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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emissions from forest fires near Mexico City" *by* R. Yokelson et al.

R. Yokelson et al.

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Author's reply to interactive comment by P. DeCarlo:

P. DeCarlo has made an excellent point that secondary processes will affect the PM that is observed in the outflow. We are basically in agreement with his comment, which we do not reproduce at this point. However, we note three additional issues. (1) secondary aerosol formation must be considered in both the industrial emissions and the fire emissions. (2) Additional mixing with fresh or aged fire emissions can occur after the MC-area plume is transported away from the area. (3) Once we are discussing secondary formation the idea of strict source apportionment is less rigorous.

To add these important issues to the paper we have inserted the word "primary" before the word "particles" or "PM" as needed throughout the revised text. We also added a sentence to the abstract to describe how secondary aerosol formation may affect our estimates. Most importantly, we added the following text to the end of section 3.5.

This text appears right after our existing discussion of the possibility that the MC plume mixes with fires from the Yucatan.

"Even if the MC plume does not mix with additional downwind fire or urban emissions, the particles observed hours to days downwind from MC will reflect both the primary emissions from our study area and secondary processes such as oxidation, coagulation, and secondary organic and inorganic aerosol formation. Secondary processes make a strict source apportionment less rigorous. For instance gases from fossil fuel sources can condense on biomass burning particles and vice versa. Biogenic emissions can condense on both types of particles. A biomass burning particle can coagulate with a particle generated from fossil fuel combustion making a larger particle with an ambiguous source. Particle constituents could evaporate and then recondense (with or without oxidation) onto other particles (Robinson et al., 2007). A full analysis of these issues would require a modeling study similar to that of Olcese et al. (2007)

However, it is of interest to consider secondary processes (ignoring mixing of the two particle sources considered in this paper) and then roughly re-estimate the mass contribution of the two sources to the downwind plume. The secondary process with the most potential to alter source PM/CO ratios is secondary aerosol formation. Secondary aerosol formation is promoted by the presence of large amounts of condensable gases or high levels of O3, which can convert less-volatile NMOC to condensable gases (Reid et al., 1998; Olcese et al., 2007; Kang et al., 2007). Both of these factors are present in abundance for both sources in our study area.

The mass ratio for primary particles to CO in the MCMA EI is 0.011. According to DeCarlo (attributed comment) and references therein (e.g. Salcedo et al., 2006) a mass ratio for PM/CO that realistically includes secondary aerosol formation in the fossil-fuel aerosol from the MC area would range from 0.04 to 0.08. This represents an increase over the MCMA EI by a factor of 4-8. PM/CO is also likely to increase in the biomass burning aerosol. Moffet et al (2007) measured a factor of 1.6 increase in the volume of biomass burning particles aged for several hours in the MC area during

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MILAGRO. A review article on biomass burning particles by Reid et al (2005) gives numerous indications that biomass burning aerosol mass (ratioed to CO) increases by factors from 1.7 to 2.0 over 1-3 days (see also Reid et al. 1998). The range of growth factors we consider for biomass burning aerosol is much smaller than that for fossil fuel aerosol, but corresponds to the addition of equal, or slightly more, total mass. More mass could add to the biomass burning particles since the fire particles are produced at higher elevation, which implies that more O3 and UV and lower temperatures (favoring condensation) are relevant. In addition, the forest fire particles are produced in an environment likely to have higher concentrations of biogenic emissions and the NMOC gases co-emitted by fires are much more reactive than for fossil fuel combustion (Reid et al 1998, Christian et al., 2004).

We now re-estimate a range of mass fractions under the approximation of just two sources (mountain pine forest fires and MCMA). A lower limit for the fire, fine-particle mass contribution in the outflow is 44% (56% from MCMA). This is obtained by starting with our HCN-based estimate of the fire contribution to study-area CO and then assuming that the PM/CO mass ratio in the MCMA EI should be multiplied by eight and our fire PM/CO multiplied by 1.6 to account for secondary aerosol formation. The upper end fire contribution is obtained by assuming a mass-growth factor of 2 for biomass burning and 4 for the MCMA aerosol. In this case the fire contribution is estimated as 67% (33% MCMA contribution). The midpoint of this range corresponds to 55% of the particle mass in the MC-area outflow being due to the mountain fires. Of course, other assumptions, additional downwind data, or a detailed modeling exercise could lead to adjustments in these estimates."

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