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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Vertical profiling of aerosol hygroscopic properties in the planetary boundary layer during the PEGASOS campaigns" *by* B. Rosati et al.

Anonymous Referee #1

Received and published: 13 July 2015

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.

General recommendations:

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.

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.

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.

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.

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.

Specific comments/questions:

Throughout: "Data" is plural. "Datum" is singular. Use "data are" instead of "data is".

Throughout - especially in Abstract: report data with $\pm$ standard deviation.

p. 9460 line 26: With significant industrial sources in the Po Valley, I'd expect to see plumes of fresh, nonhygroscopic aerosol like this.

p. 9461 line 9: replace "spread" with "variability"

p. 9462 line 14-16: I disagree with this conclusion. The significant changes in hygro-

scopicity 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.

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.

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 nonhygroscopic fraction is tenuous (and certainly doesn't belong in the abstract - p. 9447 line 23).

One other strong possibility is that hydrophobic SOA coatings may inhibit hygroscopic growth within the WHOPS instrument, resulting in an overestimation of the nonhygroscopic 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.

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.

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

p. 9472 line 6: double negative; change “neither/nor” to “either/or”

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

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 9445, 2015.