

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

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Specific Comments:

P3248, L3: The particle growth caused by the uptake of ethanol was studied, too.

Line 2 changed to:

Continental summer-time aerosol in the Italian Po Valley was characterized in terms of hygroscopic properties and the influence of chemical composition therein. Additionally, the ethanol affinity of particles was analysed.

P3248, L4: The relative humidity condition for the measurement of the HGFs should be presented.

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Line 4 changed to:

The campaign-average minima in hygroscopic growth factors (HGFs at 90% relative humidity) occurred just before and during sunrise from 03:00–06:00, but more generally, the whole night shows very low hygroscopicity, particularly in the smaller particle sizes.

P3249, L3: In the results and discussion section, the relation of the lowest HGFs to the formation of organosulfates is not discussed.

Please see further parts of this document.

P3249, L18: “(CCN)” may need to be added because this abbreviation appears later.

Changed the line to:

Additionally, hygroscopicity can determine the particles ability to act as a cloud condensation nucleus - CCN (Hanel, 1976; Hegg et al., 1993; Svenningsson et al., 1994; McInnes et al., 1998; McFiggans et al., 2006; Anttila et al., 2009).

P3250, L22-27: The references and the explanation of this sentence do not match.

All references report both AMS and HTDMA data.

P3250, L28-P3251, L1: The reference(s) reporting the result should be added.

This sentence refers to the references in L25-27

P3251, L5: The expression “HTDMA-AMS tandem” is not appropriate, if the authors intend to state that HTDMA and AMS were operated in parallel. Further, the meaning of the abbreviation “AMS” is not given here.

Changed to:

However, field applications of HTDMA and aerosol mass spectrometer (AMS) running in parallel have been rather less abundant so far (Gasparini et al., 2004; Mochida et al., 2008; Juranyi et al., 2010; Jones et al., 2011; Raatikainen et al., 2010).

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P3251, L18: The “CPC” should be spelled out because it appears for the first time.

Changed to:

The HTDMA configuration used during the campaign consisted of two Hauke type differential mobility analysers (DMAs), an aerosol conditioner (heated Gore-Tex humidifier) and a condensation particles counter (CPC model 3772) with sample flow of 1 Lmin<sup>-1</sup>.

P3252, L15: It seems that “The transfer functions...” is also a reason for “MDF is...”.

Changed to:

Because the TDMA’s overall transfer probability depends on the GF of the particles, MDF may be smoothed and skewed.

P3252, L17: “broadened” instead of “smoothed” seems appropriate.

Smoothing in this context refers to the loss of fine details of measurement distribution function

P3252, L17-19: The sentence implies that the effect of multiply charged particles on the measurement of GF has been corrected. If it is true, a brief explanation should be given because it is not explained explicitly in the paper by Gysel et al. (2009).

Line 17 concerning the multiple charging has been removed. It only applies to the laboratory studies using nebulizer when the amount of doubly charged particles can be significant. In the ambient measurement, however, the effect is negligible.

P3253, L4-5: It is not explained how the error was estimated.

Added to L5:

Uncertainties of growth factors were estimated for 50 nm particle size based on relative growth factor change between consecutive dry size laboratory measurements for different compounds (Vaattovaara et al. 2005). The estimation was carried out based

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on the 0.1 nm uncertainty in the particle diameter measurements, i.e. 0.1/50).

P3253, L25-27: The type of the Aerodyne AMS (e.g., HR-ToF-AMS) should be given.

Corrected to HR-ToF-AMS.

P3254, L1-3: The collection efficiency used in this study should be explained, with the justification for it.

For mass concentration calculations, an empirical particle collection efficiency (CE) factor of 0.5 was used, already widely found to be representative for ambient particles in many AMS studies (Jayne et al., 2000; Canagaratna et al., 2007, Middlebrook et al., 2012) and the value of 0.5 was further validated by good inter-comparison with off-line ion mass concentration measurements obtained during the field study (Decesari et al., 2013).

P3255, L10-11: If the number of the factors is arbitrarily, the reason for the use of five factors should be explained.

Please see answer to Referee 1, where the 5 factor solution is presented and discussed.

P3255, L21-24: Data used for the explanations should be noted.

If the Referee refers to the detection of deep convective clouds, we followed their evolution in North Italy using the METEOSAT images.

P3256, L3-7: The air circulation patterns of Po Valley WNW, West1, and West2 are not explained explicitly.

“West” reflecting a longer range transport from western Europe and the Atlantic (two different zones, West 1 “Western Europe” and West 2 “Atlantic”) and “PoV” describing a weaker circulation with more local (Po Valley) component.

P3256, L12: If “PoV WNW” is identical to “Po Valley WNW”, same abbreviation should

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be used. If not, the characteristics of “PoV WNW” should be explained.

Changed to the same abbreviation P3256, L24-P3257, L1: The meaning of “overall HGF values” is not clear.

Overall HGF values = values averaged between the measured sizes, as mentioned earlier in this chapter. The line has been modified to:

The second part of campaign (5 July 2009 to 11 July 2009) shows less variability and higher general (averaged) HGF values, ranging from 1.25 to 1.4.

P3257, L2: Some HGF values (overall mean HGF) at night in the last two days seem to be lower than 1.3.

Should be 1.25 – changed.

P3257, L19: The word “interpolated” may be more appropriate than “extrapolated”.

Changed to “interpolated”.

P3257, L20-22: It is not explained whether the HGFs were lowest regardless of the particle sizes. If the times for the sunrise were earlier than 06:00, the expression “just before” may be inappropriate.

It is explained that the deepest drop occurred especially in the smaller sizes in the time between 3 and 6am, thus including the dusk (just before the sunrise) and the sunrise as well.

P3257, L22-23: The explanation is difficult to follow. If the increase in the HGFs with time is the main point, the differences of the HGFs of the particles with same diameters should be explained.

Line changed to explain better the difference in the HGF between the sizes:

The HGF difference between the measured sizes was biggest at night with HGF 1.18 recorded for the smallest sized particles (35 nm) and HGF 1.38 recorded for the largest

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sizes (165 nm).

P3258, L12: The time at which the small minimum was observed should be explained.

Sentence removed (reference to the older version of the figure).

P3259, L11: According to Fig. 3., the peak of the OGF with the value of 1.13 appeared later (05:00).

The HTDMA minimum is at 03:00 and the OTDMA maximum at 05:00. Both occur at low temperature close to temperature minimum at 04:00 when total organics, sulphate and nitrate showed their highest values. At 03:00 OOA1 is partly causing HTDMA minima. Actually, the OGFs has already increased over 1.11 at 03:00 when OOA1, OOA2 and SV-OO are high but the maximum is seen later because PMF factors of OOA2 and HOA increase until 05:00 while other organics decrease slightly. At the same time, HGF slightly increases. Overall, GFs changes are small from 03:00 to 05:00.

P3259, L12-13: It seems that the “fraction” of BH particles is discussed. This is not explained explicitly.

Line changed to:

The BH fraction of HGF tracks the HOA signal the closest.

P3259, L14: It is not clear what “HGF” here means. If it corresponds to “overall mean HGF” in Fig. 2a, the diurnal pattern should be presented. Further, clear evidence to support the anti-correlation should be presented. Presentation of the correlation coefficient is worth considering.

Line changed to:

“OGF diurnal variation seems to follow roughly AMS organic mass load, while generally contrasted with HGF diurnal pattern, especially in BH and LH range. “

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P3259, L18-21: The explanation after “although...” is difficult to follow. The part may need to be reworded.

Reworded to:

It is also worth mentioning that so called “Cooking Aerosol” (COA) factor concentration is steadily increasing from around 18:00. However, the hygroscopicity and affinity to the ethanol of COA is very similar to both HOA and SV-OOA, thus no visible changes in HGF could be observed.

P3259, L21-22: If the diurnal variation pattern of OGFs is discussed in this sentence, this should be noted.

Reworded to:

At the same time, OGF diurnal pattern is similar to SV-OOA and OOA1.

P3259, L22-23: It is not easy to see whether the changes in sulphate/organics and sulphate/ nitrate ratios were small from Fig.3. It is not clear why the degrees of the changes are explained in this section.

Removed reference to sulphate/nitrate ratios from this section.

Generally, OGFs follow the total organic mass trend while the regional OOA2 concentration dominated at the measurement site.

P3259, L29: It is not explained how the presence of moderately aged aerosol is inferred. Further, it is not explained at which periods they might have been present.

Changed to:

The average 50nm OGF and HGF is plotted with the total AMS organic mass and the HGF-PDF in Fig. 4 where OGF increases when moderately aged, regional (OOA2) aerosol is present (Fig. 5), especially when HGF reaches values around 1.2.

P3260, L3-5: The meaning of “consistent” is not clear. A more explicit explanation is

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preferable.

Changed to:

Generally, the OGFs and HGFs variations are consistent with the relative proportions of organics, sulphates and nitrates, along with changes in the oxygenated level of the organics.

P3260, L14-15: The chemical form of nitrate measured using the AMS is specified as “nitric acid” without justification. Further, this interpretation contradicts the explanation later in this paragraph.

Changed to:

The strong diurnal signal is driven by the nitrate (i.e. ammonium nitrate, based on the high HGF values in accumulation mode sizes) the temporal trend, but is also notably influenced by the organic contribution.

P3260, L17-18: What “thermodynamically” means is not clear. If the statement here is based on the low HGFs, this point should be noted more explicitly. It seems that “nitrate” or “ammonium nitrate” instead of “nitric acid” should be discussed here. P3260, L18-21: The explanation of this sentence is difficult to follow. P3260, L21-24: The authors seem to consider the possibility that the nitrate signal was originated from organonitrates. However, this point is not explained explicitly. High load of inorganic nitrate during the night-time is not supported by the data, if inorganic nitrate and organonitrates cannot be distinguished using the AMS.

L 17-24:

Removed reference to nitric acid and reworded:

It is worth noting that the 35 nm and 50 nm HGF values (i.e. Aitken mode size particles) are low but the 110 nm and 165 nm HGF values (accumulation mode size particles) are high at night (Fig. 5), thus supporting the domination of highly hygroscopic nitrates

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(i.e. ammonium nitrate) in the accumulation mode sizes but the “lower hygroscopicity nitrates” in the Aitken mode sizes. Possible reasons for the low hygroscopicity of particulate nitrate in the small particles are: a) coating by poorly hygroscopic organic compounds, and b) the actual chemical nature of nitrate in Aitken mode particles is organic (nitrate esters), which is consistent with the decrease of OGFs observed between midnight and ~6 AM. In fact, in previous experiments (Vaattovaara et al., 2009) it was found that OGFs of particulate organic matter decrease in high NO<sub>x</sub> conditions and the ethanol affinity of organonitrate is apparently lower than that of the SV-OOA components forming in low-NO<sub>x</sub> conditions. Therefore, our hypothesis of the organonitrate formation provides explanation for both the low HGFs and also the lowering of OGFs in the late night hours. Generally, the formation of organonitrates is expected to be probable, especially in the environment with a high load of NO<sub>x</sub>, NO<sub>y</sub> and organics. Typically, that kind of high load conditions are observed during night time at SPC station. Importantly, NO<sub>3</sub>-initiated oxidation chemistry with alkenes is able to form organonitrates at night (e.g. Atkinson et al. 2000) without sunlight.

After L24 the following text will be added:

Additional data supporting the organonitrate hypothesis using the ATOFMS is included in the supplementary materials.

P3260, L28: The sentence is written as if  $3.2 \mu\text{g m}^{-3}$  is the maximum concentration of nitrate.

Changed to:

Total organic concentration was the highest during night-time and its maximum also corresponds with the high concentration of nitrate,  $3.2 \mu\text{g m}^{-3}$ , occurring around 04:00 (see also Fig. 8).

P3261, L8-9: It is written as if the presence of HOA in the BH fraction is a fact. Similarity in the diurnal patterns itself is not sufficient evidence to state that it is a fact. and P3261,

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L13-14: The dominance of SV-OOA in the LH particles shouldn't be stated as a fact without clear evidence.

In answer to both questions above: This is also supported by the increase in OGF values in the 50 nm size range.

P3261, L17: Whereas the expression “regional OOA2 concentration...” is used in page 3259, the expression “local OOA2” is used here.

On page 3261, line 17 changed to:

After midnight however, local OOA1 contribution increased while regional OOA2 decreased during the night.

P3261, L19: It is not clear to what the degree of the diurnal variability of the MH fraction is compared.

The MH fraction of HGFs exhibited higher diurnal variability in size range from 35nm to 75 nm than 110-165nm, with the strongest pattern seen in the smallest sizes.

P3262, L5-6: It is not very clear why influences of other organic fractions on the peak of OGF can be ruled out.

The OGF increase to 1.14 on the evening before midnight seem to be mainly due to the increase of highly ethanol soluble SV-OOA (the change of other organics and inorganics is minor).

P3262, L6: High growth factor does not necessarily mean high solubility of the solute. The growth factor could also be controlled by the molecular weight of the solute.

Word “solubility” changed to “affinity to”

P3262, L10-11: Anti-correlation is not obvious. It is important to check if the correlation coefficient is negative.

Changed to:

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Figure 6 shows that the hours of the day when the AMS organic mass reaches a maximum (between midnight and early morning) are characterized by decreasing OGF values. This behavior seems to be partly related to a high nitrate/organics ratio (see supplementary material).

P3262, L15: It is important to check if the correlation coefficient between HGF and OGF is negative.

Correlation coefficient obtained was low (-0.3) but statistically significant (t value well below critical).

Line 15 changed to:

The OGF is generally anti-correlated to HGF exhibiting low (-0.3), but statistically significant negative correlation coefficient. The data are of different temporal resolution which made the direct comparison more difficult to perform.

P3263, L13-14: This sentence is difficult to follow. If the increase in the HGFs with time is the point, differences of the HGFs of the particles with same diameters should be explained.

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.

P3263, L16-18: This part may not be appropriate to explain the suggestion of the presence of organonitrates and organosulfates because it is based on the analysis of Case2 time period.

Reworded to:

Diurnal behaviour of HGF and OGF values suggest that the Aitken mode aerosol par-  
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ticles can contain the organonitrates during night time and the organosulphates during day time. The 50 nm OGF shows minima and the 50 nm HGF shows maxima at noon when organosulfates are suggested to form. Additionally, the minima are seen in the 50 nm OGF and HGF values during later hours of the night when organonitrates are suggested to form.

P3263, L22-25: The word “strongest” is not appropriate because the definition of the strength of the patterns is not clear.

Reworded to:

The most distinctive pattern was seen in the reduction in the MH mode from approximately 80% in 165nm sized particles to 20–40% in 35nm sized particles while the LH mode contribution increased from less than 5% to more than 30% over the same size range.

P3263, L15-17: This inference should be addressed in the results and discussion section. Technical Corrections

It has been addressed in the revised version of manuscript.

Note, that The 50 nm OGF shows minima and the 50 nm HGF shows maxima at noon when organosulfates are suggested to form. Additionally, the minima seen in the 50 nm OGF and HGF values during nights when organonitrates are suggested to form.

P3259, L12: The word “HFG” seems incorrect.

Corrected to: “HGF”.

P3259, L22: The word “OO1” seems incorrect.

Corrected to: “OOA1”.

P3259, L28: The expression “plotted against” seems incorrect. Corrected to:

“Plotted with”

## References

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/13/C4163/2013/acpd-13-C4163-2013-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 3247, 2013.