Biogenic Versus Anthropogenic Sources of CO in the United States

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1. Introduction

Carbon monoxide (CO) is emitted to the atmosphere by combustion, and is also produced within the atmosphere by oxidation of volatile organic compounds (VOCs). Anthropogenic CO emissions presently contribute a ±0.20 W m⁻² radiative forcing of climate change according to the Intergovernmental Panel on Climate Change [2007], mainly through chemical effects on the concentrations of tropospheric ozone and methane. CO is also a toxic gas at high concentrations and hence the subject of regulation. The U.S. Environmental Protection Agency (EPA) (Current emissions trends summaries from the NEI, 2007, available at http://www.epa.gov/ttn/chief/trends/) claims that U.S. anthropogenic emissions of CO have been decreasing on average by 2.6% y⁻¹ since 1990, but there is large uncertainty in the EPA inventory. Observations in urban air suggest that EPA estimates of on-road vehicular emissions, accounting for 2/3 of the detailed 1999 EPA National Emission Inventory (NEI 99) for CO, are 50% too high [Parrish et al., 2006; Warneke et al., 2006]. We use here boundary layer observations from the ICARTT aircraft campaign over the eastern U.S. in summer 2004 to better quantify the U.S. anthropogenic source of CO and compare it to the natural source from oxidation of biogenic VOCs emitted by vegetation. As we will see, the anthropogenic source has decreased to the point that the biogenic source now dominates in summer.

2. ICARTT Aircraft Campaign

ICARTT was a coordinated multi-aircraft atmospheric chemistry field program over eastern North America and the North Atlantic in July–August 2004. The NOAA WP-3D aircraft [Fehsenfeld et al., 2006] and the DC-8 aircraft [Singh et al., 2006] flew extensive boundary layers legs across the eastern U.S. over the July 1–August 15 period, typically at 300m over land. The two aircraft showed agreed in their CO measurement to within ±5% (G. Chen, personal communication, 2005; http://www-air.larc.nasa.gov/missions/intexna/meas-comparison.htm) and are used here as a single data set. Other aircraft measurements used in this paper include propane, nitrogen oxide radicals, reactive nitrogen oxides (NOₓ), propane, HCN, and CH₂CN. Surface measurements of CO were also taken during ICARTT from Chebogue Point on the southern tip of Nova Scotia (44°N, 66°W) to observe outflow from the northeastern U.S. [Fehsenfeld et al., 2006; Millet et al., 2006a]. See above references for instrument details.

3. Model Description

We simulate the ICARTT observations with the GEOS-Chem global 3-D model of tropospheric chemistry (version 7.02; http://www.as.harvard.edu/chemistry/trop/geo/) driven by assimilated meteorological observations from the Goddard Earth Observing System (GEOS-4) of the NASA Global Modeling and Assimilation Office (GMAO). The model is applied to a global simulation of ozone-NOₓ-VOC-aerosol chemistry. A general description of GEOS-Chem is given by Bey et al. [2001] and a specific description of the coupled oxidant-aerosol simulation as used here is given by Hudman et al. [2007]. The horizontal resolution is 2° × 2.5°. There are 30 vertical layers including 12 below 10 km and 5 below 2 km. The
4. ICARTT Constraints on CO Sources

[7] Figure 1 compares simulated and observed mean CO concentrations in the boundary layer (0–1.5 km altitude) during ICARTT. The model using NEI 99 emissions shows a consistent 20–50 ppbv overestimate across eastern North America that matches the spatial distribution of the anthropogenic CO source. Surface observations at Chebogue Point show a similar overestimate (Figure 2).

[8] The model overestimate of CO reflects either excessive sources or insufficient boundary layer ventilation. A strong argument against the latter is that the model reproduces successfully the observed shapes of the mean vertical profiles for propane (auxiliary material Figure S1), acetylene [Xiao et al., 2007], and formaldehyde [Millet et al., 2006b] during ICARTT. Chemical loss of CO from oxidation by OH is slow relative to boundary layer ventilation and is therefore of little consequence.

[9] The chemical source of CO in the model from VOC oxidation is well constrained by the successful simulation of formaldehyde (HCHO) observations aboard the DC-8 aircraft [Millet et al., 2006b]. The entire chemical source of CO from VOC atmospheric oxidation, according to current understanding, passes through HCHO as an intermediate. Most of the boundary layer HCHO during ICARTT was from isoprene oxidation [Millet et al., 2006b], as previously observed in eastern North America [Shepson et al., 1991; Lee et al., 1998]. Millet et al. [2006b] shows that GEOS-Chem, including the same VOC sources as here, simulates the DC-8 HCHO observations by A. Fried et al. (Formaldehyde over North America and the North Atlantic during the Summer 2004 INTEX campaign: Methods, observed distributions, and measurement box model comparisons, submitted to Journal of Geophysical Research, 2008) (hereinafter referred to as Fried et al., submitted manuscript, 2008) with no significant bias. Co-located HCHO observations by Snow et al. [2007], aboard the DC-8, were 30% lower than Fried et al. (submitted manuscript, 2008) but highly correlated, and we use this difference as an estimate of the possible error in our biogenic CO source estimate (Table 1).

[10] It thus appears that the model bias in Figure 1 is due to an excessive fuel combustion source in the NEI 99 inventory, and this is consistent with the spatial structure of the bias. Chemical production from oxidation of anthropogenic VOCs is only 14% of that source and is probably not overestimated since the model shows no bias for propane during ICARTT (auxiliary material Figure S1) and is too low for ethane and acetylene [Xiao et al., 2007, also Global budget of ethane and constraints on North American sources from INTEX-A aircraft data, manuscript in preparation, 2008]. We conclude that CO anthropogenic emission is greatly overestimated in the NEI 99 inventory.

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Table 1. CO Sources Over the Contiguous United States for 1 July to 15 August 2004

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<th>Source Type</th>
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</tr>
<tr>
<td>Oxidation of anthropogenic VOCs</td>
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*Not including the oxidation of methane and minor long-lived VOCs (such as methanol and acetone) which provide a background source throughout the troposphere (this source is included in the GEOS-Chem simulation).

*Constrained by the ICARTT observations as discussed in the text. This is 60% lower than the source of 11.5 Tg given by the EPA NEI 99.

*Including 6.7 Tg from isoprene oxidation and 1.6 Tg from oxidation of other biogenic VOCs (monoterpenes, 2–3 alkenes). The 30% uncertainty is constrained by ICARTT observations of HCHO as discussed in the text.

North American fires during ICARTT are mainly outside the contiguous United States; Alaskan and Canadian fires emitted 19 Tg CO during this period [Turquety et al., 2007].
Figure 1. Mean CO concentrations in the boundary layer (0–1.5 km altitude) during ICARTT (July 1–August 15, 2004). (left) Observations averaged over the 2° × 2.5° GEOS-Chem model grid are compared to model results using the (middle) U.S. EPA NEI 99 emissions and (right) anthropogenic CO emissions reduced by 60%. Model results are sampled along the flight tracks at the time of the flights.

Figure 2. Surface air CO concentrations at Chebogue Point during ICARTT. Observations (black) are compared to model results using NEI 99 anthropogenic emissions (green) and with these CO emissions reduced by 60% (blue). Yellow bands are periods of U.S. outflow diagnosed by Millet et al. [2006b]. Overestimate near day 220 is due model misplacement of a large Alaskan/Canadian biomass burning plume.
correlated with isoprene, pointing to an error in these mechanisms (Ren et al., submitted manuscript, 2008). This problem requires further investigation and implies that the CO enhancement from biogenic VOCs is greater than shown in Figure 4.

5. Conclusions

[14] Application of the GEOS-Chem model to simulate ICARTT aircraft observations for CO over eastern North America in July–August 2004 shows that U.S. anthropogenic CO emissions are 60% lower than the U.S. EPA inventory for 1999 (NEI 99). EPA (online report, 2007) reported a mean 2.6% y⁻¹ decrease of CO emissions over the 1990–2004 period; this would imply a 12% decrease for 1999–2004, insufficient to account for the bias. Parrish [2006] and Warneke et al. [2006] found from analysis of urban CO data that on-road sources in the NEI 99 inventory are 50% too high. Our analysis implies that other anthropogenic CO sources from off-road vehicles and industry must also be overestimated.

[15] Our resulting best estimate of U.S. anthropogenic CO emissions for the ICARTT period (July 1–August 15, 2004) is 4.6 Tg, which combined with our best estimate of the secondary source from oxidation of anthropogenic VOCs (1.8 Tg) yields a total anthropogenic source for the period of 6.4 Tg. This can be compared to the CO source from oxidation of biogenic VOCs, which is well constrained during the ICARTT period by the successful GEOS-Chem simulation of aircraft observations of HCHO [Millet et al., 2006b]. We find a biogenic source of CO for the ICARTT period of 8.6 Tg (6.7 Tg from isoprene, 1.6 Tg from other VOCs). The anthropogenic CO source in the United States is thus lower than the biogenic source during summer.

[16] The simulated enhancement of CO concentrations from biogenic sources in the model is comparable to that from anthropogenic sources and weaker than one would expect on the basis of biogenic VOC emissions. This is because of model suppression of OH when isoprene concentrations are high. Observations of OH during ICARTT do not show such isoprene-driven OH titration. A possible reason could be the presence of a large biogenic OH source from ozonolysis of biogenic VOCs missing from current models [Goldstein et al., 2004; Farmer and Cohen, 2007; Kuhn et al., 2007]. This model bias mandates further investigation but it does not affect the constraints on CO sources derived here.

Figure 3. Scatterplot of simulated versus observed CO concentrations at 0–1.5 km altitude during ICARTT. Model results are from the simulation using NEI 99 anthropogenic CO emissions (top) and the simulation with these emissions reduced by 60% (bottom). Reduced-major-axis regressions (black) and y = x lines (dotted black) are shown. The Pearson correlation coefficient and the regression line parameters (with ± 95% confidence interval calculated by the bootstrap method) are given as legends.

Figure 4. July mean enhancements of CO concentrations at 0–2.5 km altitude from (left) anthropogenic and (right) biogenic North American sources, as determined by difference between the standard simulation and simulations with these sources shut off in the domain (130°–70°W, 25°–50°N).
[17] Acknowledgments. This work was supported by the NASA Tropospheric Chemistry Program and by the NOAA Office of Global Programs. We thank Tom Ryerson of NOAA for useful comments on this manuscript.

References


