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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Total Observed Organic Carbon (TOOC): A synthesis of North American observations" *by* C. L. Heald et al.

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General Comments:

The paper presents a very interesting overview of an important topic: the organic carbon budget of the troposphere, at least in the vicinity of North America. The overview generally achieves its goal of integrating the available information regarding this topic, and hence is quite valuable. The analysis methods currently in use for gas-phase and particularly aerosol phase organic carbon in the atmosphere have experimental problems that lead to significant accuracy problems. The authors reasonably account for these problems (with some exceptions discussed below.) I think that the conclusions are generally valid and the paper should be published after some fairly significant revisions are made. These revisions are specifically discussed below.

Major Specific Comments:

1) The discussion beginning on line 26, pg 17834 and the discussion relating to Figure 5a seems to indicate that there is no firm lower limit for the TOOC in the vicinity of North America. In Figure 5a Trinidad Head lies significantly below a group of several other of the less-polluted data sets. Trinidad Head is expected to be one of the cleanest sites in the temperate Northern Hemisphere since it receives inflow form the largest, nearly source free region in that hemisphere. However, the lower TOOC distribution at Trinidad Head appears to be largely due to the lack of measurements of ethane and formaldehyde during that study. If the likely contribution of these two species are added to the Trinidad Head values, then Trinidad Head would join the adjacent group of less-polluted data sets. I suspect that this group of data sets can be taken as a lower limit for the concentration of TOOC in the temperate Northern Hemisphere. The value of this paper would be significantly increased by extending the discussion of the cleanest data sets in this regard.

2) Page 17840, lines 17-23 - Here the discussion focuses on differences in the TOOC levels observed at Chebogue Point in 2004 (not 2005 as stated) compared to measurements made at the same site 11 years earlier. The larger 1993 concentrations are attributed to "plumes" and to different averaging times. However, this discussion should be expanded to consider two additional effects. First, the 2004 measurements missed the contribution of ethane, since that species was not measured. Second, Chebogue Pt. receives inflow of polluted air masses from North America, and North American emissions of anthropogenic VOC are believed to have decreased substantially over those 11 years. For example, the most recent EPA emissions estimates (http://www.epa.gov/ttn/chief/trends/index.html) suggest that, although total VOC emissions have declined by only about 20%, highway vehicle emissions (likely the major source for air masses leaving the northeastern US) were 7.8 and 4.3 E+6 US tons in 1993 and 2004, respectively. Hence, less concentrated plumes are to be expected in 2004.

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3) Page 17841 - The discussion of the photochemical clock relationships should be strengthened (or perhaps better, eliminated altogether). The analysis of de Gouw et al. showed that the aerosol OC (not TOOC) increased as the toluene/benzene ratio decreased. The toluene/benzene "photochemical clock" is designed to follow chemical processing over a period of a couple of days. The toluene/benzene did indeed show that aerosol OC increased on that time scale. However in the absence of deposition processes, there is no reason to expect that TOOC will evolve significantly during that time period. Certainly, TOOC will not increase, since TOOC processing primarily follows a gas-phase to aerosol phase path, which gives no change in TOOC. A week decrease of TOOC with time is expected due to oxidation of TOOC to CO or carbon dioxide, which I suspect proceeds slowly on the scale of the toluene/benzene "photochemical clock", or deposition of aerosol OC, which is not expected to correlate with the toluene/benzene "photochemical clock".

4) Page 17844 - The discussion of Figure 7 should be strengthened. The correlation of TOOC with the biogenic tracers is generally weaker than the correlation with CO shown in Figure 6. The biogenic tracers, upon which Figure 7 is based, likely also correlate with CO due to similarity of source regions, and similarity of dilution and mixing processes (wind ventilation in source regions, boundary layer evolution, etc.) Unless the authors can show that the correlations in Figure 7 are stronger than those due to simply the correlation of both TOOC and the biogenic tracers with CO, then Figure 7 provides no indication of a biogenic variability to TOOC, or any other useful information.

5) There is one clear experimental problem in the aerosol OC measurement field that deserves thorough discussion in the Future Directions Section. There is substantial evidence that indicates anthropogenic sources provide the dominant source of aerosol OC in many urban to rural environments. Yet, Carbon 14 measurements indicate that modern carbon sources make substantial, usually dominant contributions, even in urban areas where it is difficult to understand such a contribution. This contradiction

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seems to point to some experimental problem somewhere that should be addressed in the "Future".

Minor Comments and Technical Corrections:

1) Pg. 17832, lines 14-17 - The authors refer to mobile platforms that "pursued different air masses and plumes ... and also sampled different amounts of clear air depending...." This description is unfortunate in that it can be taken to imply that the troposphere is composed primarily of homogeneous, clear air, traversed occasionally by interesting plumes. Such is not the case; the troposphere is actually a very heterogeneous environment composed entirely of plumes of varying history that are in the process of intertwining and finally mixing. This description should be revised to present a more accurate picture.

2) Pg. 17837, line 13 - By the time I got to this sentence, it was not clear to me to which data set "this location" referred.

3) Pg. 17843, line 1 -The authors note that "The variability of TOOC at remote sites is not as well predicted by CO and the TOOC/CO slope is systematically lower." Can this behavior be taken as an indication that TOOC has a shorter atmospheric lifetime than CO? Is this worth a comment?

4) The legend of Table 1 needs work. I cannot tell what most of the techniques were; the "dot" symbol is not defined.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 17825, 2007.

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