

# Review of Wu et al., “Vertical variability of the properties of highly aged biomass burning aerosol transported over the southeast Atlantic during CLARIFY- 2017”

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## 1 Overall

This is a well-done study of aerosol in an undersampled region. There are numerous interesting findings. It is a valuable addition to the literature. It will undoubtedly be useful for people modeling the effect of very aged BB aerosol on climate.

I have a bunch of minor issues that should be addressed, but nothing that requires wholesale rewriting. There were a couple of points where I would have appreciated more thorough investigation, including the possibility of sampling artifacts, further examination of rBC to OA ratios, and the thermodynamics of  $\text{NH}_4\text{NO}_3$ .

## 2 Two related issues with nitrates

The manuscript concludes that most of the nitrate in the aerosol is inorganic. That may well be true, but the evidence offered is a bit slim, as it relies on the relative fractions of ions at  $m/z = 30$  and  $m/z = 46$ . This analysis depends on either a lack of interference at  $m/z = 30$  and  $m/z = 46$  or on the frag table being correct. The former is a bit shaky, since  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_6$  are at  $m/z = 30$  and  $\text{CH}_2\text{O}_2$  and  $\text{C}_2\text{H}_6\text{O}$  are at  $m/z = 46$ . Given the highly oxidized aerosol,  $\text{CH}_2\text{O}$  is likely to be plentiful. The frag table is of course designed for general ambient aerosol and can have striking problems with unusual composition. It is curious that the standard frag table (as of Squirrel 1.62G) assumes there is nothing but  $\text{NO}_2$  at  $m/z = 46$ . At  $m/z = 30$  there is an indirect dependence on getting the  $m/z = 28$  peak right and an assumption that the organic fraction is 2.2%.

(To be fair, I did take a quick look at an arbitrary bit of AMS data from ORACLES, where it appeared that  $\text{C}_2\text{H}_6$ ,  $\text{CH}_2\text{O}_2$  and  $\text{C}_2\text{H}_6\text{O}$  were negligible.  $\text{CH}_2\text{O}$  is too close to  $\text{NO}$  to identify, but the peak was so narrow that significant  $\text{CH}_2\text{O}$  is unlikely. Curiously, there was a bit of  $\text{CH}_4\text{N}$ , but not enough to skew the  $\text{NO}/\text{NO}_2$  ratio.) The upshot is that I'd like you to mention that there is some uncertainty in the  $m/z30/46$  ratio due to the possibility of organic interference (in addition to the uncertainty in the  $m/z30/46$  ratio of organic nitrates.)

The phrase “concentrations of nitrate, ammonium and sulfate ... were governed by the thermodynamic equilibria between their relative mole fractions rather than acidity” isn't clear. The acidity is due to their relative mole fractions. You seem to be saying that concentrations of  $\text{SO}_4^-$ ,  $\text{NO}_3^- + \text{HNO}_3$ , and  $\text{NH}_4^+ + \text{NH}_3$  are essentially constant and the only change with altitude is that the particulate  $\text{NH}_4\text{NO}_3$  rises as temperature drops and RH rises. Another possibility might be that  $\text{NH}_3$  is limiting and is more plentiful at higher altitudes.

But the thermodynamics of the  $\text{NH}_3 + \text{HNO}_3 \longleftrightarrow \text{NH}_4\text{NO}_3$  system have been well known for decades; there is no need to simply wave your hands and say your data are consistent with the thermodynamics when you could do a pretty simple test, going back to Stelson and Seinfeld (1982) or just use the online E-AIM model 4 which uses the work of Friese and Ebel (2010).

Such modeling is particularly relevant because sampling semivolatile aerosols through an aircraft inlet is prone to artifacts. Sampling from aircraft exposes aerosols to a very rapid rise in temperature (due to ram heating as the air is accelerated to aircraft speed) and to extremely intense turbulence. Then there are a few seconds at the temperature of the aircraft interior before entering the instrument. So when sampled, the equilibrium of the  $\text{NH}_{3v} + \text{HNO}_{3v} \leftrightarrow \text{NH}_4\text{NO}_{3p}$  system will be quite far from ambient. The question is how the time scales for chemical adjustment compare with the transit time within the inlet system. I'm not really sure how to answer. Seinfeld and Pandis (2006) have a section on timescales in the  $\text{NH}_{3v} + \text{HNO}_{3v} \leftrightarrow \text{NH}_4\text{NO}_3$  and conclude that its on the order of minutes in typical situations. Adjustments within particles take microseconds to milliseconds; the limiting factor is the diffusion rate from the aerosol surface to air far from particles. So perhaps aircraft sampling isn't a problem at all, but inlet turbulence is not part of the Seinfeld and Pandis (2006) calculation and would drastically change the effective diffusion rates.

### 3 Detailed comments

**Lines 21–22** The statement “thickly coated black carbon” doesn't belong in the abstract. It sounds like something you'll present in the paper, but you never

actually present any data about coating thickness, just referring to a paper in prep.

**Line 60** “semi-permanent” misspelled

**Line 77** “obscured” isn’t exactly right—the aerosol plume is quite visible to the satellites, but the cloud deck makes the intervening aerosol difficult to interpret quantitatively.

**Line 89** What do you mean by “close”? This can easily be quantified, with a statement like “limited data beyond 1000 km from the coast” or something such.

**Line 130** “across a complete range of ion mass-charge ( $m/z$ ) ratios” is meaningless. Did the AMS go to  $m/z = 5000$ ? Just say what masses were scanned. You should also mention the software used for analysis.

**Line 155** A refractive index of  $1.54 - 0.027i$  does not appear in the cited Peers et al. (2019) paper. They concluded that the best value was  $1.51 - 0.029i$ . Something is in error here.

**Line 158–160** The description of SMPS operation is confused. You make reference to Zhou et al., a Ph.D. thesis, so there’s no “et al.”, and it has little to do with airborne sampling. More plausibly, you used Jingchuan Zhou’s inversion scheme and scanned voltages over a 1 minute period. What standards were used to determine whether conditions were constant enough? PCASP concentrations varying no more than 10% or something such?

**Line 167** Impactors deal with aerodynamic diameter. To remove particles  $> 1 \mu\text{m}$  geometric diameter, you must be assuming a particle density. What is it?

**Line 183** I suspect the Lance et al. (2010) isn’t what you meant here. Lance (2012) recommend physical changes to the CDP as well as calibration and operation procedures. The modifications to the optics she recommends are pretty standard now, so I suspect your CDP used them, but you ought to mention that.

**Line 183 (and throughout the paper)** The units  $\text{g m}^{-3}$  and  $\text{g } \mu\text{m}^{-3}$  are ambiguous, since sometimes they refer to cubic meters in the air and sometimes to standard cubic meters (the concentration if the air were at a standard temperature and pressure.) Here I expect you’re using actual volume, but usual

practice for AMS measurements is to use standard volume. Please be explicit about what units you use and what definition of “standard” you use.

**Line 210–211** I expect that aerosols were detected at all altitudes in all 3 periods. Do you mean that pollution aerosols were present in both BL and FT during period 3?

**Line 228, 253**  $\text{NH}_4^+_{\text{predicted}}$  is not a real quantity and is not discussed in Zhang et al. (2007). That paper does talk about  $\text{NH}_4^+_{\text{neu}}$ , which is the  $\text{NH}_4^+$  concentration if all acids in the aerosol were neutralized. Calling it “predicted” suggests that there is some reason to believe that full neutralization should be the case, which is not at all true. if  $[\text{NH}_4^+] = \text{NH}_4^+_{\text{neu}}$ , then it is likely that an excess of  $\text{NH}_3$  vapor is present.  $[\text{NH}_4^+] > \text{NH}_4^+_{\text{neu}}$  says that there is either a measurement error or that there are un-measured acid species present (presumably organic).

**Line 230** Nitrate formation is not suppressed by un-neutralized  $\text{SO}_4=$ , it simply remains as gas phase  $\text{HNO}_3$ .

**Line 247–249** You speculate that lower fraction of OA in aged BB is due to evaporation or oxidation of OA during aging or is due to formation of secondary inorganics. But since you have BC and CO, both of which should be largely conserved, you have the data confirm or rule out the inorganics. You should take a stab at it.

**Line 255** Or the amount of  $\text{NO}_3$  was simply limited by the available  $\text{NH}_3$ . If it’s really thermodynamics of the  $\text{HNO}_3$ ,  $\text{NH}_3$ ,  $\text{NH}_4\text{NO}_3$ , and  $\text{H}_2\text{O}$  system, it ought to be straightforward to do a simple plausibility test with model 4 of E-AIM (Frieze and Ebel, 2010) (<http://www.aim.env.uea.ac.uk/aim/model4/mod4t.php> ).

**Line 274** “assume” is an inappropriate word; those papers argue that there’s evidence that  $f_{60}$  lasts longer in the FT.

**Line 278** This paper does not actually provide evidence that  $f_{60}$  is lost by oxidation during transport. You don’t present any information about what  $f_{60}$  is at the source. I have no doubt that  $f_{60}$  was higher at the source, but you’re making a claim without evidence here. Indeed, one of the lessons of Jolleys et al. (2015) is that  $f_{60}$  is highly dependent on fuel and burning conditions. The fairly complete combustion indicated by high MCE is likely to mean that the carbohydrates that make up the  $m/z = 60$  signal were largely oxidized.

- Line 286–287** It should be noted that your  $f_{44}$  is at the extreme of the data in Aiken et al. (2008) and from very different sources, so the linear fit and error estimates may not be terribly accurate.
- Line 289–290** This is circular reasoning. High  $f_{44}$  is the reason you know you have high O/C and OM/OC.
- Line 297** I’m a bit amused that you use the American spelling of “sulfate” in a European journal, then use the English spelling for “smouldering”.
- Line 299–300** The text here does not match the description in the supplement or figure 5. The latter two say that BC:CO and OA:CO in the FT were determined from the slope of the relationships, not by subtracting out the background value. Using the slope is more robust to variations in the background levels, so is a good way to do it.
- Line 300 (and Supplement S1)** I appreciate that you’re using ODR fits rather than conventional least squares, but ODRs are quite capable of exhibiting artifacts, particularly when the variables have different units (in this case,  $\mu\text{g m}^{-3}$  and ppmv). There’s a nice short discussion in the Wikipedia page. For the good correlations you have, it probably makes little difference, but you could easily recast BC to a mole ratio with air or CO ppmv to  $\mu\text{g m}^{-3}$ . Or you could wade through Warton et al. (2006) or something similar.
- Line 315–316** The statement “It is likely that observed BC/ $\Delta\text{CO}$  values in FT smoke are similar to values at source.” is likely true, but it should be acknowledged that CO has a lifetime of about a month in the FT due to reaction with OH. That lifetime is pretty long compared with your transit times and may be longer since there are a lot of other things for OH to react with.
- Line 355** Note that the only absorption instrument in SAFARI-2000 was a single-wavelength PSAP. They had to assume an absorption Ångström exponent to get SSA at other wavelengths.
- Lines 397–401** It’s little irritating to see hand waving here when it could be modeled pretty easily. You might be right that  $\text{NH}_4\text{NO}_3$  would double given the temperature difference, but it could easily be checked for plausibility. Just ignore the organics; they’ll be so much less hydrophilic than the sulfate that they won’t be responsible for much water.

**Lines 402–407** More hand waving that could be quantified. Given the additional mass of  $\text{NH}_4\text{NO}_3$ , what would be a plausible increase in diameter?

**Line 445** ~~spay~~ spray

**Supplement line 24** It might be nice to actually say what the background CO concentrations was in the FT.

**Supplement lines 59–70** This analysis depends on either a lack of interference at  $m/z = 30$  and  $m/z = 46$  or on the frag table being correct. The former is shaky, since  $\text{CH}_2\text{O}$  and  $\text{C}_2\text{H}_6$  are at  $m/z = 30$  and  $\text{CH}_2\text{O}_2$  and  $\text{C}_2\text{H}_6\text{O}$  are at  $m/z = 46$ . Given the highly oxidized aerosol,  $\text{CH}_2\text{O}$  is likely to be plentiful. The frag table is of course designed for general ambient aerosol and can have striking problems with unusual composition. It is particularly troubling that the standard frag table for Squirrel 1.62G assumes there is nothing but  $\text{NO}_2$  at  $m/z = 46$ . At  $m/z = 30$  there is an indirect dependence on getting the  $m/z = 28$  peak right. I haven't used a C-ToF, but that peak is so big on an HR-ToF that it seems to be a bit nonlinear. High CO from the aerosol can also screw that up, but I don't think your OA concentrations were that large.

## References

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