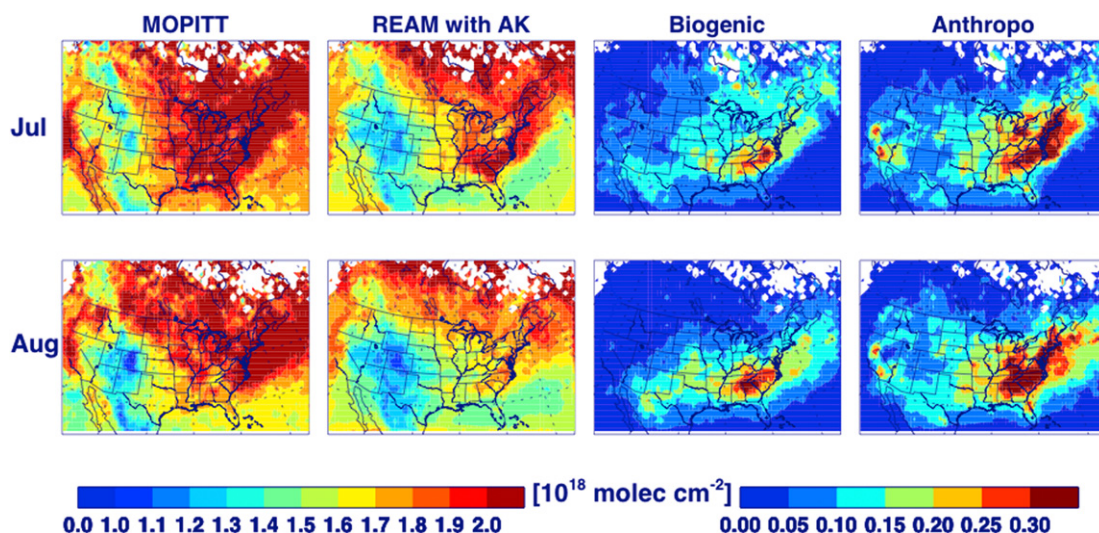
Fig. 7. Monthly mean CO columns for July–August 2006, from MOPITT CO (the first column), REAM CO with *AK* (the second), and the contribution of BIOS (the third) or ANTS (the fourth) to CO columns. Only measurements with the a priori fraction of <50% and CO concentration at 500 hPa >40 ppbv are used. The corresponding model-simulated CO columns are sampled at the same time and locations as the MOPITT measurements.

that the contribution of ANTS to CO column enhancements of the total (between 6.3% and 8.9%) is larger than BIOS (4.5–5.8%) for July 16–18 over the region (Fig. 4a). The model results also show ANTS to be more important than BIOS for other periods, August 16–18 and August 19–21 (ANTS: 6.1–7.7% and BIOS: 4.1–5.9%, not shown). However, for July 19–21, days which saw higher surface temperatures than the other dates in July–August 2006 (Fig. 3b), the contribution of BIOS to total columns (5.7–7.0%) are comparable to ANTS (5.9–8.1%, Fig. 4b). On July 20, the contribution of BIOS to the CO column (6.3%) is equal to ANTS (Fig. 4b).

4.2.2. High CO periods from TES

Even though the geographic coverage of TES is not as complete as that of MOPITT, we use TES measurements in the lower troposphere to examine the model CO because MOPITT CO is shown to have a high bias in the lower troposphere over NA (Emmons et al., 2007) as described in the Section 2.2. We first examine CO comparisons between the REAM (with *AK*) CO values and the TES CO

concentrations at 800 hPa. We do this in the lower troposphere because more than half of photochemical CO production by short-lived hydrocarbon takes place between the surface and 800 hPa (Pfister et al., 2008). TES measurement sensitivity to CO often peaks in the lower troposphere (Luo et al., 2007).

The REAM CO values are less than corresponding TES measurements in the lower troposphere over the eastern US (polluted region, Figs. 5 and 8). The low values of the REAM simulations are possibly due to the large reduction of anthropogenic CO emissions. The REAM model also underestimates the lower tropospheric CO over the Gulf of Mexico and over the Atlantic below latitude 30°N (Figs. 5 and 8). This is likely due to model boundary conditions in the lower troposphere, particularly along the eastern boundary over low latitude region (Fig. 8). This will be discussed more in Section 4.2.4 and 4.3.

The REAM CO concentrations are less than TES CO in the lower troposphere by 6.5 and 3.8%, respectively, over the region with relatively high correlation coefficients ($R = 0.66$ and 0.75) for July
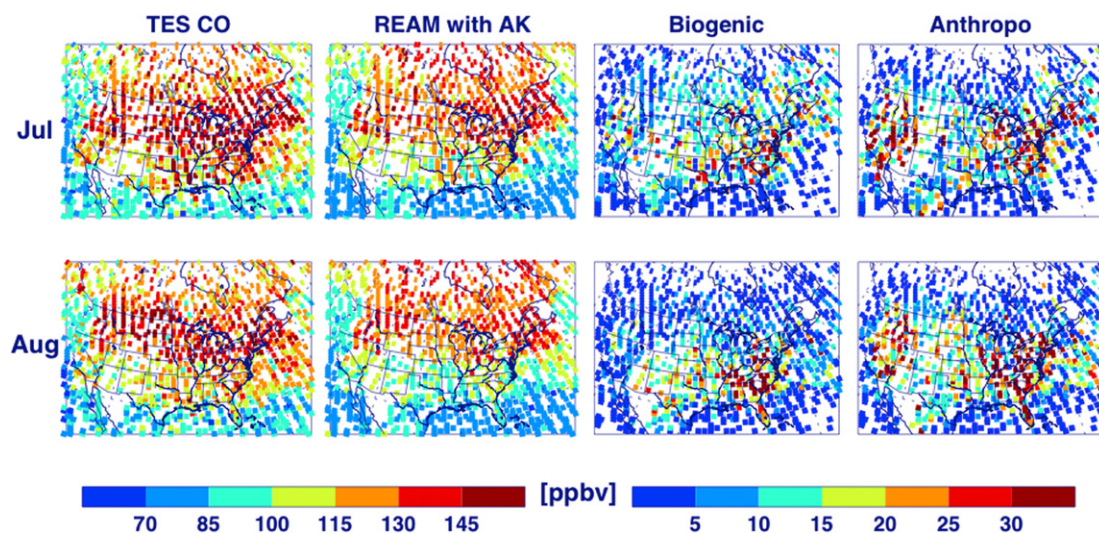

Fig. 8. Monthly mean CO at 800 hPa for July–August 2006, from TES (the first column), REAM with *AK* (the second), and the contribution of BIOS (the third) or ANTS (the fourth) to 800 hPa CO. Only TES CO data with a degree of freedom of >1.0 and CO concentration at 500 hPa >40 ppbv are used. The corresponding model results are sampled at the same time and locations as the TES measurements.

16–18 and 19–21 (Fig. 5). The model CO is also lower than the 800 hPa TES CO by 5.7% and 4.8% with correlation coefficients ($R = 0.72$ and 0.67) for August 16–18 and 19–21 (not shown). However, in general, the elevated values of CO observed by TES, particularly over the contiguous US, are also seen in the REAM simulations (Fig. 5).

The regions of high CO caused by ANTS and BIOS over the eastern US are sometimes indistinguishable at 800 hPa due to the long lifetime of CO (~ 2 months) (Fig. 5). Compared with the REAM simulation (without AK), BIOS contributes 8.9 and 8.1% of the total at 800 hPa over the region for July 16–18 and 19–21. The ANTS contribution to the tropospheric CO at 800 hPa is 8.0 and 9.4%. Over the same region, BIOS impact CO concentrations at 800 hPa by 6.3 and 7.1% and ANTS affects the CO by 9.3 and 9.5% for August 16–18 and 19–21 (not shown). The contribution of ANTS to the lower tropospheric CO (at 800 hPa) is larger than BIOS except for July 16–18. The contributions to CO concentrations at 800 hPa from ANTS and BIOS over the US and the neighboring Atlantic are between 20 and 70 ppbv (Fig. 5). This is larger than mean uncertainties of the TES CO retrievals (<20 ppbv), indicating that CO enhancements by both sources could be inferred from the TES measurements.

4.2.3. Contributions of both sources to CO vertical profiles

We also look at the vertical distribution of CO (to 100 hPa) from two TES special observations on July 20 (S1: over the northeastern US and the Atlantic, S2: over the Midwestern of the US and Texas, the second row of Fig. 5). The corresponding REAM simulations on July 20 are analyzed to determine the vertical impact of both BIOS and ANTS on tropospheric CO (Fig. 6). The vertical distribution from TES in the lower troposphere reasonably matches that from REAM (with AK, Fig. 6).

Over low latitude regions, the low values of CO from REAM, when compared to TES observations (S1 and S2), are apparent in Fig. 6. CO enhancements in the free troposphere (Fig. 6), seen in the TES retrievals and REAM simulations are primarily due to the lower tropospheric CO enhancements from BIOS and ANTS followed by lifting from convective activities, a process described previously (Choi et al., 2005, 2008a).

Compared with the tropospheric CO from the REAM simulation (without AK), BIOS contributes 4.9 and 7.8% to the total CO and ANTS contributes 9.9 and 6.3% along the tracks of the two special observations (S1 and S2). The contribution of BIOS to tropospheric CO is smaller than ANTS for the Atlantic/Northeastern US special observation (S1) but larger than ANTS for the Midwestern US special observation (S2) (Fig. 6). The differences between the standard simulation and two sensitivity tests with BIOS or ANTS turned off show the large contributions of two sources to tropospheric CO (<70 ppbv) in the lower (below 700 hPa) and upper troposphere (200–300 hPa), particularly during the first special observation (S1).

4.2.4. Monthly-averaged MOPITT and TES CO observations

The contributions of BIOS and ANTS to tropospheric CO over NA and the Atlantic are estimated on a monthly basis. Fig. 7 shows monthly-averaged MOPITT-observed and REAM CO columns and model derived CO column enhancements attributed to each source for July–August 2006. A comparison between REAM (with AK) and MOPITT CO columns shows good correlation ($R = 0.75$ and 0.76) with mean biases (8.7 and 7.9%). Over only the contiguous US, the correlation coefficients increase to 0.90 and 0.91 for July and August 2006.

Over NA and the Atlantic, a total CO column (without AK) comparison of the standard simulation and sensitivity tests with either BIOS or ANTS turned off in July yields mean differences of 4.5

Table 2
Relative contribution of anthropogenic and biogenic sources to CO in the lower troposphere (800 hPa) and total CO columns over North America for July–August 2006.

	Anthropogenic		Biogenic	
Month	July	August	July	August
800 hPa	8.3%	9.3%	7.4%	6.4%
CO column	5.1%	5.7%	4.5%	4.1%

and 5.1% (Table 2). The comparison of the standard simulation and sensitivity tests (either BIOS or ANTS turned off) in August produces mean difference of 4.1 and 5.7% (Table 2). This suggests that ANTS is a stronger contributor to the CO column enhancements than BIOS over the region. The impact of ANTS on CO column enhancements is larger than BIOS by 13.3 and 39.0% for July and August 2006.

The TES measurements are useful for quantifying CO in the lower troposphere. Fig. 8 is similar to Fig. 7, but with TES measurements at 800 hPa compared with REAM results. We find that the REAM CO (with AK) and TES CO are strongly correlated ($R = 0.75$ and 0.74). Compared with 800 hPa TES CO data, the REAM simulations are lower by 8.3% in July and 7.5% in August (Fig. 8). This low bias in the REAM results compared to TES was discussed previously (Section 4.2.2).

Another trend is that the effects of ANTS on CO enhancements in the lower troposphere are larger than BIOS (Fig. 8). In a comparison of 800 hPa CO from the REAM simulation (without AK) and sensitivity tests, the mean contribution of ANTS for July–August 2006 (8.3 and 9.3% of the total CO) is larger than BIOS (7.4 and 6.4%), which indicates that the contributions of ANTS are larger by 12.2 and 45.3% than BIOS (Table 2).

4.3. Contributions of both sources to altitudinal CO fluxes

Over the broad geographic region looked at for this study, ANTS dominate CO production. The resulting CO can then be transported off NA. From the MOPITT and TES measurements (Figs. 7 and 8), we see that CO tracers flow out along the east coast of the US and Canada in July and they are more broadly spaced out into the Atlantic in August. In order to characterize the pattern change of CO export from NA, CO fluxes through eastern model boundaries are estimated using REAM. We focus on longitudinal flux change as a function of latitude and altitude as in a previous study (Choi et al., 2008a). The export fluxes of CO (9.0–9.4 Gmol d^{-1}) from NA in the boundary layer in this study (Table 3) are significantly smaller than those seen previously (Choi et al., 2008a), mainly due to the reduction of ANTS in this study. The vertically (up to 13.5 km) CO exports over the latitude range of 20–55°N are also calculated using REAM for July–August 2006 (Fig. 9). The west to east CO transport appear north of 33°N in July and north of 27°N in August, which reflect the difference in wind fields in the troposphere between July and August.

The results from the standard simulation and sensitivity tests (BIOS or ANTS source turned off) indicate that the contribution of ANTS to exported CO flux is larger than BIOS (Fig. 9) for July–August 2006. These results also indicate that BIOS and ANTS enhance longitudinal CO exports from NA by 2.8 and 3.3 Tg CO for July and

Table 3
Import and export fluxes of CO (in Gmol d^{-1}) in the boundary layer (<2.5 km) over North America (20–62°N) for July–August 2006.

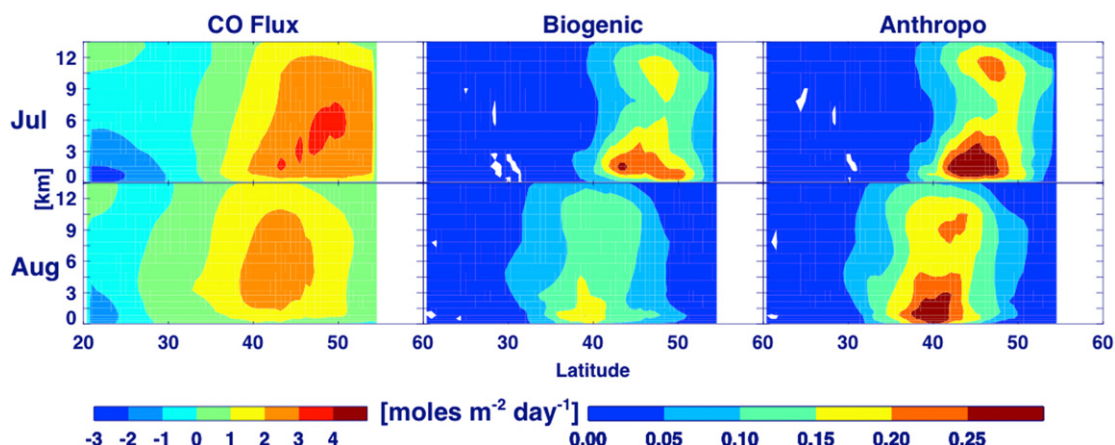|	Import		Export	
Month	July	August	July	August
<2.5 km	2.1	0.8	9.4	9.0

Fig. 9. Monthly mean CO exports in the eastern boundary (Fig. 1) for July–August 2006 are shown (the first column), and increased CO exports by BIOS (the second) or ANTS (the third). Positive values indicate flux from West to East.

2.7 and 3.9 Tg CO for August along the eastern boundary. The enhanced CO exports by ANTS are larger than BIOS by 18 and 44% for July and August. Despite the large reduction of BIOS in August (Table 1), the amount of enhanced export by BIOS in August is similar to that in July. This is likely due to preferable wind fields (westerlies) for longitudinal outflow in August (the first column of Fig. 9). In the upper troposphere, the peaks of enhanced CO export caused by both sources are shown at about 10.5 and 8 km for July and August (Fig. 9). The altitude of maximum export in the upper troposphere in August is lower than in July, likely because cloud top heights in July are greater than in August over NA, which is supported by outgoing longwave radiation data (http://www.cdc.noaa.gov/data/).

5. Conclusions and discussion

This study has analyzed the sources and distribution of tropospheric CO using *in situ* surface CO measurements from the SEARCH network, CO columns estimated from MOPITT and lower/upper tropospheric CO data from TES for July–August 2006, as well as CO fields from the REAM model. The REAM model uses a 50% reduction in fossil-fuel CO emissions (4.0 Tg CO) from EPA99 over the US (Parrish, 2006; Warneke et al., 2006) and biogenic VOC emissions (4.3 and 3.5 Tg CO for July and August) scaled by EPA AIRS measured isoprene concentrations. Using these emissions, the REAM model reasonably simulates the *in situ* SEARCH surface CO ($R = 0.52-0.64$), the MOPITT-observed CO column ($R = 0.75-0.76$), and TES lower tropospheric CO ($R = 0.74-0.75$) with high correlation coefficients in the model/data comparisons.

The 50% reduction of fossil-fuel CO emissions from EPA99 is likely to be too much, based on the low bias over the eastern US (source regions) in the comparison of simulated lower tropospheric CO with TES (Fig. 8). Furthermore, a possible change in anthropogenic VOC emissions over the US since 2000 may affect CO and OH concentrations, and in turn, impact CO production by BIOS and ANTS. Thus, an inverse modeling study needs to be carefully performed to quantify the amount of fossil-fuel CO emissions. Regardless of potential errors in emission estimates, the horizontal and vertical structure of CO, and the characterization of the outflow from NA provide new insights into tropospheric pollution development and transport.

On a monthly basis, the REAM model is also used to simulate observations of CO columns from MOPITT over the eastern US and the Atlantic. Results of the simulations show that regional BIOS and ANTS are the cause of enhanced CO column values ($\geq 2.0 \times 10^{17}$

molecules cm^{-2}). The simulated CO enhancements are larger than MOPITT retrieval uncertainties of about 2.0×10^{17} molecules cm^{-2} (Choi et al., 2005). REAM is also used to simulate TES observations of lower tropospheric CO, and the results show that BIOS and ANTS increase CO concentrations, by amounts that are comparable to or larger than TES retrieval uncertainty. The REAM model shows that the contribution of ANTS to CO at 800 hPa and CO column is larger than BIOS by 12–46% and 13–39% over NA and the Atlantic for July and August of 2006.

During hot summer days, July 16–21, the contribution of BIOS to CO column or lower tropospheric CO on a daily basis is as large as, if not larger than, that of ANTS, suggesting that it might be inaccurate to use CO as an anthropogenic tracer during hot days. During hot summer days, the REAM-simulated tropospheric CO enhancements (20–70 ppbv) over the region are from BIOS and ANTS followed by convective activities. These enhancements can be larger than TES measurement uncertainty.

The CO tracers flow out along the east coast of the US and Canada in July based on MOPITT and TES CO measurements and they flow more broadly into the Atlantic in August (Figs. 7 and 8), which is captured in the REAM simulation. REAM shows that the winds in August are more preferable compared to July for longitudinal export of CO. As a result, despite source estimates indicate that CO productions by BIOS in August is significantly smaller than in July, the REAM simulations of CO export by BIOS for July and August are similar. The contribution of ANTS to enhanced CO export is larger than BIOS by 18 and 44% for the July and August of 2006.

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