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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Free Tropospheric Aerosols at the Mt. Bachelor Observatory: More Oxidized and Higher Sulfate Content Compared to Boundary Layer Aerosols" *by* Shan Zhou et al.

Anonymous Referee #2

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The manuscript submitted by Shan Zhou and coauthors describes in detail a subset of a NR-PM1 aerosol chemistry dataset acquired at a high altitude sampling site, Mount Bachelor Observatory during the summer of 2013. It focuses on a few days where no apparent fire influence was observed at the site and uses this data to:

- Describe typical background summer conditions at MBO - Analyze how boundary layer dynamics modulate the chemical characteristics of the aerosol observed. - It then puts these measurements into a larger context of other NR-PM1 measurements at high altitude sites as well as aircraft observations.

The available field data presented is fairly sparse and this affects the robustness/representativeness of the conclusions, as discussed below. Nevertheless, the authors provide adequate context in most cases to support their findings. The technical quality of the analysis is excellent, and provides additional insights into sources composition that are often missing in comparable publications. Given that these are the first AMS measurements under background conditions at a key high altitude site in North America, these results are important and useful, despite the small coverage.

The classification of air masses into BL/FT used in the manuscript is based on previous publications by the same authors and gives sensible results, although some more detail on the impact of the uncertainty of the assignment on the conclusions would be desirable. The summary of AMS observations at Mountain Sites is a useful addition and valuable for future high altitude studies. Also in this case the sample is at present fairly small, especially if one focuses on measurements that are clearly of free tropospheric air. May this publication help encourage further contributions.

Major comments:

Line 66: It would be useful to know what the criteria were to determine the clean/remote analysis periods. Line 118 mentions that <120 ppb CO and <25 Mm-1 at STP were observed, but those seem more descriptive (it clearly worked) than prescriptive. Can the authors explain if this based on back trajectories? Chemical markers? Other?

Line 110: Given that the two factors found are in good agreement with the factors found in Zhou et al, 2017, it would seem that focusing on the temporal evolution of these two for the full six week deployment would be a good way to improve statistics, especially regarding the BL/FT split (which should not really depend on the presence or absence of additional BB aerosol). PMF analysis in the presence of very large BB plumes can be challenging, but the analysis presented in Zhou et al, 2017 seems robust enough that this could work, and considerably strengthen the findings regarding e.g. daily trends and average FT composition. So I would encourage the authors to consider this possibility.

Line 151: The authors write that NH4 and SO4 are relatively comparable in the FT and BL, but this seems to contradict the acidity gradient described later (based on NH4/SO4 molar ratios), please clarify. Furthermore, the conclusion that the sources of SO4 are the same in the FT and BL is not really supported by the different size distributions observed (and the explanation given there). Given that sulfate concentrations in the BL are going to be a strong function of BL height and FT exchange, a direct comparison of these concentrations is not very meaningful, suggest removing.

Line 166/Fig 2: Constructing diurnal profiles based on six days of data is less than ideal, and the trends are somewhat obscured by the different times at which the PBL rose above the sampling site . Again, I suggest extending the PMF analysis for the full length of the deployment (Line 220) to spot check at least for some of the variables the robustness of the trends shown. That might also allow to filter for days where the BL/FT switch happened at consistent times and hence improve the robustness of the aerosol trends

Line 186: It should be mentioned that Lee et al, “Substantial secondary organic aerosol formation in a coniferous forest: observations of both day- and nighttime chemistry”, Atmos. Chem. Phys., 16, 6721–6733, 2016, doi:10.5194/acp-16-6721-2016, reported the same trends in particulate organic nitrated at the Whistler “middle altitude site” with likely very similar forests sources as at MBO . The authors may also consider adding this dataset to Fig 6 as well, although the lower sampling altitude makes it less comparable to other high altitude observations.

Line 196: The MSA analysis is well done and a nice addition to the manuscript. Are the authors aware of the study by Sorooshian et al, “Surface and airborne measurements of organosulfur and methanesulfonate over the western United States and coastal areas” J. Geophys. Res. Atmos., 120(16), 8535–8548, doi:10.1002/2015JD023822, 2015? They measured MSA and OS at ground sites near MBO during the Summer of 2013 as well, and found broadly similar concentrations, consistent with MSA being made in the continental BL.

Section 3.4: The diurnal profiles show a fairly clear “transition zone” between FT and BL influence, and including/excluding those periods will likely strongly affect the averages found (see also Wagner et al, Atmos. Chem. Phys., 15, 7085–7102, 2015 as an example on the difficulty of properly defining the top of the BL). Such an analysis, either based on the diurnal profiles themselves or on the uncertainty of their threshold criteria, would help strengthen the confidence in the reported averages and trends, especially for the FT data.

Line 275-278: This seems mostly speculative. MSA could also be oxidized further to sulfate and/or partition to the gas phase instead of being washed out. Consider removing/shortening.

Line 295-306: Again this seems fairly speculative. There is no discernible enhancement of small particles in the (fairly noisy) sulfate size distribution presented, which is still within the envelope of the BL size distribution. So preferential activation/wash out of larger particles would suffice to account for the observed differences and nucleation is not needed to explain the difference. So consider shortening/removing.

Line 328-336: I am not following. If the average FT NH4/SO4 molar ratio is less than 0.3, the particles will be liquid bisulfate/sulfuric acid down to fairly low RH, hence the discussion of solid ammonium sulfate as presented does not seem really relevant to the findings. Please explain.

Minor comments:

Line 32: “At lower altitudes “ instead of “in lower altitudes”

Line 39: While aircraft measurements are indeed expensive, I would argue that the main advantage of mountaintop observatories are long-term, continuous measurements that are invaluable for statistics. Obviously deploying complicated instrumentation such as the AMS can be a challenge for such sites as well, but I think it is worth mentioning this.

Line 40: Given the inclusion of the Whistler site, I would suggest replacing “US” with “North America”

Line 45: Suggest adding to your list of non-AMS particle measurements: L. Ahlm et al, “Temperature-dependent accumulation mode particle and cloud nuclei concentrations from biogenic sources during WACS 2010”, Atmos. Chem. Phys., 13, 3393–3407, 2013, doi:10.5194/acp-13-3393-2013

Line 82: “the established data analysis tool” instead of “established data analysis tool”

Line 84: It would be useful to document the range of CEs observed. A histogram keyed by BL/FT influence would be appropriate, and would serve to highlight again the gradient in acidity between the different air masses sampled at MBO.

Line 131: Is the chloride associated with periods of somewhat larger inorganic nitrate? As Hu et al, Aerosol Sci. Technol., 51,735-754, doi:10.1080/02786826.2017.1296104 described, under such conditions chloride can be a vaporizer artifact, and is easily testable by reviewing the ammonium nitrate calibrations. Given the relative concentrations of chloride and nitrate, this is unlikely, but should be mentioned.

Fig 4: Suggest adding a timeseries of the ratios, with the FT periods clearly marked, that would make the point(s) better than these correlation plots.

Fig S13 (middle): Please add the background line from Cubison et al. It looks like your factors lie pretty much right on top of it, as in Zhou et al, 2017.

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