Review of "Hygroscopic properties and mixing state of aerosol measured at the high altitude site Puy de Dome (1465 m a.s.l), France" by Holmgren et al.

General Comments:

The authors present humidified tandem differential mobility analyzer (HTDMA) measurements and hygroscopic growth factors (GFs) for aerosol sampled at the French high-altitude research station, Puy de Dome. Measurements are reported for September of 2008, December-May 2009, September-February 2010, and continuously from January 2011 to December 2012. The stated goal of this paper is to explore how aerosol hygroscopic growth factors vary year-to-year, seasonally, diurnally, and with air mass type. Given the incomplete dataset for 2008-2010 it is hard to draw definite conclusions regarding whether the observed differences in GF are due to seasonally-varying aerosol characteristics or due to an analysis approach biased by inclusion or lack of data for a given season in a given year. A revised manuscript should limit the scope of the dataset to ensure an unbiased analysis. In addition, a number of speculative conclusions are drawn from the HTDMA data regarding aerosol composition and emissions source attribution that are currently not supported (some instances noted under specific comments below); if these conclusions are based on additional measurement data, they should be discussed more fully or otherwise removed. Finally, this manuscript would be greatly improved by including all of the measured HTDMA sizes (given the non-linear nature of the observed hygroscopicities) and by a more extensive and sophisticated discussion of aerosol mixing state that incorporates the GF "spread" of each mode.

Specific Comments:

1) HTDMA measurements were made at PdD at six sizes: 25, 35, 50, 75, 110, and 165 nm, but only measurements for three sizes (25, 50, and 165 nm) are reported. Given the similar GF-derived kappas reported for 25 and 50 nm particles in Table 7 and the much higher kappa reported for 165 nm, there is clearly a non-linear size-dependence to kappa. Thus, it is essential that the authors add the other 3 measured diameters to the manuscript in order to provide greater size resolution in understanding how the aerosol composition is varying.

2) In Section 3.1 and Figures 2-7 it does not seem appropriate to include a single month as the annual average for 2008 and half a year for the annual average in 2009 and 2010. This only leaves two years for assessing "year-to-year" annual average variability, which obviously cannot lead to very robust conclusions. It would make sense to me to focus on reporting average aerosol properties over the continuous 2011-2012 time period rather than on trying to identify an inter-annual trend from this dataset. Similarly, the "unbalanced seasonal sampling" identified on Pg. 6767, Lines 17-18 is a major flaw in this analysis that must be corrected, perhaps by again focusing only on the two continuous years 2011-2012 or by bringing in only the winter data from 2009-2012. As it currently stands, definitive conclusions cannot be drawn regarding GF month-to-month variability.

3) Given the large amount of size-resolved GF data being compared in the tables and in Figures 2 and 4, I recommend that the authors report the data using the hygroscopicity distribution concept as described by Su et al., Atmos. Chem. Phys., 2010 (doi:10.5194/acp-10-7489-2010). Cumulative H(kappa, Dd) vs. kappa curves facilitate the same comparisons but would also more easily convey the contribution of non-hygroscopic aerosols as well as the means and spreads of the hygroscopic modes. Similarly, since there are six different HTDMA sizes, interpolated color maps similar to those in Figure 9 of Su et al. would be an especially nice way to display this dataset.

4) I'd like to see a much more extensive discussion of aerosol mixing state beyond the current method, which defines an external mixture as when two or modes are present. For example, the spread of each mode also contains information about mixing state, and should be more fully discussed. In the end how representative is an average GF reported in these tables (and those in other studies) of the individual aerosol particles typically present at this site?

5) Please add kappa axes to Figures 1-7, 10-11 that correspond to the GF axes so that the reader is able to easily see the compositional differences across aerosol sizes without having to account for the (admittedly small) Kelvin size dependence of the GF.

Pg. 6762, Line 25-27: This statement is untrue and should be stricken. See for example, Sjogren et al., 2008, which is cited in the previous paragraph, who made measurements at Jungfroujoch during multiple, 1-month campaigns spanning different seasons in 2000-2005. Kammerman et al., 2010 (also cited in the previous paragraph) made measurements at Jungfroujoch for a continuous 13-month period.

Pg. 6763, Lines 5-6: I don't understand the meaning of the definitions "background site" and "high altitude site" in the context of the citations and the HTDMA measurements. A description of what characteristics go into these labels would be preferable.

Pg. 6764, Lines 15-19: I don't understand how the authors are calibrating their DMAs using ammonium sulfate. I would think that this is not really a calibration, but rather is a consistency check of the instrument operation using a known pure-component salt. This should be reworded or, if I'm mistaken and a calibration was performed, more details are needed.

Pg. 6769, Lines 16-22: This result is surprising since I might expect shallow boundary layers present during winter to prevent PBL air from reaching the high altitude site. Also, please provide support for the claim that "the nearly hydrophobic mode observed in winter and autumn originates from the presence of combustion aerosols emitted from heating devices".

Pg. 6770, Lines 19-22: Is there any evidence to support the statement: "in autumn and winter, the high degree of external mixing may also be explained by more wood fires in individual houses, resulting in combustion aerosol being injected high in the atmosphere due to the very strong convection in the warm outflow".

Pg. 6772, Lines 1-18: Is this discussion regarding seasonal differences in BC or in regional biomass burning supported by any measurements or observations from the site. It is mentioned on Pg. 6763, Line 10 that particulate BC, NOx, and CO2 are measured at PdD during the study period; are these combustion tracer measurements consistent with the discussion in this section over the HTDMA measurement time period? What is the observational evidence for the statement: "In winter and in PBL conditions, the contribution from biomass burning is greater than in the summer, bringing with it a high fraction of primary organics and nitrates"?

Pg. 6772, Line 25 and discussion throughout: How is the height of the PBL or RL being assessed so as to apportion specific aerosol types as deriving from the PBL or the FT? Presumably, this is coming from the vertical component of the HYSPLIT back trajectories or possible sonde-based temperature profiles?

Pg. 6773, Line 5-8: It should be easy to detect periods influenced by NPF by examining the variation in the overall particle number concentrations referenced on Pg. 6763, Line 10. It would be very interesting to know how frequently NPF events were observed during this study period in explaining the HTDMA results.

Pg. 6774, Line 2-4: I don't understand the connection between lower wind speeds and a higher PBL.

Pg. 6774, Lines 15-21: I'm surprised that the HTDMA measurements at 25-165 nm would be substantially impacted by dust, which tends to be present at larger particle sizes (>~ 0.5-5 micron diameters).

Pg. 6775, Lines 6-8: What is the basis for the statement that anthropogenically-influenced marine aerosol are more "aged" than those originating from the continental PBL?

Pg. 6775, Lines 21-25: I don't understand the formation mechanisms for "freshly formed anthropogenic aerosol" and "aged anthropogenic aerosol". What type of particles are these – organics and sulfate? "Aging" of fresh combustion particles is mentioned in this sentence as well.

Pg. 6776, Lines 10-12: The meaning of the sentence "Continental aerosol displays the same trend as smaller particles, with higher hygroscopicity in the cold season" is unclear.

Section 3.4: I do not understand the reason for using the Zhou et al., 2001 parameterization since it is not physically based and because it obscures the inherent size-dependent measurement variability by reducing the data to two arbitrary coefficients. I recommend cutting this parameterization and only including the kappa values as is currently done while also adding their standard deviation. In addition, the hygroscopicity distribution concept of Su et al., 2010 seems perfect for describing this dataset, while preserving the spread of the GF distribution and the frequency of observation.

Pg. 6777, Lines 13-18: The statement, “The parameterization and the kappa values are issued from a long term data set, and are therefore considered reliable for future use in studies in which the hygroscopic properties should be taken into account, such as for calculations of condensational sink or for calculations of size distributions at ambient humidities for calculations of optical properties. The parameterizations and kappa values are representative of western European aerosol in remote sites.”, is unfounded and should be removed.

Pg. 6778, Lines 10-11: What is the basis for this statement regarding ageing of fresh continental combustion aerosols? Is this based on elevated BC measurements?

Figure 1: How were the error bars for the MDF distribution calculated? Showing the actual data points would be a clearer way to show what the raw distribution looks like.

Figures 2 and 4: Given the overlapping uncertainty envelopes, it is hard to distinguish which color corresponds to which curve (especially at 165 nm). For example, red and magenta are nearly indistinguishable, as are purple and blue. Recasting these figures using the hygroscopicity distribution concept might be a clearer representation; otherwise, consider spinning each curve out into a separate subfigure.

The stacked bar graphs in Figure 5-7, 10-11 are very interesting and a nice contribution to better quantitative understanding of the aerosol mixing state.

Minor Comments:

Pg. 6760, Line 4: Research was conducted during this period but the data set is not continuous. This should be noted here as it is on Pg. 6767, Lines 17-21.
Pg. 6760, Lines 17-20: I don’t think speculative conclusions are appropriate for an abstract
Pg. 6761, Line 12: Update to the latest IPCC report
Pg. 6762, Lines 12-13: Boundary layer aerosols often feed convectively-driven tropospheric clouds
Pg. 6762, Line 25: Again, please note that the data set is not continuous
Pg. 6763, Line 18: Remove citation to Hervo et al., 2014, which is in preparation. It is grossly misleading and inappropriate to cite a non-published paper with a publication year.
Pg. 6765, Line 1: Was the RH constant at 90% or was it varied? Why is this recalculation necessary?
Pg. 6765, Lines 22-26: Is this referring to the GF and sigma for each mode or for the entire PDF?
Pg. 6766, Line 5: Reference Figure 8 here.
Pg. 6766, Line 5: What is the “oceanic modified” air mass type referring to? How is the air mass modified?
Pg. 6770, Line 5: What is “modified sea salt”?
Pg. 6772, Lines 23-24: Stating that the less hygroscopic fraction increases during the day at the expense of the hygroscopic fraction does not tell the reader whether there a more less hygroscopic particles present or just fewer hygroscopic particles present during the day.

Pg. 6773, Line 19: What height was used to initialize the back trajectory?
Pg. 6775, Line 16: Does CNN refer to “cloud condensation nuclei (CCN)”?
Pg. 6778, Line 27: I don’t think “realistic” is the correct word here, as ambient RH conditions can vary from dry air masses to moist air masses.
Pg. 6780, Line 29: Strike the Hervo et al., in preparation reference since it is not yet accepted for publication.
Table 1 could be moved to the supplementary material as it is not directly relevant to the discussion.
In Tables 2-4 and Figures 1-7, 10-11, please explicitly note that GF is GF(90%RH) in either the caption or the Table heading / Figure axis labels.