Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-1018-RC2, 2020

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Direct links between hygroscopicity and mixing state of ambient aerosols: Estimating particle hygroscopicity from their single particle mass spectra" *by* Xinning Wang et al.

Anonymous Referee #2

Received and published: 30 January 2020

General:

This paper describes tandem measurements of particle composition and particle hygroscopicity using an HTDMA and an ATOFMS. This paper then suggests that the particle mass spectrum can be used to determine the growth factor. While the HTDMA/ATOFMS work is interesting on it's own, I have several reservations about the use of mass spectra to predict the growth factor in this work that must be addressed before the work can be considered for publication.

Printer-friendly version

Discussion paper

Major Comments:

1. The authors claim that they can predict the growth factor from the mass spectra, but they mainly just showed associations between particle types and growth factors, not that the spectra provide a degree of predictability.

2. The authors also did not explore whether ion peak areas such as sulfates and nitrates, which are critical for particle water uptake, were better predictors of growth factors than the particle types themselves.

3. This paper is missing critical information about how the ATOFMS data was treated and analyzed and what criteria were used to assign particle types and ascribe a growth factor.

4. I don't understand the authors' claim regarding particle effective density as a predictor for particle hygroscopicity. Can the authors show a theoretical reason for such a claim?

Specific Comments:

Abstract:

1. Lines 31-32: The authors need to explain why the higher effective density correlates with the hygroscopicity.

2. Lines 32-34: The authors need to revise this statement or revise their work to show a degree of predictability of the GF was achieved.

3. Lines 37-39: I don't understand this claim that back-trajectory analysis is consistent with particle hygroscopicity. The authors need to clarify this statement.

Introduction:

1. Lines 47-49: This sentence is very vague. The authors should discuss heterogeneous and multiphase reactions that would affect particle hygroscopicity.

2. While the coupling of techniques was discussed, the authors need to add discussion of growth factors observed in ambient environments and what has been learned about how composition drives hygroscopicity in tandem experiments.

Methods:

1. The data analysis methods for the ATOFMS measurements are missing yet are a critical component of this work. What clustering method was used? Art2a? What vigilance factor, learning rate, and number of iterations were used? How were particle types assigned?

2. What size range did the ATOFMS hit particles? Usually 250 nm is on the lower end of what the instrument can see for certain inlet configurations, what is the detection efficiency of the ATOFMS at this lower size?

3. What were the hit rates for the different growth factors? This will be important for assessing how representative the observed particles are of each growth factor.

4. Lines 166-167; Lines 191-194: the authors mentioning assigning a GF for ambient particles that match particles observed during HTDMA-ATOFMS spectra. What was the criteria for matching particles and assessing their similarity? Was a threshold dot product used to assess similarity as was done for prior ATOFMS studies (e.g., [Pratt and Prather, 2009]).

5. Lines 171-174: I have not heard of treating ATOFMS data this way. It is well-known that the instrument is sensitive to ionization potential energies ([Gross et al., 2000]) and usually relative intensities are used to work with such spectra. The authors' method of arbitrarily reducing the intensity of metals so that organics are relatively enhanced requires significant justification.

6. The authors used candidate particle types to explain hygroscopicity, but did they ever simply compare sulfate and nitrate peak areas to the growth factor data to see if those soluble compounds could explain their results better than different particle types?

Results:

1. The particle statistics mentioned in Section 3.1.1 are really hard to follow and put into context. I suggest just keeping this section focused on particle types, then moving Section 3.2.1 up and providing better statistics for the particle types that contributed to each growth factor including a description of the percentage of each particle type observed for each growth factor and what the hit rates were on the ATOFMS for each growth factor.

2. Line 207: add the following references for ATOFMS detection of biomass burning aerosol: [Pratt et al., 2010; Zauscher et al., 2013].

3. Lines 214-215 describing EC particles require a reference to prior work [Ault et al., 2010; Spencer et al., 2006; Toner et al., 2008].

4. Line 217: define NH and MH.

5. Lines 223-225: I suggest adding Figure S2 to the main text. 6. Lines 226-227: please add [Ault et al., 2011; Gaston et al., 2017; Sullivan et al., 2007].

7. I suggest also adding Figure S3 to the main text.

8. Lines 255-257: there are other ATOFMS studies showing ammonium/OC particles associated with agricultural emissions [Qin et al., 2012]. The authors should also consider that source for their observations.

9. Lines 260-261: aging does not always translate to high hygroscopicity.

10. Line 275: please also cite [Pratt and Prather, 2009]

11. Line 282-283: please site [Gaston et al., 2011]

12. The authors mention that only a few sea salt particles were observed, yet this was the only particle type where a through investigation linking the particle composition to the GF was performed. Why was this type of analysis or discussion not included for

other particle types?

13. Lines 301-302: please cite [Gaston et al., 2011; Prather et al., 2013]

14. Lines 306-307: please cite [Gaston et al., 2018] who found a similar result using ATOFMS data.

15. I had a hard time following lines 305-310, the authors need to clarify whether aged sodium nitrate contributed to the lower GF or whether other factors were responsible.

16. Section 3.1.2 seems out of place. While it is an interesting finding that the effective density showed a trend with the GF, the authors need to explain this finding a bit more.

17. Section 3.2.1 needs some statistics to show that the authors can predict the GF from the spectra alone.

18. Lines 441-442: this suggests that the authors should try comparing their GF data to peak area intensities of sulfate and nitrate.

References:

Ault, A. P., C. J. Gaston, Y. Wang, G. Dominguez, M. H. Thiemens, and K. A. Prather (2010), Characterization of the single particle mixing state of individual ship plume events measured at the Port of Los Angeles, Environmental Science & Technology, 44(6), 1954-1961.

Ault, A. P., C. R. Williams, A. B. White, P. J. Neiman, J. M. Creamean, C. J. Gaston, F. M. Ralph, and K. A. Prather (2011), Detection of Asian dust in California orographic precipitation, Journal of Geophysical Research-Atmospheres, 116, doi.org/10.1029/2010JD015351.

Gaston, C. J., J. F. Cahill, D. B. Collins, K. J. Suski, J.-Y. Ge, A. E. Barkley, and K. A. Prather (2018), The cloud nucleating properties and mixing state of marine aerosols sampled along the Southern California coast, Atmosphere, 9(52), doi:10.3390/atmos9020052.

Gaston, C. J., H. Furutani, S. A. Guazzotti, K. R. Coffee, T. S. Bates, P. K. Quinn, L. I. Aluwihare, B. G. Mitchell, and K. A. Prather (2011), Unique ocean-derived particles serve as a proxy for changes in ocean chemistry, Journal of Geophysical Research, 116, D18310, doi:18310.11029/12010JD015289.

Gaston, C. J., K. A. Pratt, K. J. Suski, N. W. May, T. E. Gill, and K. A. Prather (2017), Laboratory studies of the cloud droplet activation properties and corresponding chemistry of saline playa dust, Environmental Science & Technology, 51(3), 1348-1356.

Gross, D. S., M. E. Galli, P. J. Silva, and K. A. Prather (2000), Relative sensitivity factors for alkali metal and ammonium cations in single particle aerosol time-of-flight mass spectra, Analytical Chemistry, 72(2), 416-422.

Prather, K. A., T. H. Bertram, V. H. Grassian, G. B. Deane, M. D. Stokes, P. J. DeMott, L. I. Aluwihare, B. P. Palenik, F. Azam, J. H. Seinfeld, R. C. Moffet, M. J. Molina, C. D. Cappa, F. M. Geiger, G. C. Roberts, L. M. Russell, A. P. Ault, J. Baltrusaitis, D. B. Collins, C. E. Corrigan, L. A. Cuadra-Rodriguez, C. J. Ebben, S. D. Forestieri, T. L. Guasco, S. P. Hersey, M. J. Kim, W. F. Lambert, R. L. Modini, W. Mui, B. E. Pedler, M. J. Ruppel, O. S. Ryder, N. G. Schoepp, R. C. Sullivan, and D. Zhao (2013), Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol, Proceedings of the National Academy of Sciences of the United States of America, 110(19), 7550-7555.

Pratt, K. A., A. J. Heymsfield, C. H. Twohy, S. M. Murphy, P. J. DeMott, J. G. Hudson, R. Subramanian, Z. E. Wang, J. H. Seinfeld, and K. A. Prather (2010), In Situ Chemical Characterization of Aged Biomass-Burning Aerosols Impacting Cold Wave Clouds, Journal of the Atmospheric Sciences, 67(8), 2451-2468.

Pratt, K. A., and K. A. Prather (2009), Real-time, single-particle volatility, size, and chemical composition measurements of aged urban aerosols, Environmental Science & Technology, 43(21), 8276-8282.

Qin, X., K. A. Pratt, L. G. Shields, S. M. Toner, and K. A. Prather (2012), Seasonal comparisons of single-particle chemical mixing state in Riverside, CA, Atmospheric Environment, 59, 587-596. Spencer, M. T., L. G. Shields, D. A. Sodeman, S. M. Toner, and K. A. Prather (2006), Comparison of oil and fuel particle chemical signatures with particle emissions from heavy and light duty vehicles, Atmospheric Environment, 40(27), 5224-5235.

Sullivan, R. C., S. A. Guazzotti, D. A. Sodeman, and K. A. Prather (2007), Direct observations of the atmospheric processing of Asian mineral dust, Atmospheric Chemistry and Physics, 7, 1213-1236.

Toner, S. M., L. G. Shields, D. A. Sodeman, and K. A. Prather (2008), Using mass spectral source signatures to apportion exhaust particles from gasoline and diesel powered vehicles in a freeway study using UF-ATOFMS, Atmospheric Environment, 42(3), 568-581.

Zauscher, M. D., Y. Wang, M. J. K. Moore, C. J. Gaston, and K. A. Prather (2013), Air quality impact and physicochemical aging of biomass burning aerosols during the 2007 San Diego wildfires, Environmental Science & Technology, DOI: 10.1021/es4004137.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-1018, 2020.

Printer-friendly version

Discussion paper