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Formation of highly oxygenated organic aerosol in the atmosphere: Insights from the Finokalia Aerosol Measurement Experiments

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[1] Aged organic aerosol (OA) was measured at a remote coastal site on the island of Crete, Greece during the Finokalia Aerosol Measurement Experiments (FAME-08 and FAME-09), which were part of the EUCAARI intensive campaigns. Quadrupole aerosol mass spectrometers (Q-AMSs) were employed to measure the size-resolved chemical composition of non-refractory submicron aerosol (NR-PM$_1$), and to estimate the extent of oxidation of the OA. The experiments provide unique insights into ambient oxidation of aerosol by measuring at the same site but under different photochemical conditions. NR-PM$_1$ concentrations were about a factor of three lower during FAME-09 (winter) than during FAME-08 (summer). The OA sample was significantly less oxidized and more variable in composition during the winter than during the early summer. Lower OH concentrations in the winter were the main difference between the two campaigns, suggesting that atmospheric formation of highly oxygenated OA is associated with homogeneously photolyzed aging. Citation: Hildebrandt, L., E. Kostenidou, N. Mihalopoulos, D. R. Worsnop, N. M. Donahue, and S. N. Pandis (2010), Formation of highly oxygenated organic aerosol in the atmosphere: Insights from the Finokalia Aerosol Measurement Experiments, Geophys. Res. Lett., 37, L23801, doi:10.1029/2010GL045193.

1. Introduction

[2] Submicron atmospheric aerosols have a highly uncertain effect on climate [Intergovernmental Panel on Climate Change, 2007], and they adversely affect human health [Pope and Dockery, 2006]. Organic aerosol (OA) comprises 20–90% of the global PM$_1$ mass [Kanakidou et al., 2005], but its formation and evolution remain poorly understood [Jimenez et al., 2009]. After formation or emission, OA can re-evaporate and be further oxidized (“aged”) and transported in the atmosphere [Robinson et al., 2007]. Air-quality models tend to under-predict the concentrations of OA in the atmosphere, especially in the summer when photochemical activity is high [Volkamer et al., 2006; Goldstein and Galbally, 2007; Karydis et al., 2007] suggesting that we do not understand the aging of OA and formation of secondary OA (SOA) well.

[3] The complex OA composition prevents speciation on a molecular basis, let alone tracking the chemical evolution of its molecular components. However, aerosol mass spectrometry and factor analysis enable differentiation among several types of OA, mostly distinguished by their oxygen content and thermal volatility [Jimenez et al., 2009]. The resulting OA components include hydrocarbon-like OA (HOA), biomass burning OA (BBOA), and oxygenated OA (OOA), a more oxidized component which dominates the total OA mass in most locations [Zhang et al., 2007]. OOA can frequently be further separated into highly oxygenated OA, now referred to as low-volatility OA (LV-OOA) and less oxygenated OA, referred to as semi-volatile OA (SV-OOA) [Jimenez et al., 2009; Ng et al., 2010].

[4] Oxidation reactions after initial OA formation can affect the concentration and composition of OA. Most fresh SOA formed from gaseous precursors in laboratory experiments resembles SV-OOA [Ng et al., 2010]. After additional OH oxidation, the aged SOA can start to resemble LV-OOA. Primary OA formed in laboratory experiments, such as OA from diesel exhaust or woodsmoke, initially resembles HOA or BBOA, but upon aging can resemble SV-OOA [Jimenez et al., 2009]. Thus, SV-OOA can be created from essentially all OA precursors in the laboratory, and source strengths and mechanisms of this moderately oxidized OA can be tested on laboratory timescales. Illuminating the formation of LV-OOA is more challenging. Typical laboratory experiments only access the first few generations of oxidation [Kroll et al., 2009], and hence this highly oxidized OA cannot easily be created in laboratory experiments, especially if the experiments aim to approximate atmospheric concentration levels. Studying aged ambient OA is also difficult since it is usually mixed with fresher OA, especially if the ambient measurements are conducted close to sources. Thus, we need to conduct well-situated ambient measurements to explore the formation of highly oxygenated OA.

[5] The Finokalia Aerosol Measurement Experiments (FAMEs) were designed to study ambient OA of different photochemical ages. Finokalia is on the island of Crete, and it is an ideal location to study the aging of OA. The station is isolated and often downwind of European sources [Koulouri et al., 2008] and therefore allows the study of OA from Europe, as well as marine and Saharan aerosol. Also, the photochemical conditions are conducive to high levels of oxidation, especially in the summer [Berresheim et al., 2003].

[6] We conducted two campaigns at this site to measure OA under different conditions. FAME-08 was in the early summer (May 8–June 5, 2008) under strong oxidizing conditions. FAME-09 was in the winter (February 25–March 25,
Kulmala et al.−ion and can therefore be used as a semi-empirical measure of the extent of oxidation of the OA. The organic mass fraction at m/z 44, f_{44} = [m/z 44]/C_{OA}, where C_{OA} is the total mass concentration of the organic aerosol, can be used to estimate the oxygen to carbon ratio, (OC)_{44}, and the organic mass to organic carbon ratio, (OM: OC)_{44}, of the OA [Aiken et al., 2008].

3. Results

3.1. Bulk Chemical Composition

[11] Figure 1 shows 1-h averages of the chemical composition of dry NR-PM_{10} measured by the AMS during FAME-09, the campaign average contributions of the different aerosol components to the total aerosol mass, and the mean values of organics and sulfate during FAME-08. During March 5–7 the area experienced a Saharan dust event with PM_{10} concentrations exceeding 1000 µg m⁻³, NR-PM_{10} concentrations were extremely low during this time period, presumably because the larger Saharan particles scavenge smaller particles by coagulation and low-volatility vapors by condensation. The campaign−average total dry NR-PM_{10} concentration measured by the AMS was 3.2 µg m⁻³, a factor of three lower than during FAME-08; average total OA was 1.4 µg m⁻³, a factor of two lower than during FAME-08 [Hildebrandt et al., 2010]. The bulk composition also differed: during FAME-08 OA comprised 28% of dry NR-PM_{10} and the ratio of OA to AMS-Sulfate (OA:SO_{4}²⁻) was approximately 0.5, during FAME-09 OA comprised 43% of dry NR-PM_{10} and OA:SO_{4}²⁻ was unity.

3.2. Organic Composition

[12] Figure 2 shows 2-h averages of f_{43}, f_{44} and f_{57} as a function of time during FAME-09. Figure 2 also shows the mean values of f_{43} and f_{44}, as well as the 30th and 90th percentiles of f_{44} during FAME-08. Almost all values of f_{44} during FAME-09 are below the 10th percentile of the FAME-08 values; the OA was significantly less oxidized in the winter (FAME-09) than the early summer (FAME-08). The average f_{44} of 18.2% observed during FAME-08 corresponds to an estimated (O:C)_{44} of 0.8 and (OM:OC)_{44} of 2.2. In comparison, the average f_{44} of 10.6% observed during FAME-09 corresponds to an estimated (O:C)_{44} of 0.5 and (OM:OC)_{44} of 1.8. The organic aerosol was not only less oxidized but also much more variable in composition during FAME-09.

The size−resolved submicron aerosol composition was measured using Q−AMSs from Aerodyne Research, Inc. [Canagaratna et al., 2007]. The particles were sampled at ambient relative humidity. The particle number distribution was monitored using scanning mobility particle sizers (SMPSs) from TSI. A number of other measurements were performed during these campaigns, including PM composition from filter samples and aerosol light scattering and absorption ( nephelometers, aethalometers). Meteorological data are also available.

The Q−AMSs alternated operation between mass spectrum (MS) scanning mode and particle time−of−flight (pToF) mode every fifteen seconds. The sample averaging time was set at three minutes, and further averaging was performed in post−analysis. Data were analyzed using a standard AMS fragmentation table and batch table [Allan et al., 2004], with a few modifications. These modifications, as well as details on the calibration of the AMS, the OA detection limit and uncertainties in the AMS measurements and analysis are discussed in the auxiliary material. In summary, the average collection efficiency of the AMS was 0.85 during FAME-08 and 0.6 during FAME-09, estimated from comparison to SMPS distributions and confirmed by comparison to filter measurements. For the analysis of the organic composition (Section 3.2) we did not include data when C_{OA} < 0.3 µg m⁻³, a reasonable estimate for the OA detection limit in the Q−AMS [e.g., Drewnick et al., 2009]. Importantly, the differences observed in the organic composition cannot be explained by the expected uncertainty and variability in AMS measurements.

We focus on the OA mass spectra from the two measurement campaigns. The fragments at mass−to−charge ratio (m/z) 44 mostly correspond to the CO_{2} ion and can therefore be used as a semi−empirical measure of the extent of oxidation of the OA. The organic mass fraction at m/z 44, f_{44} = [m/z 44]/C_{OA}, where C_{OA} is the total mass concentration of the organic aerosol, can be used to estimate the oxygen to carbon ratio, (OC)_{44}, and the organic mass to organic carbon ratio, (OM: OC)_{44}, of the OA [Aiken et al., 2008].

Figure 1. Time series of total mass concentrations of NR-PM_{10} components and average concentrations (inset) measured by the AMS during FAME-09, as well as mean values of total OA and sulfate concentrations during FAME-08 (horizontal dashed lines).

2009 under milder oxidizing conditions. The OA measured during FAME-08 has been characterized in detail in a previous publication [Hildebrandt et al., 2010]. The OA observed during FAME-08 was highly oxygenated, resembling LV−OOA throughout the campaign, regardless of the source region. The hypothesis motivating FAME-09 was that wintertime OA would be less oxygenated and more variable in composition than summertime OA.

2. Experimental Procedure

2.1. Measurement Campaign

[7] Measurements were conducted at the Finokalia Station of the Environmental Chemical Processes Laboratory of the University of Crete [Hildebrandt et al., 2010] as part of the EUCAARI intensive campaigns [Kulmala et al., 2009]. Detailed results from FAME-08 have been published [Hildebrandt et al., 2010; Lee et al., 2010; Pikridas et al., 2010], and details on FAME-09 will be presented elsewhere. Here, we focus on the comparison of OA sampled during FAME-08 and FAME-09.

2.2. Instrumentation and Methods

[8] The size−resolved submicron aerosol composition was measured using Q−AMSs from Aerodyne Research, Inc. [Canagaratna et al., 2007]. The particles were sampled at ambient relative humidity. The particle number distribution was monitored using scanning mobility particle sizers (SMPSs) from TSI. A number of other measurements were performed during these campaigns, including PM composition from filter samples and aerosol light scattering and absorption ( nephelometers, aethalometers). Meteorological data are also available.

2.3. Q−AMS Measurements

[9] The Q−AMSs alternated operation between mass spectrum (MS) scanning mode and particle time−of−flight (pToF) mode every fifteen seconds. The sample averaging time was set at three minutes, and further averaging was performed in post−analysis. Data were analyzed using a standard AMS fragmentation table and batch table [Allan et al., 2004], with a few modifications. These modifications, as well as details on the calibration of the AMS, the OA detection limit and uncertainties in the AMS measurements and analysis are discussed in the auxiliary material. In summary, the average collection efficiency of the AMS was 0.85 during FAME-08 and 0.6 during FAME-09, estimated from comparison to SMPS distributions and confirmed by comparison to filter measurements. For the analysis of the organic composition (Section 3.2) we did not include data when C_{OA} < 0.3 µg m⁻³, a reasonable estimate for the OA detection limit in the Q−AMS [e.g., Drewnick et al., 2009]. Importantly, the differences observed in the organic composition cannot be explained by the expected uncertainty and variability in AMS measurements.

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Auxiliary materials are available in the HTML. doi:10.1029/2010GL045193.
This variability is another indication that the OA during FAME-08 was more aged than during FAME-09. As during FAME-08, low \( f_{37} \) (0.6% on average) suggests little or no contribution from fresh, non-oxidized OA, consistent with the remoteness of the site.

4. Discussion

A meaningful comparison of the OA composition during FAME-08 and FAME-09 requires an understanding of the similarities and differences in the aerosol sources and ambient conditions during the campaigns. Based on the footprint residence time plots from the FLEXPART model [Pikridas et al., 2010], the source regions of the aerosol sampled over the course of the two study periods were comparable. In particular, during FAME-09, the source region was categorized as marine for 61% of the campaign (38% in FAME-2008), as Saharan for 7% of the campaign (9% in FAME-08) and as continental for 32% of the campaign (53% in FAME-08). Based on the somewhat higher abundance of marine and lower abundance of continental air masses during FAME-09, we would expect OA to be more oxidized (aged) during FAME-09 than during FAME-08; however, we observe the opposite. We also stress that, during FAME-08, the aerosol from all sources was consistently highly oxygenated. Thus the lower oxidation and increased variability in composition of the OA during FAME-09 were likely not due to different source regions.

Since the two campaigns were conducted during different seasons, there were differences in the emissions. Biogenic VOC emissions are temperature dependent and higher in the summer than in the winter. Based on emission inventories [Visschedijk et al., 2007], total isoprene emissions in Europe were on average nine times higher during FAME-08 than during FAME-09, and total terpene emissions were six times higher. The isoprene and terpene emissions in Greece had similar ratios (C. Pilinis, unpublished results, 2010). However, preliminary model results using the PMCAMx-2008 model [Murphy and Pandis, 2009] suggest that the contribution of biogenic SOA to total OA sampled at Finokalia were similar during the two campaigns (about 50%) (C. Fountoukis, unpublished results, 2010). Thus, the lower biogenic VOC emissions during the winter cannot explain the difference in OA composition between the two campaigns. Differences in the emissions of other compounds were smaller. For example, total European CO, NO and NO\(_2\) emissions were on average 10% higher during FAME-09 than during FAME-08, SO\(_2\) emissions where 26% higher, and aromatic VOC emissions were similar (C. Pilinis, unpublished results, 2010). Therefore, the campaign differences were probably not mainly due to different emissions, nor different source regions, but rather due to different meteorological and photochemical conditions.

Photochemical conditions were milder during FAME-09. We approximate ambient OH concentrations using measures of UV intensity (approximated by the photolysis rate of NO\(_2\)) and O\(_3\) concentrations. The UV intensity during FAME-09 was lower and more variable than during FAME-08 (Table S1 of the auxiliary material). Using the correlations developed by Berresheim et al. [2003], the approximate mean midday OH concentrations were \(12 \times 10^3\) cm\(^{-3}\) during FAME-08 and \(5.5 \times 10^6\) cm\(^{-3}\) during FAME-09. The Berresheim correlations are derived from summer data and hence they can only provide an upper limit for FAME-09 (the slant path is higher in the winter) and a better estimate for FAME-08. Ozone concentrations were lower in the winter (FAME-09 average = 44.6 ppb) than in the summer (FAME-08 average = 53.2 ppb). Since O\(_3\) is a source of OH, we infer that OH concentrations were on average at least a factor of two (and possibly much more) lower during FAME-09. The significantly lower OH concentrations could explain more variable composition and lower average extent of oxidation of OA in the winter. Considering that ambient conditions were more humid during FAME-09 (mean RH = 73%) than during FAME-08 (mean RH = 60%), and that \( f_{44} \) was not significantly correlated with inorganic acidity (FAME-08 \( R^2 = 0.065\), FAME-09 \( R^2 = 0.015\)), it is unlikely that aqueous or heterogeneous processing played a dominant role in the formation of highly oxygenated OA during FAME-08. Furthermore, the time scale of heterogeneous OH oxidation is approximately two weeks, using the simple mass balance suggested by Robinson et al. [2006], the FAME-08 average particle size (300 nm) and diurnal-average OH concentration (\(2 \times 10^6\) cm\(^{-3}\)). Thus, heterogeneous aging appears too slow,
and most of the oxidation was probably homogeneous. We estimate that the OH exposure needed for the OA to reach the highly oxidized state observed during FAME-08 is approximately $4 \times 10^{11}$ molecules cm$^{-3}$ s [Hildebrandt et al., 2010], which is about ten times less than the exposure required for heterogeneous production of LV-OOA [Jimenez et al., 2009]. The average ambient temperature was about 9 K higher during FAME-08 than during FAME-09 (Table S1). Using the volatility distribution from FAME-08 [Lee et al., 2010], we estimate that there was about 30% more OA with effective saturation concentration $\leq 10$ μg m$^{-3}$ in the gas phase during FAME-08, which is expected to accelerate the gas-phase oxidation.

[10] In order to further explore differences in the meteorological conditions during the two campaigns, we used data from the European Centre for Medium-Range Weather Forecasts (http://www.ecmwf.int/research/era/do/get/era-interim). When considering only the grid cell containing the field site (Figure S1), average low cloud cover was 27 times higher during FAME-09 than during FAME-08 (Table S1). The average low cloud cover in a much larger domain including most of Europe was more than twice as high during FAME-09 (Table S1 and Figure S2). Thus, photochemical conditions were milder during FAME-09—not just at the field site, but also during transport to the site.

[11] The difference in OA:SO$_4^2$ during the two study periods could also be due to the different photochemical conditions, which can affect the concentrations of SO$_2$ and OA.

Previous work has shown that OH oxidation of SO$_2$ is the main source of submicron SO$_4^2$ in the area [Mihalopoulos et al., 2007]. During FAME-08, SO$_2$ concentrations and the mass ratio of SO$_2$ to sulfate were low (average SO$_2$:SO$_4^2$ was 0.06), suggesting that SO$_2$ was almost completely oxidized to sulfate before it reached the measurement site. This was not the case under the milder oxidizing conditions during FAME-09, when the average SO$_2$:SO$_4^2$ was 0.7. Furthermore, the higher extent of oxidation of the FAME-08 OA (section 3.2) suggests that fragmentation reactions were probably more significant during FAME-08 [Kroll et al., 2009]. Fragmentation reactions and increased evaporation due to higher temperatures can decrease the concentration of OA and therefore cause a lower OA:SO$_4^2$ during FAME-08.

5. Implications

[12] Organic aerosol was less oxidized and its composition was more variable under milder photochemical conditions in the winter (FAME-09) than it was in the summer (FAME-08). Since the main difference between the OA sampled during FAME-09 and FAME-08 is the more extreme photochemical conditions in the summer, we hypothesize that homogeneous photochemical aging drives the transformation from younger and more variable OA (FAME-09) to older, more uniform and highly oxidized OA (FAME-08).

[13] The range and mean values of the summer and winter OA support the hypothesis that the OOA factors emerging from PMF data analysis do not represent distinct aerosol populations but rather the lower and upper limits bounding the range of variation in degree of oxidation observed during a given campaign. Ng et al. [2010] showed that the two OOA factors from various field campaigns show progressively rising amounts of oxidation correlating with expected photochemical age. Hildebrandt et al. [2010] showed that the FAME-08 (summer) factors both fell well within the historical LV-OOA range and that the factors showed a clear diurnal variation consistent with daytime oxidation. In the winter (FAME-09) we see much greater variability and lower mean degree of oxidation with much lower photochemical age.

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