Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-41-AC1, 2018

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation and evolution of Tar Balls from Northwestern US wildfires" *by* Arthur J. Sedlacek III et al.

Arthur J. Sedlacek III et al.

sedlacek@bnl.gov

Received and published: 12 May 2018

Anonymous Referee #1 This manuscript characterizes the microphysical properties of tar balls sampled during the BBoP campaign. This is an important finding and deserves to be published. I would recommend publication of this manuscript after mandatory revision. Below are my major comments:

1) In the abstract, the sentence "Brown carbon is a poorly characterized mixture that includes tar balls (TBs)" conveys a very vague meaning and needs to be edited or removed. I suggest not to mention the word "brown carbon" here. Just defining tar balls should suffice.

We agree that this sentence was somewhat confusing. We have changed the sentence

Printer-friendly version

Discussion paper

to read, “Tar balls (TBs) are a type of brown carbonaceous particle apparently unique to biomass burning.” We have chosen to leave the term “brown carbonaceous particle” in the definition of TBs, as TBs absorb light as been well-established in the literature (e.g., our citations, Chakrabarty et al, 2010 and 2016, Alexander et al., 2008, and Hoffer et al., 2016). In this work, we tested three different TB refractive indices (RI) and found that the RI’s that gives the best agreement with that derived SSA values from our measurements were consistent with TBs exhibiting weak light absorption (i.e., m similar to the literature values 1.56 – 0.02i or 1.56 – 0.02i).

2) I like that this paper finally tackles the question of how tar balls are actually made. I like the terminology “processed primary particles”. This needs to be mentioned in the abstract. A sentence or two should also be added to the abstract on how these particles differ in composition and optical properties from those generated using heat-shock treatment in the laboratory by Hoffer et al.

We thank the reviewer for the encouraging words. We spent many hours discussing the pros and cons of labeling tar balls as “processed primary particles”. We agree that this terminology should be included in the abstract. We have added the following sentence: “Given the observed evolution of TBs it is recommended that these particles be labeled as processed primary particles, thereby distinguishing TBs formation/evolution from secondary organic aerosols.”

As for the reviewer’s comments about the laboratory results, we unfortunately cannot meet the request at this time. These initial laboratory experiments were preliminary and focused on attempting to determine a reasonable measure of the collection efficiency of the SP-AMS to laboratory generated tar balls. We accomplished this narrow task. We did not collect optical measurements in the laboratory. Furthermore, given the preliminary nature of these laboratory experiments, we are still working on interpreting any SP-AMS chemical information obtained during these studies. This information, while interesting, remains outside the scope of this work.

3) The authors determine aging using the NOX/NOY metric, which is fine. However, by parameterizing aging using this metric will make it difficult to place their findings within the accepted context of the atmospheric chemistry community. I recommend a Van Krevelen (VK) diagram if they do have the necessary data from the AMS. I think adding a VK plot would enable better comparison of this dataset with other studies.

We thank the reviewer for the relevant suggestion. The requested VK diagram for the second flight on 30 July is shown here, colored by the HROrg mass loading concentrations to differentiate between sampled plumes (high loadings) and background air (low loadings). These data were all collected with both the laser and tungsten vaporizers on. The elemental ratios have been estimated using the Aiken et al. (2008) method and the Canagaratna et al. (2015) corrections for SP-AMS laser vaporizer data have been applied. As expected, the organic dominated biomass burning particles are less oxidized (lower O:C and higher H:C) when sampled nearest to the fire (highest loadings) and more oxidized (higher O:C and lower H:C) downwind and in the background air (lowest loadings).

VK diagram insert here

While we agree with the reviewer that this information is highly interesting, we have chosen not to include it here for several reasons. First, age dependent changes in elemental ratios from biomass burns are not as well characterized or understood as that from other emission sources. Second, BBOP represented the first research flights for the SP-AMS operated with dual laser and thermal vaporizers. This instrument configuration is not as well characterized as a standard AMS. Comparisons with other studies would have to take into account the possibility of differences in instrumentation. For example, the Canagaratna et al. (2015) SP-AMS laser vaporizer corrections were obtained from laboratory studies of various organic compounds on refractory black carbon particles vaporized by the laser vaporizer, whereas the BBOP samples were for a highly externally mixed aerosol with significant mass spectral ion signals coming from both the laser and tungsten vaporizers. We are currently working on understanding the

instrumental effects on these measurements, through comparing laser on and off measurements for sequential plumes transects (which were done for this explicit purpose during BBOP) and independent laboratory studies, and will present these results in the future in another form.

Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K.S., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, M.R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J.L. (2008). O/C and OM/OC Ratios of Primary, Secondary, and Ambient Organic Aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry. Environ. Sci. Technol., 42(12):4478–4485.

Canagaratna, M.R., Massoli, P., Browne, E.C., Franklin, J.P., Wilson, K.R., Onasch, T.B., Kirchstetter, T.W., Fortner, E.C., Kolb, C.E., Jayne, J.T., Kroll, J.H., and Worsnop, D.R. (2015). Chemical Compositions of Black Carbon Particle Cores and Coatings via Soot Particle Aerosol Mass Spectrometry with Photoionization and Electron Ionization. J. Phys. Chem. A, 119(19):4589–4599

4) If the authors have optical measurements and size distribution data available, why didn't they just inverse Mie calculations to derive complex m rather than perform forward calculations of literature data? The consensus is that m varies according to fuel type and burn conditions, and using a single value for a given fuel is an incomplete basis for comparison. For example, assuming that all Alaskan duff particles have m=1.75-0.002i is neither reasonable nor rigorous.

Aerosol particle concentrations in wildfire plumes greatly exceeded the coincidence design limits of the UHSAS and PCASP probes that were used to determine size distributions in the size range relevant to scattering. Flow control to the UHSAS was not adequate to reduce particle concentrations to acceptable values. The UHSAS particle-by-particle data was not consistent with random particle arrival times and thus was of

no help in coincidence-correcting the data. The inadequacy of the particle measurements was demonstrated via Mie calculations in smoke plumes in which scattering based on UHSAS or PCASP size distributions were of order 10% to 50% of that measured with a TSI nephelometer. The variability and magnitude of the discrepancy are quite outside of the range that can be generated by a variable refractive index.

The intent of Figure 8 was not to retrieve a refractive index, but rather to show that our scattering and absorption measurements are consistent with literature values for the refractive index of weakly absorbing TBs, but not with strong absorbers. Reasonable changes in the real component of the refractive index of TBs or organics do not change this conclusion.

5) Continuing the discussion of complex m, Sumlin et al. (2017 and 2018) have shown that m associated with the organic fraction of carbonaceous aerosol varies widely as a function of burn conditions and photochemical age. This work further emphasizes that it is preferable to do inverse Mie calculations rather than rely on previously reported values. Sumlin, B. J.; Pandey, A.; Walker, M. J.; Pattison, R. S.; Williams, B. J.; Chakrabarty, R. K., Atmospheric Photooxidation Diminishes Light Absorption by Primary Brown Carbon Aerosol from Biomass Burning. Environ. Sci. Tech. Let. 2017, 4 (12), 540-545. Sumlin, B. J.; Heinson, Y. W.; Shetty, N.; Pandey, A.; Pattison, R. S.; Baker, S.; Hao, W. M.; Chakrabarty, R. K., UV-Vis-IR spectral complex refractive indices and optical properties of brown carbon aerosol from biomass burning. J. Quant. Spectrosc. Radiat. Transfer 2018, 206, 392-398.

The retrievals and retrieval software described by Sumlin et al. (2017 and 2018) are impressive. High quality data is a must in such retrievals. Unfortunately, as above, we do not have the data to pursue similar calculations for BBOP. Even if all of the instruments worked as intended, an inversion of size and scattering data to yield a refractive index would be difficult. For example, Sumlin et al. (2017 and 2018) averaged their data over 5 minutes. The plumes we sampled had significant structure within one km (10-second integration time at a sampling speed of 100 m/s), thereby not allowing

long averaging times.

6) Figure 5 shows TEM images of aggregates of tar balls. This is very interesting. Chakrabarty et al. (2016; ACP) have also observed aggregates of spheres from Alaskan Peat combustion. A paragraph is warranted on how the optical parameters (SSA etc.) would differ if aggregate morphology is accounted for in the calculations. Would schemes such as Rayleigh-Debye-Gans be appropriate?

We thank the reviewer for bringing the TB aggregates in our TEM images to our attention. The authors agree that the observation of aggregated TBs is interesting and potentially provides insight into their formation (e.g., the TBs number concentration was high enough to drive TBs coagulation). We have added the following sentence at line 159 to reflect corroboration of our observations with that reported by Chakrabarty et al., (2016). "Similar to that reported by Chakrabarty et al., (2016), agglomerated TBs are observed in some TEM images." The appropriate citation has been added to the reference list (line 346 in the original manuscript).

With respect to the impact that agglomerated TBs would have on optical properties, this is outside the scope of the current work. First, it is not clear how aggregated TBs may affect the optical properties. In contrast to soot particles, where very small spheres aggregate into larger particles that increase light scattering, aggregated $\sim$200 nm TBs may actually exhibit decreased scattered light (i.e., lower SSA) due to the decreasing scattering efficiency for larger sized particles in the visible. Second, we have not quantified the number concentrations of the aggregated TBs nor the number of TBs in each aggregate, which would have to be done prior to addressing this specific comment. Third, TBs particles are too large ($\sim$200 nm) to use the Rayleigh-Debye-Gans approximation (Sorensen, 2001, Aerosol Science and Tech), leaving a T-matrix or discrete dipole approximation (DDA) calculation as a method to explore this impact. Further work will be required to adequately address this intriguing comment by the reviewer.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-41/acp-2018-41-AC1-supplement.pdf

---

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-41, 2018.

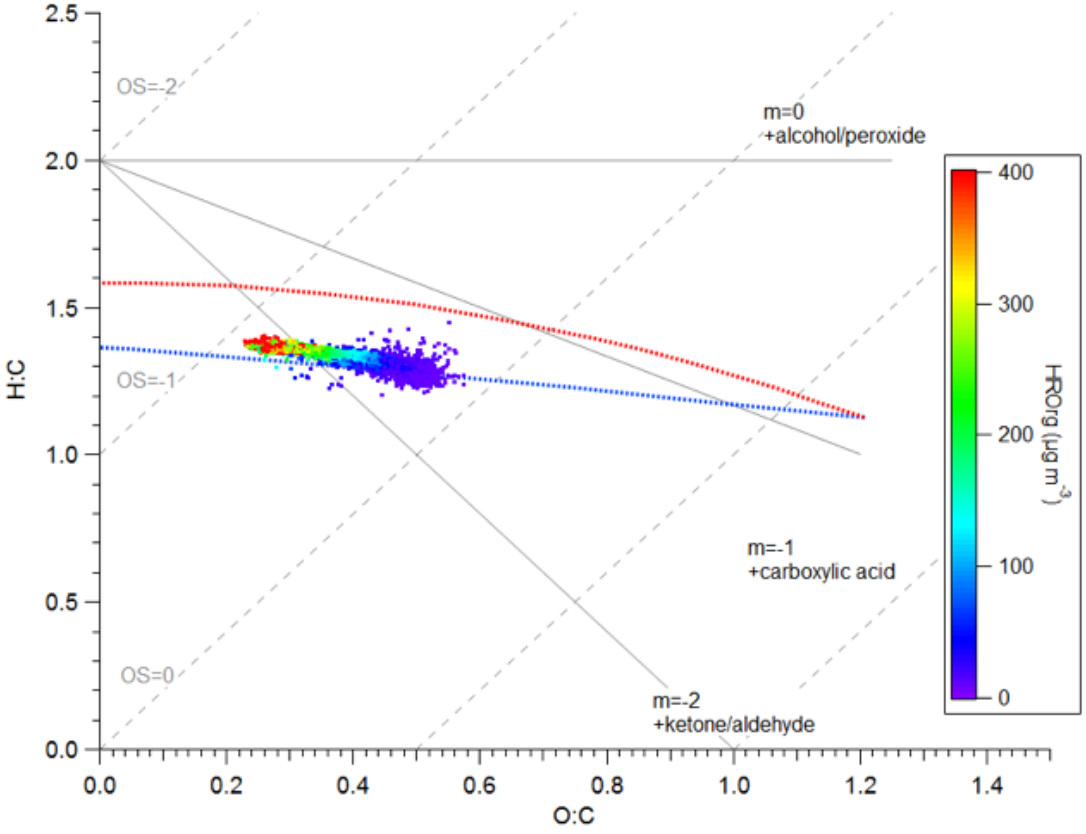

Fig. 1.

Printer-friendly version

Discussion paper