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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The fluorescence properties of aerosol larger than 0.8 µm in an urban and a PBA-dominated location" *by* A. M. Gabey et al.

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This study analyzes measurements of aerosol properties, size and fluorescence, in two locations with very different sources of particles. The primary objective of the study is to evaluate the differences in the particle size distributions and fluorescing intensities in the context of PBA versus non-PBA particles. The goal is to find metrics that can differentiate the two types of fluorescing aerosol particles (here after referred to FAP) so that, in the long run, these types of measurements can better quantify the properties of PBA, their sources, health impacts, etc. Of course, given that we also know quite little about the non-PBA FAP, being able to better characterize their properties would

also improve our ability to identify and “fingerprint” these types of particles.

Overall, the material is organized and presented concisely with each step leading logically to the next one. From the beginning it is clearly understood that the authors intend to use the F1, F2 and F3 intensities, and some relationships among them, to derive metrics that separate PBA from non-PBA FAP and, in the end, there appears to be an argument for using the F1/F3 ratio as a way to find “Borneo-like” particles in Manchester. To this reviewer, however, to end the paper with this conclusion leaves this reader, and potential user of a WIBS-like instrument, hanging, i.e. if I am now to run the WIBS in Mexico City, and find that my F1/F3 ratio distributions look neither like Manchester or Borneo, what have I learned? I think that the authors have a rich data set that could and should be pushed a bit further than they have done to this point in order to better understand exactly what are the links between the biochemical properties of the FAP and their size, fluorescence intensities as a function of wavelength and other characteristics that better differentiate PBA and non-PBA on a single particle basis, rather than on an ensemble.

The paper touches upon, but never returns to, the problem of actually determining how much fluorescing material there is in a particular particle. In the single particle soot photometer, SP2, we are challenged similarly, i.e. we have an optical diameter measured by light scattering, similar to the WIBS and an incandescence signal, related to the amount of refractory black carbon (rBC) mixed in the particle, similar to fluorescence in the WIBS that is related to the amount of UV active material mixed in a particle. In order to get a handle on the fraction of rBC in a given particle with respect to the rest of the non-refractory material, we derive a mass equivalent diameter (MED) from the rBC mass that we obtain from the incandescence signal. Here, of course is where there is a major difference between the WIBS and SP2. In the SP2 we have what we think is a fairly good relationship between rBC and the intensity of incandescence because of calibrations with rBC reference materials (these, of course, are the focus of a lot of healthy discussions). The point is, however, that we are able to compare the

ACPD
11, C386–C390, 2011

optical diameter with the MED and this gives us a relative indicator of the amount of rBC mixed with non-refractory material. We find some very significant differences from location to location, depending on the source of the rBC and their age, in these mixing indicators.

I recommend an expansion of the analysis of the current data set to take a similar approach when evaluating the Manchester and Borneo measurements. Just as in the SP-2, we look at two different incandescence wavelength to estimate the temperature, the authors are using three different fluorescence wavelengths to separate NHAD and Tryptophan type of characteristics. The obstacle to following an approach parallel to that which is used in the SP2 is that apparently there is no reference material that relates fluorescence intensity to an intrinsic property of the FAP. This raises my first three questions:

1) Why can't the WIBS be calibrated with known FAP, i.e. PAHs that are known to fluoresce and that can be produced with mono-dispersed distributions?

2) If at the moment the analysis is restricted to the use of arbitrary units (a.u.) how do the intensities measured during the Manchester trials equate to those measured during the Borneo trials? Put another way, what was the transfer standard used to calibrate the F1, F2 and F3 channels so that any differences were really in the FAP themselves and not changes or shifts in the optical or electrical system?

3) Were the background fluorescing values the same in both experiments?

In the current analysis, fluorescence is shown plotted in Figs. 7-9 with lines representing median values and quartiles, but these graphs mask what may actually be going on that makes the Borneo data distinct from the Manchester measurements. The spread in fluorescence values, that is quite large, may be linked to other processes that could be related to the source of the difference. We know for example, that there can be photon quenching effects, depending on what the fluorescing material is mixed with. Without knowing the relative fraction of fluorescence material to total non-fluorescing

ACPD

11, C386–C390, 2011

material, this effect cannot be very well assessed. So, my first three suggestions:

i) Analyze the number concentration as a function of F1, F2 and F3 fluorescing intensity.

ii) Normalize F1, F2 and F3 with the scattering intensity to get [F1], [F2], [F3] then look at the relationships between [F1], [F2], [F3], e.g., scatter plots of [F1] vs [F3] with color encoding uing the intensity of [F2]. Plot number concentration as a function of [F1], [F2] and [F3].

iii) If fluorescence is expected to be proportional to the cross sectional area of the particle, then derive a surface equivalent diameter (SED) that can be compared with the optical diameter. This can be arbitrary as well until some there is a way to better calibrate the fluorescence channels, i.e. derive a scale factor between fluorescence and Dˆ2 to get an SED < = optical diameter. The objective is to find a way to estimate a relative fluorescence fraction that is then used to more clearly compare FAPs on the same basis.

In summary, given the very limited number of data sets that have been taken thus far, the authors are in a position to set the pace on analyzing these complex measurements and raise the bar somewhat higher as a challenge to future researchers acquiring more data from the same type of instrument. This is not to cast stones at the work they have already accomplished as it has been done carefully and there is already value to their evaluation. I am recommending that before this go to press as an ACP publication, that a bit more effort be expended to extract more information than has been done to this point.

Other comments, questions, suggestions:

Abstract, line 14. Start out defining sizes as radii or diameters.

Page 533, Line 22-23. It is not clear what is meant here by the excitation and emission bands being quite well separated. They seem to have overlapping emissions and excitations. Some clarification needed.

ACPD

11, C386–C390, 2011

Page 537, Methods. Forward and side-ward light is measured. Are the two summed? Which is used for sizing? Clarify? Size range? Uncertainty? Sample line losses? Number of size bins? Is the Xenon radiation filtered to remove any light between 310-400, or 400-600nm? Are the activation wavelength really that precise? Lacking essential information here to understand the remainder of the discussion.

Page 541, Line 7. Nnon is introduced here without defining.

Page 543, Line 20. Based on what? Show a microphotograph? Explain what one looks for in a PBA.

Page 547, lines 19 – To my eye these distributions don't look log-normal. What criteria are being used to make this observation?

Page 550, Line 13 – Although in their summary the authors qualify their conclusions that PBA have a minor influence in Manchester, until they further stratify or parse their results and have a more statistically reasonable set of filter analyses, I think that this conclusion should be put on hold.

Page 551, lines 15-17: I would argue that the relationship between fluorescence and diameter is not linear, as stated here by the authors. A positive trend, yes, but on a linear-log plot, a straight line is not linear. This raises the question, what would all of these data look like on linear-linear scale plots?

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 531, 2011.