Review on "Vertical profiling of aerosol hygroscopic properties in the planetary boundary layer during the PEGASOS campaigns"

We would like to thank the referees for their detailed and constructive comments, which helped us to improve our manuscript. Our answers to the comments are given below in blue letters, while the referee comments are given in black italics. Additionally, we added the changes we made in the revised manuscript in **blue bold** letters.

Reply to Referee #1:

Overview: Hygroscopic trends are presented from measurements within the evolving boundary layer in the Po Valley, Italy, and in the fully mixed layer in the Netherlands during the PEGASOS 2012 campaigns. Results from the Po Valley conform to expectation – that newly evolving boundary layer aerosol comprises hygroscopic aerosol with a large nitrate fraction contributed by nighttime HNO3 chemistry and cool temperatures. Nitrate fraction decreases as temperatures increase (volatilization) and photochemistry takes place (presumably adding SOA), resulting in suppressed hygroscopicity. It is noteworthy that the hygroscopicity of aerosol in the fully mixed layer is similar to that in the aged residual layer. The hygroscopic fraction of aerosol sampled in the Netherlands was high, though no composition data are presented to offer an explanation. In general, the data presented here are limited (one sampling day for each location), but the text contains excessive detail and should be edited for length. Correlations between hygroscopicity and composition are sparingly presented, and should be expanded. Nonetheless, the detailed probing of an evolving mixed layer (for the Po Valley site) is a unique dataset and worthy of publication. I recommend that the presentation of AMS data be integrated with hygroscopicity results, and that AMS data be more fully utilized in explaining hygroscopicity trends from the Po Valley, while decreasing the detail of the hygroscopic results sections. The paper is recommended for publication after revisions and additions.

We rewrote and restructured sections 4 and 2.3 to make the discussion clearer and more compact (see answers below for more details) as well as the abstract and the conclusion. In particular, we put more emphasis on connecting hygroscopicity and chemical composition data, whenever the latter are available (see section 4). We also decided to exclude data from the Monte Cimone mountain site in Italy and shortened the discussion on possible contributors to the non-hygroscopic mode.

General recommendations:

1) *Overall the paper would benefit from significant compression. As written, the text contains excessive detail and is much longer than necessary. Data from the Netherlands seem somewhat out of place, and the absence of AMS data limits their value. The authors might consider focusing solely on presenting the Po Valley flight in detail, as there is enough presented there to stand on its own – especially once the authors expand the discussion of aerosol composition and utilize more AMS data to explain hygroscopicity trends.*

As mentioned above, we shortened the paper. However, we kept the data from the Netherlands in the paper to show the contrast to the results from Italy. Even though we do not have airborne AMS data available for this flight, the AMS ground measurements are presented and are valuable to complement the WHOPS results.

2) *The connections made between composition and hygroscopicity are rather limited. Presumably you have a wealth of data available from the HR-AMS, including things like the organic oxidation state. What is the average O:C ratio for organics in the residual layer, compared with*

the new mixed layer, for example? The paper would benefit a great deal from expanding the connections between hygroscopicity and composition. On a related note, hygroscopicity results (e.g. 4.1.1, 4.1.2, 4.1.3) are unnecessarily and awkwardly divorced from composition results (e.g. AMS, MAAP, etc). The paper would benefit greatly from co-presentation of hygroscopicity and composition data so that the reader can more naturally make connections between the two, without waiting until the "closure" section.

We added O:C ratio values for the three different layers and the corresponding organic κ values obtained by applying the parametrization from Duplissy et al. (2011). These organic κ values differ only slightly from the overall mean value of 0.11 that we had previously used. Nevertheless, we adapted all results using the actual O:C ratio measured in a certain layer as input for the κ and closure calculations.

Revised text: Page 9459; lines: 6-10:

The κ values for the organics were inferred from the measured O:C ratio using the relationship between O:C and κ value reported in Duplissy et al. (2011) for organics in atmospheric aerosols in three different environments.

Added text: Page: 9469; line: 8:

The O:C ratio inferred from the HR-ToF-AMS measurement (using the method presented by Aiken et al., 2007) was found to differ slightly between the three layers with values of 0.45 ± 0.03, 0.55 ± 0.03 and 0.50 ± 0.05 for the newly forming ML, the RL and the fully developed ML, respectively. The corresponding κ values were estimated to be 0.09, 0.14 and 0.12 in the newly forming ML, the RL and the fully developed ML, respectively (see Sect. 3 for more details on the method to estimate the κ value). The mean O:C ratio of the organics measured at the SPC ground site was 0.60 ± 0.03, which translates to a kappa value of 0.17.

Revised text: Page: 9473; lines: 24-25:

The O:C ratio of the organic matter measured by the AMS was 0.48 ± 0.02. The corresponding κ value of the organic matter is estimated to be 0.11 (Sect. 3). The measured composition of PM1 (Fig. 12) as a whole translates to an average κ value of 0.28 (Eq. 5). This agrees within uncertainty with the WHOPS-derived κ value of 0.25 in the lowermost flight level at 100 m AGL (see Table 3).

3) The Zeppelin was only operated on one day with low wind speeds, low cloud coverage, and *clear skies. I would expect this combination of conditions to be most ideal for formation of an aged residual layer, and that this enhanced residual layer would have a disproportionate impact on the fully mixed layer by midday. It should be mentioned that these results are therefore not generally applicable to the Po Valley and Netherlands, but instead likely represent a maximum impact of residual layer on mixed layer aerosol.*

Indeed, the presented flight days show only one possible scenario for summertime conditions in the Po Valley or the Netherlands. When looking at the Po Valley for example, the measurement day - 20 June 2012, was certainly hotter (27.5 °C) than the average for this period of the year (22.1 ± 3.1 °C for June in San Pietro Capofiume, reference period: 1961 - 2005). However, the climate is changing rapidly in this region of the world, with a positive trend in temperatures of 0.60°C per decade in summertime.

Therefore, the measurements during PEGASOS cannot be considered representative for the late XX century climatology of the Po Valley, but can be more representative of what the climate is becoming. [source of the climatological data: ARPA Emilia-Romagna]. Such conditions favour strong vertical mixing and the residual layers' entrainment.

The representability of the results for the flight above Cabauw in the Netherlands is discussed in Sect. 4.2.4, where the results are compared against existing literature data.

4) *Hygroscopicity results (e.g. 4.1.1, 4.1.2, 4.1.3) are quite long and excessively detailed. Stick to the main points, let the figures do the talking, and try to condense these sections substantially.*

We shortened these sections for the revised manuscript.

5) *Does the WHOPS instrument adjust refractive index once particles have been humidified? Uptake of water (RI=1.33) lowers overall RI, meaning comparatively less light scattering for the same size particle. This would lead to systematic underestimation of GF, and introduce discrepancies between HTDMA and WHOPS. It would be worth doing a sensitivity study to see how much an error of 0.2 in RI would impact your GF and kappa calculations – just to put HTDMA/WHOPS discrepancies into perspective.*

Revised text: Page: 9454; line: 23:

The index of refraction of the grown particles gradually approaches the index of refraction of pure water (m_{H2O}=1.333) with increasing hygroscopic growth factor. This effect is accounted for in our data analysis approach as detailed in Rosati et al. (2015).

6) *Specific comments/questions:*
Throughout: "Data" is plural. "Datum" is singular. Use "data are" instead of "data is".
Throughout - especially in Abstract: report data with ± standard deviation.

Grammatical errors were corrected. Standard deviations have been added in the abstract and main text where appropriate.

7) *p. 9460 line 26: With significant industrial sources in the Po Valley, I'd expect to see plumes of fresh, non-hygroscopic aerosol like this.*

In Section 4.1.2 we argue that the non-hygroscopic particles are unlikely to originate from combustion sources. The true nature of these particles – dust, tar balls or biological particles – remains speculative.

Revised text: Page 9460; line: 26:

An exception is the measurement taken at around 12:45 LT and 100 m AGL, when the mean κ was considerably lower due to a strongly increased fraction of non-hygroscopic particles (see Fig. 6) likely originating from a local source.

8) *p. 9461 line 9: replace "spread" with "variability"*

We changed this in the revised manuscript.

9) *p. 9462 line 14-16: I disagree with this conclusion. The significant changes in hygroscopicity at lower altitudes are likely primarily caused by the change in nitrate mixing state. Nitrate fraction is enhanced at low temperatures in shallow boundary layers in the morning, owing to nighttime HNO3 chemistry. Nitrate fraction drops significantly during the day due to volatilization of ammonium nitrate – the result of both increased temperatures and dilution with the deepened*

mixed layer. While an enhancement in externally-mixed hygroscopic growth might indicate strong local influence, a general decrease in hygroscopicity doesn't necessarily.

We agree with this conclusion and changed the text as follows:

Revised text: Page: 9462; line: 14-16:

This can be explained by the differing chemical composition of the particles in these layers, with a very strong nitrate fraction in the new ML which decreases in the fully developed ML.

Revised text: Page: 9468; line: 15-20:

During IHP1/2 a clear difference between the mass fractions in the new ML with a high nitrate fraction of 20–22% (Fig. 8a and c) and the RL with a nitrate contribution of only 5% (Fig. 8e) were observed. This increased nitrate fraction in the new ML can be explained by the accumulation of nitrate species overnight at low temperatures, which are formed in the nocturnal surface layer and are then entrained into the new ML after sunrise. The nitrate drop in the fully developed ML is due to volatilization of nitrate species as a result of both, increased temperature and dilution.

10) *p. 9463 line 26-29: BC in heavily anthropogenically-influenced areas is almost entirely coated with secondary material. For example, results from the SP2 and ATOFMS in the Los Angeles Basin indicated that the vast majority of rBC was coated – even at short photochemical ages (<1h). See Metcalf et al., 2012 and Hersey et al., 2013 (JGR-Atmospheres). So it's highly conceivable that you may have observed coated BC particles here. Nothing to really change here, but I think you're on the right track in considering coated BC.*

We added the proposed citations to the revised manuscript.

11) *p. 9464 line 15 to 9465 line 5: My concern with investing in a long discussion of mineral dust and biological material is that you have no composition data to back it up. Unless you can support these possibilities with very strong presentation of HYSPLIT back-trajectories that suggest dust influence or something like seasonal pollen count data to support biological material, any suggestion that they contribute to the non-hygroscopic fraction is tenuous (and certainly doesn't belong in the abstract - p. 9447 line 23).*

We shortened this discussion and clarified that these are only possible contributors. We also deleted the sentence from the abstract.

12) *One other strong possibility is that hydrophobic SOA coatings may inhibit hygroscopic growth within the WHOPS instrument, resulting in an overestimation of the non-hygroscopic fraction and overall underestimation in apparent GF and kappa. I'm guessing that the humidification time constant in the instrument is on the order of a few seconds, while equilibrium with water vapor for coated particles can take minutes or hours. See Shiraiwa et al., 2011 (Proceedings of the National Academy of Sciences 108 (27), 11003-11008) and Koop et al., 2011 (Physical Chemistry Chemical Physics 13 (43), 19238-19255) for more discussion.*

The residence time of the particles in the humidification system of the WHOPS is approximately 20 s (details on the humidification system are presented in Rosati et al., 2015a). The study by Sjogren et al. (2007) shows that 10-20s are sufficient to reach a stable hygroscopic growth factor for most investigated examples, while >40 s were needed for some extreme systems. Therefore, we think that 20 s should be sufficient for most aerosol particles to reach their equilibrium growth factor including complete deliquescence.

Revised text: Page: 9454; line: 3:

Alternatively, the size-selected dry particles are humidified before being directed to the WELAS to measure the wet optical response (residence time at the high RH ~ 20 s).

13) *p. 9466 line 6-8: This might support the dust option. I see that the characteristic humidification time in the HTDMA is longer than in the WHOPS (line17-29). It may be that particles are exposed to elevated RH for longer in the HTDMA, causing some of those coated, diffusion-limited particles to come closer into equilibrium with water vapor in the HTDMA than in the WHOPS. It's worth checking. These diffusion inhibition issues are always something that should be considered with SOA and aged, coated particles, and in your case might counteract some of the ammonium nitrate volatilization issues.*

There has been a misunderstanding in this paragraph. What we meant is that the humidification time in the WHOPS is longer than in the HTDMA, however, the time in the dry section of the WHOPS is shorter compared to the HTDMA. Therefore, losses of ammonium nitrate in the WHOPS should be smaller as particles have less time to evaporate.

We changed the text in the revised manuscript as follows:
Revised text: Page: 9466; line: 17-24:

Gysel et al. (2007) provided strong evidence for ammonium nitrate artifacts in the dry part of the HTDMA measurement, which resulted in underestimated hygroscopic GFs. The HTDMA employed in SPC featured smaller residence times in the range between 10-15s, which should minimize nitrate evaporation losses, however, they can still not be fully excluded. GF measurements done with the WHOPS are most likely less susceptible to ammonium nitrate evaporation, as the residence time in the dry part of the instrument is shorter due to higher flow rates.

14) *p. 9466 line 28-29: possibly, but I think the physical arguments from humidification and ammonium nitrate volatilization are bigger issues here.*

We included additional supporting arguments for the other hypothesis.

Revised text: Page: 9466; line: 26-28:

Another possible reason could be that the particles at the ground (measured in the surface layer) and at 100 m AGL were not exactly the same due to e.g. direct influences by local emissions. This hypothesis is also supported by measurements of the particles' optical properties on this flight day, presented in Rosati et al. (2015b). A comparison of the scattering and extinction coefficients between the airborne and ground based measurements, shown in Fig. 4 and 8 in the stated paper, respectively, also illustrate differences between the two altitudes, which are independent on the hygroscopicity measurements and associated artifacts.

Rosati, B., Herrmann, E., Bucci, S., Fierli, F., Cairo, F., Gysel, M., Tillmann, R., Größ, J., Gobbi, G. P., Di Liberto, L., Di Donfrancesco, G., Wiedensohler, A., Weingartner, E., Virtanen, A., Mentel, T. F., and Baltensperger, U.: Comparison of vertical aerosol extinction coefficients from in-situ and LIDAR measurements, Atmos. Chem. Phys. Discuss., 15, 18609-18651, doi:10.5194/acpd-15-18609-2015, 2015b.

15) *p. 9472 line 6: double negative; change "neither/nor" to "either/or"*

We changed this in the revised manuscript.

16) *p. 9473 lines 7-8: or water-uptake-inhibited, coated particles*

We consider it unlikely that hygroscopic growth is fully inhibited on a 20 s time-scale (see comment above).

Reply to Referee #2:

General comments:
The manuscript presents a case study of aerosol properties in the atmospheric boundary layer measured from an airborne platform in two places for one day in each location. Suite of instruments on-board of the airship allowed measurement of hygroscopicity and chemical composition including estimate of equivalent black carbon mass concentration. The flights were performed in the vicinity of ground sites equipped to provide similar measurements. The authors discuss measured hygroscopic properties of 500 nm aerosols, results of composition-hygroscopicity closure studies as well as intercomparison with ground sites. It should be noted that experimental data on hygroscopic properties of ambient aerosols are scarce, especially for the larger (few hundred nanometres) aerosols in the atmospheric boundary layer. Undoubtedly, the results of this work could be published in ACP, however only after the manuscript has undergone appropriate revision.
The manuscript needs to be re-arranged to separate description of the instrumentation and methods from the results and conclusions; it seems to be burdened with trivial statements and unsupported speculations, which should be avoided. Technical aspects of the current work may be presented in the Supplement to keep the main manuscript concise and focused. The authors are advised to secure help from a professional editor to improve readability of the manuscript.

We rewrote and restructured sections 4 and 2.3 to make the discussion clearer and more compact (see answers below for more details) as well as the abstract and the conclusion. We also decided to exclude data from the Monte Cimone mountain site in Italy and shortened the discussion on possible contributors to the non-hygroscopic mode. The detailed changes are presented below.

Specific comments:

1) *Please use generally accepted abbreviation for altitude in meters above ground: m a. g. l. or m AGL.*

We changed all occurrences of **m a. g**. to **m AGL.**

2) *PP 9447-9448, Abstract: The abstract needs major revision to better reflect actual work done and substantiated conclusions reached; currently a reader gets an impression of much broader experimental data basis for the claimed conclusions. Also, it would be advisable to be more scrupulous in descriptions, for example "flown just after sunrise" looks like an exaggeration for the flight started 3 hours after sunrise.*

We adapted the abstract to be more precise.

3) *P 9448, L 17: References to entire IPCC reports are not practical; please site the specific reference(s) in the IPCC 2013.*

As we refer to chapter 7 (Clouds and Aerosols) in the IPCC 2013 we changed the reference to: *Boucher, O., D. Randall, P. Artaxo, C. Bretherton, G. Feingold, P. Forster, V.-M. Kerminen, Y. Kondo, H. Liao, U. Lohmann, P. Rasch, S.K. Satheesh, S. Sherwood, B. Stevens and X.Y. Zhang, 2013: Clouds and Aerosols. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.*

4) *P 9450, L 12-14: There is at least one instrument for size resolved hygroscopicity measurements that was built and deployed earlier than DASH-SP, see: Hegg, D. A.,*

Covert, D. S., Jonsson, H., and Covert, P. A., 2007: An instrument for measuring sizeresolved hygroscopicity at both sub- and super-micron sizes, Aerosol Sci. Technol., 41, 873–883.

Revised text: Page: 9450; line: 12-14:

The first instrument built for this special task is the aerosol hydration spectrometer (AHS; Hegg et al., 2007). The setup comprises two optical instruments, one to get a dry optical and the other one a humidified optical response. However, the measurement is performed for a polydisperse size distribution rather than investigating the hygroscopic properties of aerosol particles with one specific diameter. The differential aerosol sizing and hygroscopicity spectrometer probe (DASH-SP; Sorooshian et al., 2008) on the other hand, is constructed using a combination …

5) *P 9452, L 5-13: Please describe state variables measurement (temperature, humidity, wind speed, etc.) that has been made on board of the airship; including type of sensors, time response, averaging, etc.*

We propose to present details on instrumentation together with mean values of the potential temperature and relative humidity, as requested in comment 19, in the supplementary material (please see response to comment 19 for more details).

6) *Please provide a short description of inlets for the WHOPS, AMS, and aethalometer. Are they isokinetic? Any estimates of transmission efficiency?*

We included a short description of the inlets for each instrument.

Revised text: Page: 9455-9456; line: 28; 1:

The particles were sampled through a 1500 mm long tube (4 mm ID), ending about 200 mm below the bottom hatch of the Zeppelin. A constant pressure inlet, consisting of an orifice that is pumped with variable flow and installed between the aerosol inlet and the AMS, was used to regulate the downstream pressure to 800 hPa independent of upstream pressure. This ensured constant sampling conditions for the AMS. Within the AMS, the particles pass a critical orifice and an aerodynamic lens, which focuses particles of sizes between 100 and 700 nm into a narrow beam.

Revised text: Page: 9453; line: 24:

Briefly, particles are collected through an isokinetic inlet developed for an average flight velocity of 50 kmh^{-1} before they reach the WHOPS. Then they are dried…

Revised text: Page: 9457; line: 1:

The aerosol was collected through the same isokinetic inlet and sampling line as for the WHOPS.

7) *P 9453, L 4-7 and 17-18: Please elaborate how the mixing layer depth was retrieved from the ceilometer data. Automated algorithms to retrieve atmospheric boundary layer height from ground based remote sensing measurements (lidar, sodar, ceilometer, radar wind profiler, etc.) are notoriously unreliable. Since the mixing layer depth is one of the key parameters in interpretation of the results, its retrieval procedure should be presented. Is there any radiosonde data from SPC meteo station or Hague Airport available for flight days? Radiosonde derived mixing layer depth could provide useful "hints" for interpretation of ceilometer data.*

Radiosonde data is available for the two measurement days, however, during the time of the flight only one launch was performed and consequently, only one data point is available from these measurements. Therefore, we decided to use the continuous measurements from remote sensing instruments. Additionally, we added a new figure to the supplement, illustrating height profiles of the potential temperature (Θ) as measured on board the Zeppelin (see answer to comment 18 below).

Added text: Page: 9453; line: 6:

Retrieval of the estimated mixing layer height is performed by operating on a graphical interface presenting the maximum gradient points in the signal daily plot. In this way, the operator solves the ambiguities related to multiple relative maxima often present in the ceilometer signal (e.g., Angelini et al., 2009). The typical imprecision due to the operator's choice amounts to 3 pixels, i.e. ±45 m.

8) *PP 9453-9455, Section 2.3.1: The description of how the WHOPS works is not complete; please describe "wet" part. Also see comments to PP 9461-9465 and PP 9465 L 24-26.*

Revised text: Page: 9453-9454; lines: 21-25; 1-7:

On the Zeppelin the WHOPS was used to determine hygroscopic GF. All instrument specifications, as well as associated calibration and data analysis procedures, are presented in detail in Rosati et al. (2015). Briefly, particles are collected through an isokinetic inlet developed for an average flight velocity of 50 kmh^{-1} before they reach the WHOPS. They are then dried (RH<10%) and size selected in a differential mobility analyzer (DMA). In a next step, the dry particles are guided directly to a WELAS 2300 optical particle spectrometer (WELAS; Palas GmbH, Karlsruhe, Germany) to measure the dry optical response. Alternatively, the size-selected dry particles are humidified before being directed to the WELAS to measure the wet optical response (residence time at the high RH ~20 s). Multiply charged particles appear as a distinctly separated mode in the optical size distribution measured by the WELAS and are discarded from the further data analysis. Hygroscopicity measurements are typically performed at RH=95%, where the uncertainty in the humidity measurement is estimated to be ±2%. Since the RH to which particles were exposed to varied only between ~94-96% during both flight days, no further RH corrections were applied to the results.

9) *P 9453, L 24-25: What is "dry" RH? Was it controlled/measured in any way?*

The dry conditions were always characterized by RH<10%. This RH was continuously monitored throughout all measurements. The revised section 2.3.1 includes now these details (see also response above to comment 8).

10) *P 9454, L 3-8: Please provide short description of measuring protocol (timing, averaging, size change and wet/dry sequences, etc.) for the WHOPS operation.*

Added text: Page: 9454; line: 8:

Particles with a dry mobility diameter of 300 nm or 500 nm were alternately probed during 250 s per size, whereof 150 s were used for the wet-mode and 100 s for the dry-mode. The results were averaged for each flight segment (probed layer) at a constant flight altitude. This ensured that each GF-PDF shown in Figs. 5, 7, 12 and 15 is based on more than 90 detected particles.

11) *P 9454, L 16-19: Any DMA has a well-known artefact of "double sized, double charged" particles – any corrections for this artefact implemented in the WHOPS procedure?*

Added text: Page: 9454:

Multiply charged particles appear as a distinctly separated mode in the optical size distribution measured by the WELAS and are discarded from the further data analysis.

12) *P 9454, L 21-25: For absorbing aerosols the real part of the refraction index found via the presented technique is biased low; so, strictly speaking, this retrieved parameter is not the real part of refraction index.*

Indeed, the effective index of refraction that we retrieve is not just the real part of the index of refraction but also dependent on the absorbing properties of the analysed particles. Therefore, we use the term "effective" and propose to clarify the definition as follows:

The term "effective index of refraction" has been clarified:

The qualifier "effective" is used because the true index of refraction is slightly different due to simplifications such as assuming an imaginary part of zero, spherical particles and a homogenously internally mixed aerosol (see Rosati et al., 2015, for more details).

13) *P 9454, L 26 - PP 9455, L 11: This paragraph belongs to the Results and Discussion section. Figure 2 does not show "the temporal variability". Please try to correct the "effective" index of refraction for absorbing nature of the aerosols in both locations when comparing to other measurements of the refractive index.*

Figure 2 illustrates the temporal variability of the effective index of refraction shown as the distribution of the values found throughout the campaign. We moved Fig. 2 to the supplement. The results for the effective index of refraction are now only briefly mentioned in the main text as they are for the most part only of technical interest for the data analysis approach. The comparison of the observed effective index of refraction to literature data has been deleted as it does not exactly reflect the true real part of the index of refraction. With that it becomes obsolete to correct the effective index of refraction for the absorbing nature of the aerosol, which would have required plenty of assumptions too.

14) *P9455, L 12-23: Please provide short description of measuring protocol (timing, averaging) used on ground site HTDMA's.*

Revised text: Page: 9455; lines: 12-14:

The SPC site was equipped with a hygroscopicity tandem differential mobility analyzer (HTDMA; see e.g. Swietlicki et al., 2008) in order to determine the hygroscopic properties of particles with 4 different dry diameters between 35 and 200 nm. Each scan to record a GF-PDF at a fixed dry size lasted 500 s in total, thus providing a time resolution of 1.8 measurements per hour for each dry size.

15) *P 9456, L 28 - PP 9457, L 6: Please provide short description of measuring protocol (timing, averaging) for AE42 aethalometer.*

Added text: Page: 9457; line: 1:

eBC concentrations were logged with a time resolution of 2 min and averaged for the time needed to probe a certain layer.

16) *P 9458, L 8: Looks like unfinished sentence?*

Revised text: Page: 9458; line: 8-10:

For a composition-hygroscopicity closure, the κ values derived from the GF measurements (WHOPS) are compared to those derived from the chemical composition measurements (AMS and aethalometer).

17) *P 9459, L 18-19: Please provide a short description of the flight pattern (linear, box, spiral or ramp ascend/descend, etc.) and a distance from the ground site during measurements, if in excess of a few kilometres.*

Revised text: Page: 9459; line: 17-18:

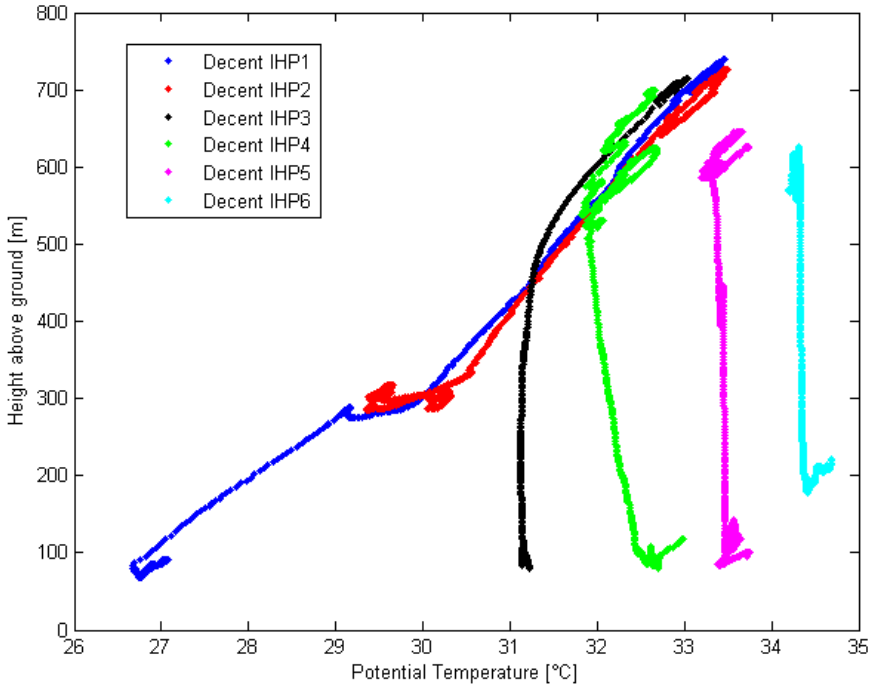
The vertical flight pattern performed on the 20 June 2012 is shown in Fig. 3 and was obtained by flying spirals at selected constant heights and straight ascends and descends. During this day vertical profiles were measured within 5 kilometres horizontal distance from the SPC site …

18) *P 9459, L 23-25: Figure 3 shows time trace of Th and RH, rather than vertical profile. It might be beneficial to present vertical profiles of Th and RH measured on descent (minimal influence of the airship body?) to help the readers get another (independent) pattern of the mixing layer depth evolution (see also comment P 9453, L 4-7 and 17-18).*

Revised text: Page: 9459; line: 24-25:

Figure 3 depicts the temporal evolution of potential temperature (Θ) and RH observed during the flight at different altitudes. The shaded area denotes the estimated mixing layer height provided by Ceilometer-Lidar data.

We propose to include the following figure illustrating height profiles of the potential temperature (Θ) to the supplementary material.



Supplement:

Height profiles of the potential temperature (Θ) during the flight on 20 June 2012 in the Po Valley are presented for all height profiles IHP1-6 using only data from the Zeppelin descents. These data provide an independent measure of the mixing layer height, showing that only during IHP1 and 2 a clear layering of the PBL is visible with a mixing layer height of approximately 300 m AGL.

19) *PP 9460 - 9461: Section 4.1.1 needs to be revised. It is not clear why IHP3 has been excluded from discussion – it seems to be in line with general pattern of growing ML. It might be beneficial to present values for all flight legs separately in Table 2; please include also averaging time, mean RH and Th (or T) for each leg. It would be interesting to see GF (corrected to 95%) measured at the ground site for each leg as well.*

We revised the explanation on why IHP3 and IHP4 were excluded from most figures and discussion (see revised text). Averaged values of potential temperature and RH for each probed layer at a constant level are included in a new table in the supplement. The SPC-GFs corrected to RH=95% for each profile are now included in the revised Table 2, as presented below (response to comment 20).

Revised text: Page: 9460; line: 23-25:

After ~11:00 LT a second set of profiles was performed. To study particles in the fully developed ML the results from IHP5/6 (~12:30–14:00 LT) are considered, while IHP3 and IHP4 are excluded as the ML had not reached its maximum height and could, therefore, be influenced by the RL or the entrainment zone between the layers.

Supplement Table 1:

	Altitude	*Layer*	*Zeppelin*	*Zeppelin*
			Θ [°C]	*RH [%]*
IHP1/2	*100 m*	*New ML*	*26.0 (±0.6)*	*60.1 (±2.0)*
	700 m	*RL*	*33.0 (±0.9)*	*39.4 (±3.1)*
IHP5/6	*100 m*	*Fully developed ML*	*33.4 (±0.6)*	*31.5 (±3.1)*
	700 m	*Fully developed ML*	*33.6 (±0.5)*	*36.5 (±4.2)*

Mean potential temperature (Θ) and relative humidity (RH) during IHP1/2 and IHP5/6 with respective standard deviations representing the temporal variability. Results are presented for two different altitudes, 100 m and 700 m AGL. Measurements of the temperature (Pt100-Sensor; OMEGA; 15s time respond), RH (HMP45-Sensor; Vaisala; 15s time respond), height above ground, wind-speed and direction (all three retrieved by measurement of the pressure using sensors #239 and #270; Setra) were continuously recorded on board the airship. All of these measurements were logged with a 100 Hz frequency and finally averaged over 10 data points.

20) *The "upper" leg of IHP4 seems to be "odd" in sense that airship altitude was not kept constant, at the same time the airship was in the vicinity of the ML top; it is quite possible that part of the leg was within the ML or the entrainment layer. For this reason, IHP4 should not be classified/averaged as flown in "fully developed ML" here and in subsequent sections of the manuscript.*

After a thorough analysis, we decided not to include IHP4 for the calculations of the fully developed ML as indeed it cannot be clearly classified as part of this layer. Consequently, we adapted Fig. 5,7, 8 and 9 and all instances in the manuscript were the fully developed ML is defined. Also, the mean values

of the GF and κ in the fully developed ML were recalculated including only IHP5 and 6. However, we want to note here, that the differences are minimal.

Adapted Table 2:

	Altitude		*Zeppelin-WHOPS*	*Zeppelin-WHOPS*	*Zeppelin-AMS + Aethalometer*
			GF(95%)	κ_{WHOPS}	κ_{chem}
Size			*500 nm*	*500 nm*	*PM1*
IHP1/2	*100 m*	*New ML*	*1.88 (±0.19)*	*0.34 (±0.12)*	*0.26 (±0.06)*
	700 m	*RL*	*1.61 (±0.16)*	*0.19 (±0.07)*	*0.22 (±0.05)*
IHP5/6	*100 m*	*Fully developed ML*	*1.49 (±0.15)*	*0.14 (±0.06)*	*0.19 (±0.04)*
	700 m	*Fully developed ML*	*1.63 (±0.16)*	*0.20 (±0.08)*	*0.20 (±0.04)*
			SPC-HTDMA	*SPC-HTDMA*	*SPC-AMS + MAAP*
			*GF(95%)**	κ_{HTDMA}*	κ_{chem}
Size			*200 nm*	*200 nm*	*PM1*
IHP1/2		*New ML*	*1.61 (±0.22)*	*0.19 (±0.04)*	*0.31 (±0.08)*
IHP5/6		*Fully developed ML*	*1.60 (±0.21)*	*0.18 (±0.04)*	*0.21 (±0.06)*

*HTDMA uncertainty calculated assuming 2% accuracy in the RH measurement.

21) *The hypothesis of an aerosol layer with special properties at 100 m AGL in presumably convective boundary layer around 12:45 seems to be far-fetched; it should be corroborated by measurements, if any available, like significant change in total aerosol concentration, scattering, extinction, etc.*

We do not have any other data supporting our hypothesis and, therefore, we decided to delete the sentence on page 9460-9461, lines 26-27 and 1.

22) *PP 9461 - 9465: Section 4.1.2 needs to be revised. Description of how aerosol mixing state could be inferred from the WHOPS measurements should be moved to Section 2.3.1. It is not clear what "kind" of PDF is shown in Fig. 5: total sum/area of a PDF should come to 1.0 (or 100%), neither seems to be the case with all presented GF-PDFs. Non-hygroscopic mode that is present in all and every GF-PDFs measured by the WHOPS is really surprising; it looks rather like an artefact of the instrument. Ambiguity of relationship between the "wet" scattering cross section and GF is a major limitation of the WHOPS (as it is discussed in WHOPS introductory paper, Rosati et al, 2015). It is assumed, that the WHOPS is operated within certain "safe" limits of dry sizes, effective refractive indices, and growth factors where "sigma"-GF relationship is unambiguous. The problem is that these "safe" limits were found under approximation of non-absorbing aerosol; for absorbing aerosol these "safe" limits should be different, possibly not including the whole range of effective refraction indices observed in the current work. Detailed study of this problem is obviously beyond the scope of the current work, but it should be discussed in Section 2.3.1.*

The description of the mixing state retrieval has been moved from Section 4.1.2 to the experimental Section 2.3.1.
Normalization of the GF-PDFs: the GF-PDFs do actually have unit area. Subtle deviations from unity may occur due du inaccurate graphical reproduction.

The non-hygroscopic mode is indeed surprising. However, we are confident that the non-hygroscopic mode is not an artefact. Already for the technical paper (Rosati et al., 2015a) we assessed but discarded various potential problems. Several arguments are:

- The non-hygroscopic particles never appeared when e.g. measuring laboratory generated ammonium sulfate aerosols. Therefore, it is not a problem of the optical sizing of non-absorbing particles.
- The optical sizing is a single particle measurement. Thus the optical sizing of the non-absorbing particles will not be affected by the presence of absorbing particles.
- Light-absorbing particles, which would also have a different index of refraction than that applied in the data analysis are a potential problem. Candidates are e.g. black carbon containing particles. We performed a sensitivity analyses to estimate at which GF such BC containing particles would show up in the WHOPS (also considering bias between mobility diameter and volume equivalent diameter for fractal-like particles). We came to the conclusion that most BC-containing particles would not show up exactly at GF=1, except for a minor fraction with exactly matching "compactness" and coating thickness.
- The optical properties and shape of light-absorbing particles do vary from particle to particle and with time and in space. Therefor it is not expected that such BC-containing particles, or some other issue with inappropriate assumption for the optical calculations, would always produce an artefact non-hygroscopic mode that always appears at the same GF. However, the non-hygroscopic mode observed in this study consistently appears at GFs very close to unity.

23) *P 9464 L 29 - PP 9465 L 2: "Influence of Saharan dust intrusion . . . can be expected for the day of the Zeppelin flight" – so what is exactly HYSPLIT show? This is the only ground for a rather far-reaching conclusion of dust presence and its effect on aerosol hygroscopicity.*

Revised text: Page: 9464; line: 29:

The HYSPLIT model for Saharan Dust Intrusions (specific analysis by "Spain HYSPLIT"; http://www.ciecem.uhu.es/hysplit/; not presented here) predicted Saharan dust all the way down to the lowest atmospheric layer (100 m AGL) near the SPC site. However, we do not have additional data to support these calculations.

24) *P 9465 L 19-21: Direct comparison of the airborne measurements with MTC ground site seems to be not very relevant here due to (a) horizontal separation of 100 km (over 5 hours' travel time with 5 m/s winds), (b) "MTC is situated at a much higher elevation than the Zeppelin NT was flying", and (c) ground site measurements are always affected by local ground layer/sources (e. g. see current manuscript P 9660 L 26-28).*

We agree with this statement and removed the part describing any MTC data from the revised manuscript and Figs. 1, 7 and 9 as well as Table 2.

25) *P 9465 L 24-26: This limitation of the WHOPS should be described earlier, in Section 2.3.1 and reflected in the abstract.*

This limitation was on purpose mentioned along with the results rather than buried in Sect. 2.3.1 because it is relevant for correct interpretation of Fig. 7. We did not move it in the revised manuscript.

Due to this limitation we did not include any results from the 300 nm particles in the abstract. Accordingly, we consider it unnecessary to add a statement about this limitation in the abstract.

26) *P 9467, L 4-6: Please elaborate how "differences . . . are influenced by data inversion algorithms".*

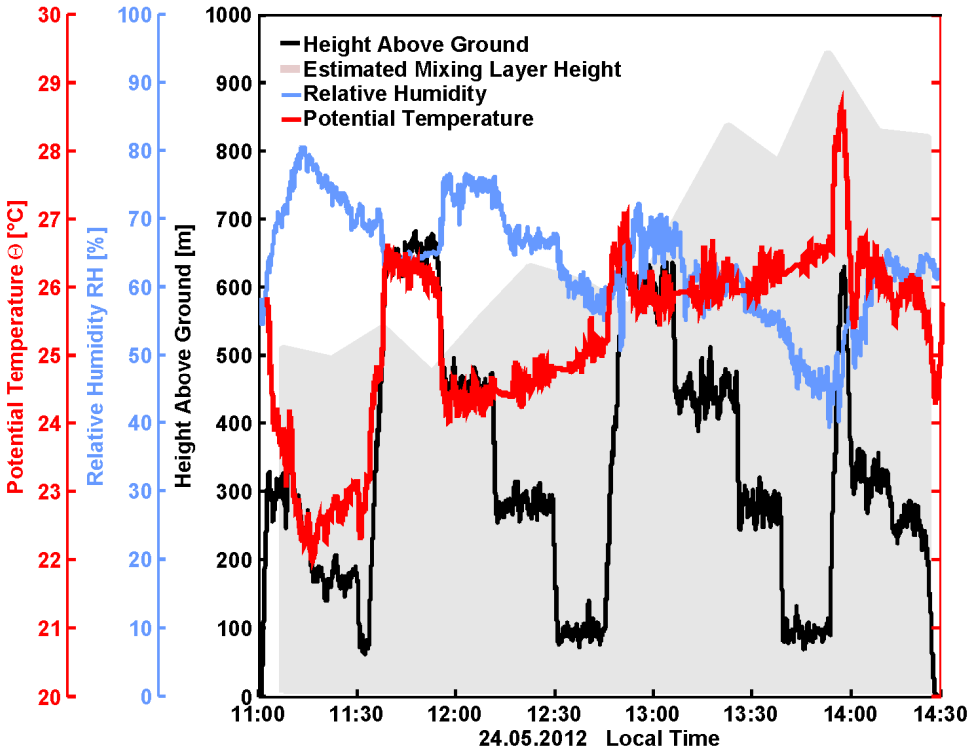
This was in a paragraph about data from the MTC site and has been removed from the manuscript. (An extensive discussion about the potential and limitations of HTDMA inversion algorithms is given in Gysel et al., 2009).

Gysel, M., McFiggans, G. B., and Coe, H.: Inversion of tandem differential mobility analyser (TDMA) measurements. *J. Aerosol Sci.*, **40**, 134-151, doi:10.1016/j.jaerosci.2008.07.013, 2009

27) *P 9471, L 17-21: It might be beneficial to present vertical profiles of Th and RH; see comment to P 9459, L 23-25. Trace for Th in Figure 10 looks like the time series was smoothed or filtered, if so, please explain why, and, if possible, present un-filtered version.*

In contrast to the flights in Italy, the conditions in the Netherlands did not vary substantially throughout the day and therefore we propose to omit profiles of Θ.

We revised Figure 10 (see below) using un-filtered data. Small adjustments had to be done for rapid altitude changes but instead of smoothing the whole-data set the few instances were corrected and the rest of the data is presented as measured on board the Zeppelin.



28) P 9471, L 21-24: see also comment to P 9453, L 4-6 and 17-18.

Added text: Page: 9453; line: 18:

The retrieval of the mixing layer height from the LD40 ceilometer backscatter profiles is based on a wavelet algorithm (Hay et al., 2007). The algorithm determines the height of the maximum in the gradient in the backscatter profile. The difference in backscatter in a small range below and above the retrieved height is used as an estimator for the quality of the retrieved height. Retrieved mixing heights with the highest quality index have comparable accuracy to radiosonde retrieved heights and have an estimated accuracy on the order of 50 m.

29) P 9472, L 22-24: "GF-PDFs between a GF of 0.9 up to 3.2 are visible . . ." – please change wording in this and subsequent phrases.

Revised text: Page: 9472; line: 22-24:

The GF-PDFs range between values of 0.9 until 3.2, which can be attributed to the presence of particles with very different hygroscopic behaviour.

30) PP 9475-9477, Conclusion: the Conclusion needs to be revised in a similar manner as the Abstract (see comment to PP 9447-9448).

We revised the conclusion.

Reply to Referee #3:

This manuscript describes interesting and unique results from measurements of aerosol hygroscopicity, supplemented by particle composition measurements of non-refractory and black carbon components. The measurements were made from an airship, which allowed careful evaluation of particle properties with respect to the dynamically changing planetary boundary layer. The data are really unique and of broad interest. There are no other measurements that enable both the spatial and temporal variation of aerosol hygroscopic properties in a growing PBL to be explored at these resolutions. The manuscript is unnecessarily difficult to follow, however, and needs revision for brevity and clarity. In particular, it needs to focus on specific elements of the data–the variation in hygroscopicity with evolving particle composition as a function of PBL development–and ignore speculative side-topics such as dust contributions. The manuscript now reads like "these are all the interesting things that we saw", rather than "this is an interesting and important phenomenon that we found in two locations and quantified". These data are really fascinating, and much very good analysis has been done. But the manuscript is unnecessarily disorganized, and needs focus and restructuring to be more concise and precise, and to focus on a few key conclusions rather than trying to explain every detail of the data. Some suggestions, which are not comprehensive, follow.

We rewrote and restructured sections 4 and 2.3 to make the discussion clearer and more compact (see answers below for more details) as well as the abstract and the conclusion. We also decided to exclude data from the Monte Cimone mountain site in Italy and shortened the discussion on possible contributors to the non-hygroscopic mode.

Comments:

1) *The manuscript is peppered with imprecise language. For example, on p. 9454, line 15, the OPC technique allows for "mostly unambiguous" attribution of particle diameter to scattering cross-section. Does this mean the method is "somewhat ambiguous"? Can this ambiguity be quantified?*

A detailed description on the possible ambiguities can be found in Rosati et al. (2015).

Added text: Page: 9454; line: 16:

Residual uncertainties with regard to the Mie oscillations amount to less than 7% in the GF (for more details see Rosati et al., 2015).

2) *What are the uncertainties in the hygroscopicity method? Can a numeric value be placed on them? For example, what are the uncertainties associated with interpolating diameters from the look-up table? In situations involving Mie theory, it is not possible to propagate uncertainties from first principles. In these cases, it is appropriate to use a Monte Carlo simulation with a range of input values to determine how the various uncertainties in these parameters propagate through to the final value. I suggest this method be applied, summarized in the main text, and detailed in the supporting material. Use calculated uncertainties for every number in every table and on every graph. Without uncertainties data are meaningless.*

In the technical paper about the WHOPS (Rosati et al. 2015) all relevant uncertainties influencing the WHOPS data analysis are presented, and a final uncertainty for the GF is stated.

Added text: Section 2.3.1:

As described in Rosati et al. (2015) the GF uncertainty for dry particle diameters of 500 nm is approximately ±10% below GF=3.

3) *The acronym "WHOPS" is unfortunate. In the U.S., this is a pejorative term for the descendants of Italian immigrants. While it might be too late to change the acronym from an earlier publication, the authors should be aware of this and minimize its use in the U.S.*

We were unaware of the similarity to the term “wop” (singular) or “wops” (plural) that you refer to. While we regret this coincidence, we introduced the term already for the technical paper (Rosati et al. 2015) and, therefore, it will be hard to change it now. However, we thank the reviewer for mentioning this fact.

4) *More language imprecision (p. 9457 line 10): the AMS "roughly measures particles smaller than 1 um". Use the actual transmission efficiency of the inlet, and say, "the AMS detects particles with diameters < 0.7 um vacuum aerodynamic diameter" or whatever the number is.*

Revised text: Page: 9457; line: 10-13:

As the AMS has a transmission of close to one for particles with aerodynamic diameters between 50 nm and 600 nm, and most of eBC is assumed to be present in the size range below 1 µm, we refer to the chemical composition as of PM_1 (particulate mass with an aerodynamic diameter smaller than 1 µm) in the following.

5) *P. 9458, line 20, "pairing", not "paring".*

We corrected this mistake in the revised manuscript.

6) *P. 9461, lines 9-10, "less spread" relative to what? What "discrepancy" is being discussed? It’s very hard to follow the logic of this paragraph.*

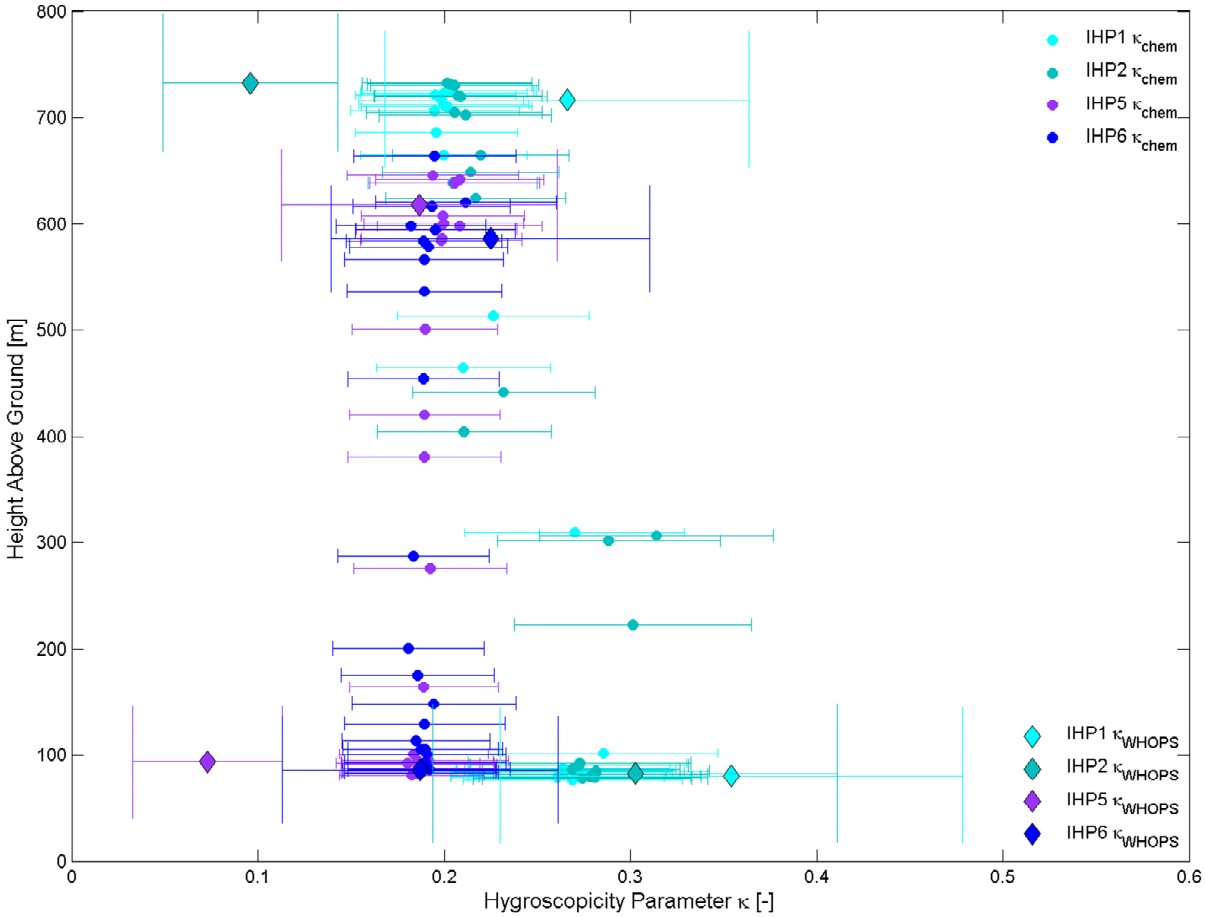
Revised text: Page: 9461; line: 9-10:

In the fully developed ML, hygroscopicity results show less variability with no clear pattern between the altitudes. The values amount to κ_{WHOPS}=0.14±0.06 and κ_{chem}=0.19±0.04 at 100 m AGL and κ_{WHOPS}=0.20±0.08 and κ_{chem}=0.20±0.04 at 700 m AGL.

7) *In section 4, the results are described with extreme detail. Can one example be shown from each measurement area (the Netherlands and the Po Valley), and then the remaining data compiled into different types of plots? I would find vertical profiles of the parameters, with different lines showing the evolution of the profiles, to be more informative than the time plots for which I have to estimate altitude from the altitude plot, then go to the parameter of interest and try to get a value. Since the evolution of the particle hygroscopicity with vertical growth of the PBL is of most interest, it would make sense to use altitude as the independent parameter for the plots.*

Section 4 has been revised for the new manuscript focusing on the main interesting points. Figure 4 contains both, the hygroscopicity results and the altitude (as dashed black line) in order to facilitate the attribution of the measured results to a certain layer and therefore altitude. Presenting the WHOPS data by using the altitude as the independent parameter does not seem the best solution for us as the resolution of the instrument is rather low.

In the figure below we present a possible plot illustrating the hygroscopicity results as height profiles, but we are of the opinion that Fig. 4 from the ACPD paper shows a better representation of the data and we propose not to change the plot.



8) *p. 9465, line 4. Mineral dust is brought in as an explanation for large, non-hygroscopic particles. This needs more support. Are there ground or LIDAR measurements showing a dust contribution? In the next paragraph, biological material is discussed. This is all speculation. These paragraphs could be condensed to read, "the non-hygroscopic fraction of 500 nm particles may be attributable to dust, plant materials, or other components commonly found extending into the accumulation mode from the coarse mode." The digression to speculative discussion detracts from the main points of the paper.*

We shortened the discussion on possible contributors to the non-hygroscopic mode as, like you mentioned, these are only assumptions.

9) *p. 9465, lines 24-25. Here we learn that growth factors < 1.5 for particles with diameters <300 nm are not detected "reliably". Why is this not detailed in the instrument description, and why are "unreliable" data being shown and discussed?*

The full measurement of the 300 nm particles is, as you mention, not reliable. However, this refers only to the fraction GF<1.5. The measurements above this limit are reliable and are therefore shown in Fig. 7 and discussed. In this way, we can provide another size-dependent information of the hygroscopic fraction (GF>1.5).

Revised text: Page: 9465; line: 24-25:

Note that the WHOPS cannot reliably detect particles with GF<1.5 and D_{dry}=300 nm, as described in Rosati et al. (2015). Thus, only the reliable number fraction describing GF>1.5 for this diameter is presented in Fig. 7.

10) *p. 9469, lines 25-28. More speculation without conclusion.*

We bring up two hypotheses for the discrepancy between the HTDMA observation and other results. One is from the literature; one is our own. Unfortunately, we cannot prove or discard one or the other.

11) *Section 4.2. This section does not contribute much to the story of the evolution of particle hygroscopicity with the growing PBL. The conditions are quite different from the Po Valley, and no firm conclusions are drawn from the measurements. It might be wise to exclude these observations from the manuscript and focus on the more comprehensive and interesting Po Valley analysis, from a region with much larger air quality problems and radiative forcing implications.*

We kept the results from the Netherlands as only few data on the hygroscopicity of atmospheric particles in the 500 nm size range are available. Furthermore, while we could not probe both the developing mixing layer and the residual layer, we could still show the homogeneity of the aerosol properties within the developing PBL. However, we shortened this section substantially for the revised manuscript.

12) *There are many typographic errors and a revised manuscript would benefit from thorough editing by a native English speaker.*

We did a thorough revision for the new manuscript.