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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hygroscopic and chemical characterisation of Po Valley aerosol" *by* J. Bialek et al.

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Major comments.

1. The authors suggest in the abstract (P 3249 lines 5-12) that the More Hygroscopic (MH) mode undergoes a "transformation" into a LH and BH mode. This statement implies that the aerosol particles that comprise the MH mode undergo some sort of physical or chemical process that changes some of them to LH and some to BH aerosol. It is highly unlikely that any process could selectively transform some particles to BH and some LH. While I think that condensation of organic, non- or less hygroscopic coating material is a plausible explanation for the reduction of MH particles to LH, it is far more likely that the BH mode has some source other than transformation of MH

particles. This result is explained in more appropriate language on page 3263 lines 1-6. Consider revising these specific conclusions presented in the abstract.

Reworded to:

The analysis of the HGF probability distribution function (PDF) reveals a transformation of a predominant "More Hygroscopic" (MH) mode with HGF of 1.5 around noon, into a "less hygroscopic" (LH) HGF of 1.26. Another mode, a "barely hygroscopic" (BH) with HGF of 1.05 appears during the night and, in addition, a new, externally mixed BH ultrafine mode (HGF $\sim$1.2) appears and persists through the night. Both modes can be related to the production of fresh POA particles (like HOA + BC).

2. The authors use PMF factor analysis with "focus on a 5-factor solution." While a 5-factor solution appears to be appropriate for Case 2, it seems that Case 1 would be more appropriately described by a 4-factor solution. The OOA 1 and OOA 2 factors in Case 1 closely follow one another, suggesting that those two factors describe essentially the same variability in data and indicating that they would be best represented as a single factor. Is there a compelling reason why the authors applied 5 factors to Case 1? The authors might consider an appendix with details on the method for choosing the best PMF solution to describe variability in AMS data.

The PMF analysis was performed for the duration of the campaign for 1 to 7 factors, and is described in detail in Supporting Information. It was found that the PMF solutions with factor numbers greater than 5 provided no new meaningful information and instead resulted in a splitting of the existing factors. The five factor solution was thus chosen as the optimal solution following a number of considerations, including correlations between the chosen AMS PMF solution and measurements taken using the other techniques, specifically with Aerosol time of flight Mass spectrometer data (see methodology for example used in Dall'Osto et al., 2013).

As regard of OOA1 and OOA2, whilst the two factors do indeed present similar temporal trends during case 1, the overall temporal variability during the field study is very

different. Hence, because they represent different types of OOA, we keep them separate (please see Attached figure 1).

3. The authors do a thorough job of presenting main results of the study, but provide little physical explanation for the observed trends. For example, the maximum concentrations in case 2 occurred early in the morning, with a decrease in concentration after that. Meteorological data are available - is this the result of a shallow inversion? Consider adding brief statements following presentation of main findings that propose explanations for observed trends, in order to aid the reader in better understanding the factors affecting aerosol formation and hygroscopicity in the Po Valley.

The decrease in concentration can be indeed attributed to the changes in the BL height. Line 17, 3256, added:

During these days, the boundary layer meteorology followed a typical diurnal evolution for July in the Po Valley, characterized by a transition from a stable, shallow nocturnal surface layer to a 1500 m - thick convective mixing layer between 8:00 to 13:00 (local time) (Di Giuseppe et al., 2012)".

4. It is an important result that GF is lowest when nitrate is highest. There is also significant HOA present during this time. It is possible that organosulfate/nitrate production or hydrophobic coating layers are responsible for this behavior, but these phenomena are typically photochemically produced. What mechanism do the authors suggest forms organonitrates/organosulfates or hydrophobic coatings at night?

Some of organonitrates and hydrophobic organic compounds concentrations spikes may be driven by repartitioning of semi volatile compounds to the particulate phase as temperature decreases at night. Importantly, NO3-initiated oxidation chemistry with alkenes is additionally able to form organonitrates at night (e.g. Atkinson et al. 2000) without sunlight, while organosulfate formation would need solar radiation. HOA mass fraction is not dominating the organics at night and thus it could not be responsible for the low HTDMA values at night.

Minor Comments:

Consider distinguishing times as Local Time (LT)

Described as LT in revised manuscript.

3248 Line 6-10 in abstract is confusing as written. Consider rewording.

Reworded to:

The average HGFs recorded during the low HGF period were in range from 1.18 (for the smallest, 35nm particles) to 1.38 (for the largest, 165nm particles). During the day, the HGF gradually increased to achieve maximum values in the early afternoon hours from 12:00–15:00, reaching 1.32 for 35 nm particles and 1.46 for 165 nm particles.

3248 Line 13-14 - Clarify what "low diurnal temporal patterns" refers to

Reworded to:

Case 1 exhibited weak diurnal temporal patterns, with no distinct maximum or minimum, and was associated with moderate non-refractory aerosol mass concentrations (for 50% size cut at 1 μm) of the order of 4.5 μgm$-$3.

3248 Line 16 - remove "to" in typically to 50% of the mass

Corrected.

3248 Line 17 - non-refractory mass

Corrected as suggested

3249 1-10 - Do these results apply to both cases and just case 2? Please clarify which results are generally applicable to the entire study and which apply to just one case.

Lines changed as follows:

Surprisingly, the lowest HGFs occurred for the period when nitrate mass reached peak concentrations (case 2). This may suggest formation of organonitrates, which

significantly decreased the OGF. Coincident with the peak in nitrate was a peak in Hydrocarbon-like Organic aerosol (HOA) and Semi-Volatile Oxygenated Organic Aerosol (SV-OOA) and analysis of the HGF probability distribution function (PDF) reveals an existence of a predominant “More Hygroscopic” (MH) mode with HGF of 1.5 around noon, and two additional modes, one with a “less hygroscopic” (LH) HGF of 1.26, and another with a “barely hygroscopic” (BH) mode of 1.05. Generally, the analysis points to an internal mixture of larger size inorganic species, mainly nitrates, coated with a hydrophobic organic layer which suppresses water uptake. In addition, a new, externally mixed BH ultrafine mode appears and persists through the night.

3250 22-29 - It would be helpful here to give a range of GFs previously reported for SOA.

Changed to:

In general, all SOA is found to be slightly hygroscopic, with water uptake less than that of typical inorganic aerosol substances. HGF values reported in the laboratory studies ranged from 1.05 (for the fresh SOA) to 1.2 (for highly oxidized SOA).

3259 5 - "that" should be "than"

Corrected to “than”.

3259 6-14 - Is there size-resolved PTOF AMS data to shed light on these trends? I expect that inorganics dominate the larger sizes and organics the smaller sizes, but size-resolved data to confirm would be nice.

Unfortunately PTOF AMS data were not available for the current study. However, Five-stage Berner low-pressure impactor samples were collected concurrently to the on-line measurements over 12 hour periods (day & night) and chemical analyses confirmed that inorganic ions are enriched in the accumulation mode (0.14 – 1.0 μm) with respect to the quasi-ultrafine mode (50 – 140 nm). This behaviour contributes to explain the lowering of HGFs towards smaller sizes. The same analyses indicate that quasi-

ultrafine particles actually contain nitrate and sulphates. However, the variations (day vs. night) in the inorganic-to-carbonaceous mass ratio for the small particles could not be determined accurately by these analyses because of the analytical errors, and therefore were not presented in the paper.

3259 22 - OOA1?

Corrected to OOA1.

(related to Major Comment 3 above) Could precipitating systems in 4.1.2 have contributed to the decrease in aerosol mass in late morning during Case 2? Or is boundary layer deepening the major cause?

The decrease in concentration is indeed caused by changes in the BL height. The explanations will be introduced in the script.

(related to Major Comment 3 above) Fig 3 - SV-OOA is typically considered a marker for early-generation SOA products. Why then does it show such little diurnal variability?

Under typical polluted continental conditions, SV-OOA follow the classical diurnal trend with a minimum in afternoon hours, which is in fact observed in the days between 9 and 11 July (Fig. 5). On the other hand, the previous days (Fig. 3) were more ventilated with a reduced excursion in temperature and especially in relative humidity. These factors are probably to be blamed for the “less classical” diurnal trend for SV-OOA.

References:

Atkinson, R., Calvert, J.G., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J. and Yarwood. G. (2000) The mechanism of Atmospheric Oxidation of the Alkenes, Oxford Univ. Press., Oxford, UK.

Di Giuseppe, F., A. Riccio, L. Caporaso, G. Bonafé, G. P. Gobbi and F.Angelini, "Automatic detection of atmospheric boundary layer height using ceilometer backscatter data assisted by a boundary layer model", Q. J. R. Meteorol. Soc. 138: 649–663,

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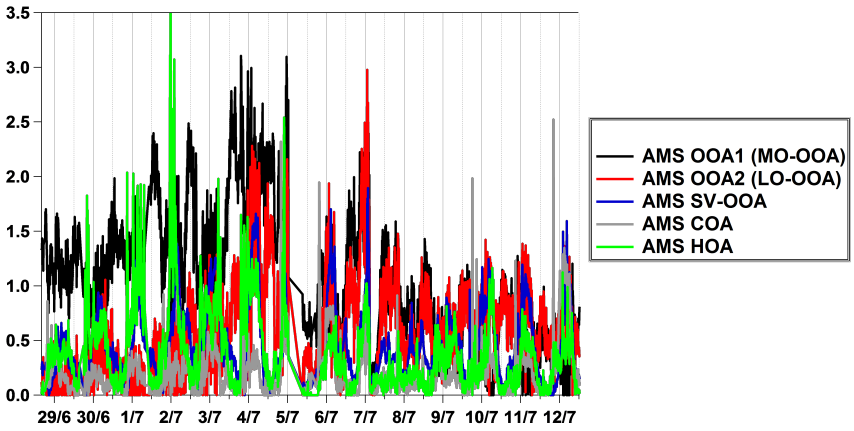

Fig. 1. 5-factor PMF analysis for the duration of the whole campaign.