Atmos. Chem. Phys. Discuss., 5, S4279–S4281, 2005
www.atmos-chem-phys.org/acpd/5/S4279/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on “The characterisation of pollution aerosol in a changing photochemical environment” *by* M. J. Cubison et al.

Anonymous Referee #3

Received and published: 2 December 2005

General Comments:

This paper combines a number of advanced methods to analyze the aerosol and gases downwind of London in a summer field study. The measurements provide information on aerosol size distributions, composition, and hygroscopicity, as well as photochemical age of the air mass. The results are quite interesting and the authors provide a self-consistent explanation of the changes in aerosol properties with age due to oxidation and condensation. This is a well-done study and is appropriate for publication in Atmospheric Chemistry and Physics. I have a few comments to be addressed.

Specific Comments:

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

EGU

1. Page 10070, lines 20-30: I do not follow this discussion. It seems like the authors are saying at first that the sulfate:organic ratio increases with particle size, that this is a reflection of condensational growth, and leads to a reduced influence from organics as the aerosol is processed. But then it is said that SOA production is faster than SO2 conversion to sulfate. It seems that these are contradictory statements. I find the discussion from here up to section 4.4 rather confusing.

2. Page 10074, lines 6-19:

A. When it is stated that "after ˜1-2 days photochemical age virtually all the organic content is oxygenated in nature", what does this mean? Does this mean that the C/O ratio ˜ 1 for the aerosol? Does it mean that each organic compound has at least one functional group?

B. If one calculates the number of collisions of OH radicals with 100 nm particles using an upper limits of [OH] = 3 x 106/cm3 (for 12 hrs per day) and t = 2 days, assuming a mean thermal speed of OH of 600 m/s, mean organic molecular weight of 300 g/mol, and density of 0.9 g/cm3, each organic molecule undergoes approximately one collision. So if "totally oxygenated" in 1-2 photochemical days means one functional group per molecule, this could be explained by heterogeneous oxidation of the primary particles. However, since there would be many more carbons available for reaction (for MW = 300 the carbon number ˜21), the degree of oxygenation should continue to increase for weeks. Since the observation is that the degree of oxygenation does not change significantly after 1-2 photochemical days, this calculation supports the idea that SOA is responsible for the increase in OOA.

C. Continuing with the point made above, it seems that the conclusion that the major source of OOA is SOA is consistent with the organic aerosol being highly oxygenated and essentially saturated with functional groups (C/O ratio ˜1). Has this ratio been calculated from the AMS data? If this is so, then it explains why there is no further oxidation after 1-2 photochemical days. This would also be consistent with the likely composition of SOA formed in this urban setting. I would imagine that the SOA is primarily from aromatics, which are known to form SOA (probably as oligomers) from reaction products such as tetraols and multifunctional hydroxycarbonyls that have C/O ratios ˜1.

3. Page 10076, line 26-page 10077, line 10: The suggestion that the urban aerosol undergoes no further aging after ˜1-2 photochemical days is surprising to me. I would think that as the aerosol enters rural regions it would accumulate biogenic SOA. Are the authors suggesting that the absence of further changes in the aerosol is because no more SOA accumulates or that the accumulating SOA is the same composition everywhere, in urban, rural, and remote areas? It seems to me that urban and biogenic SOA should be very different in chemical composition. Would the AMS be able to observe these differences?

Technical Comments:

4. Figure 3. If I understand this figure correctly, the circles are all outliers. I suggest stating this in the caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 10055, 2005.