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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Measurements of coarse mode and primary biological aerosol transmission through a tropical forest canopy using a dual-channel fluorescence aerosol spectrometer" *by* A. M. Gabey et al.

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The authors exploit a dual-excitation-wavelength particle fluorescence spectrometer developed by Kaye and collaborators (Kaye et al, 2005; Foot et al., 2008), called the Wide Issue Bioaerosol Spectrometer, version 3 or WIBS-3, to measure concentrations of fluorescent particles in a tropical rainforest in Borneo, Malaysia. The WIBS-3 measures the undispersed fluorescence of single particles flowing through an optical cell

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and excited by the sequential firing of two xenon sources with peak emission around 280 nm and 370 nm, optimal for exciting the fluorophores tryptophan (280 nm excitation) and NADH (370 nm excitation) found in many biological particles. The WIBS-3 has been developed to be relatively low-cost and portable (Foot, 2008) so that it can be used in a variety of applications. The authors find diurnal variations in fluorescent particles, which they assume are Primary Biological Aerosol or PBA. The diurnal variations appear to be consistent with times of increased release of fungal spores.

The authors define a Primary Biological Aerosol (PBA) as "an aerosol particle that is discernibly all or part of a living organism." Because the authors then write that the category includes (among others) "animal and plant fragments," their definition would be more clear as: "A Primary Biological Aerosol (PBA) particle is defined as an aerosol particle that discernibly is or was all or part of a living organism." Do they consider Primary Biogenic Aerosol and Primary Biological Aerosol to be equivalent? Because particles may be mixtures of biological and nonbiological materials, it seems that some definition regarding these mixed particles (possibly in terms of mass fraction) is needed. Also, because biological materials can degrade with time, we wonder how much degradation can occur before a material would no longer be termed PBA if it were in an aerosol particle? For example, roughly what fraction of typical humus, if aerosolized, would be PBA?

The authors state, "It was assumed that PBA are the only fluorescent aerosol in the coarse mode and that to be recorded as such, their fluorescence must exceed an instrument-defined minimum threshold in either channel."

This statement raises several questions and concerns. 1) What data was used to determine the fluorescence thresholds needed to support the above assumption, so that the measurements can be used to make quantitative statements about the number concentration of fungal spores or other PBA? What types of fungal spores, bacteria, wood fragments, cellulose particles, etc., were used in the calibration to determine these thresholds? The work of Kaye et al (2005) is cited; however, this paper shows

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results for two bacteria, and one pollen, but no fungal spores. The lack of any indication that known fungal spores were measured with the WIBS-3 as test particles, in a paper that emphasizes fungal spores, is of concern. In a companion paper, Gabey et al, 2009 (submitted to Biotropica), measurements for asymmetry parameters of several types of fungal spores measured with the WIBS-3 are presented. But they say nothing about the fluorescence of these spores, which must have been measured at the same time if they were calibrating the system as a whole. Sivaprakasam et al (Opt. Express, 2004) included Sporisorim cruentum as test particles for their dual-excitation-wavelength LIF aerosol detector, and found these fungal spores to have a very weak fluorescence. In Fig. 3 of the Sivaprakasam paper, Sporisorium spores appear to have fluorescence that is not much stronger than kaolin, a mineral dust, and so their one fungal spore is placed in a category of non-fluorescing interferants. As Sivaprakasam stated, "The two interferents, kaolin and S. Cruentum both show a pattern distinctive from all the other samples marked by particularly low fluorescence in all channels." That data raises further questions, e.g., how do the fluorescence cross sections from recently released spores compare to those of aged fungal spores? How much variation is there in the fluorescence cross sections of fungal spores from different fungi?

2) We question the rationale for using the same fluorescent thresholds for particles having diameters that range from 2 to 20 micrometer, where the volume varies by a factor of about 1000. The number of fluorophors in a particle is proportional to volume if the fluorophors are uniformly distributed. Thus, for particles of mixed composition, the molecular fraction of fluorors in a small particle would have to be proportionally larger than that in a large particle, for the same fluorescence intensity to be emitted. Consequently, having the same fluorescent threshold for all particles will distort "PBA" concentrations derived from the atmospheric data. In the work of Sivaprakasam (2004; 2007) both the elastic scattering and fluorescence excited at the two wavelengths are used in their classification schemes. Sivaprakasam (2004) calculated the fluorescence cross sections (proportional to the ratio of fluorescence to volume) for their 16 types of test particles made of different materials. Sivaprakasam (2007) wrote: "Our data

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was analyzed using a Baysian classifier algorithm which was trained to pick out the simulants of interest . . . where the classifier could use the elastic scattering and fluorescence". Gabey et al classify particles into PBA and non-PBA based solely on fluorescence intensity. The data in the Sivaprakasam papers, especially the scatter plots, suggest fluorescence intensity alone is not adequate when the particle sizes vary over a wide range. The data in the paper under review reinforce this concern. In Fig. 6 the ratio of the "non-PBA" to "PBA" particles decreases by over two orders of magnitude as the particle size increases from 0.8 um to 20 um. We suggest that this enormous decrease in the ratio is an artifact of the definition chosen for PBA, where the fluorescence from the particles is not normalized by either particle volume or cross section. We note that for homogeneous particles the dependence on particle size is typically somewhere between the cross section and the volume, depending upon a variety of factors such as the particle size, wavelength of light, concentration of absorbing molecules, total absorption by the particle, and re-absorption by other fluorophores of the initially emitted (from the molecule, not the particle) fluorescence (Hill, 2001).

3) Even if the fluorescence thresholds were based on something like fluorescence-to-scattering ratios, and on measured data for fungal spores, etc., we still question whether the assumption that "PBA is the only fluorescent aerosol in the coarse mode" is valid. Bauer et al (2008) found that fungal spores contribute only 2%-8% of organic carbon at an urban site in Europe (Vienna). Elbert et al 2007 (paper referenced by the authors) estimate that in pristine tropical rain forests, fungal spores may account for 25% to 45% of coarse particulate matter. Fluorescence spectra of atmospheric aerosol (Pinnick et al, 2004; Pan et al, 2007) illuminated with 266-nm light (similar to the 280-nm excitation channel WIBS-3) exhibit many different spectra, where about 90% of the spectra could be clustered into one of 8 to 10 clusters with the distance metric chosen. The measurements were not made in a jungle environment, but two of the measurement sites were in the east coast of the USA, where large trees and other vegetation are plentiful. In those papers various fluorophors known to be present in at-

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mospheric aerosol were listed for most of the main spectral categories observed. Some of the wide range of organic-carbon fluorescent compounds that could contribute to the spectra measured include: a) tryptophan, vanillic acid (a tracer for biomass burning) and naphthalene derivatives for spectra that have the 345 nm peak typical for proteins and bacteria; b) ferulic acid and other known fluorors in cellulose for the peak near 450-nm and which may also have contributions from NADH; c) humic acids and humic-like-substances, as well as polycyclic aromatic hydrocarbons (PAH) for the spectral clusters that are typically most populated (although we note that reported spectra of humic substances appear over a remarkably large range); d) phenols and other benzene derivatives for our category with the peak emission at the shortest wavelengths (Although we note that fluorescence generated from benzene by the 280-nm light used in the WIBS-3 should be negligible and this is consistent the WIBS-3 not recording fluorescence from polystyrene.). For 266-nm excitation, only a relatively small fraction of particles that fluoresce have spectra characteristic of tryptophan (the dominant fluoror in biological particles). The large variations in the fluorescence spectra measured by Pinnick (2004) and Pan (2007), and the huge numbers of non-biological fluorescent organic-carbon molecules known to occur in the atmosphere, make us question further the validity of the assumption that all particles with fluorescent intensity exceeding some threshold are PBA, even below a canopy in Borneo. Heald et al (2009) suggest that PBAs may be the dominant source of organic aerosol in the tropics. And it seems likely that PBAs contribute a higher fraction of aerosol in a tropical rainforest site in Borneo than in less-remote areas in the USA. On the other hand, forest fires in Borneo and other parts of Indonesia are not uncommon. Even if they were, we would expect combustion aerosols would be important. Air pollution from China can travel 1000's of km to the western USA, and smoke from forest fires in Alaska can travel to the east coast of the USA. Cigarette smoke can have fluorescence spectra very similar to those of bacteria (Hill et al., 1999). We also expect that particulates containing humic acids and humic-like-substances, which can be formed by biodegradation of plant matter in the soil, likely contribute to the fluorescent fraction of coarse particles. Regarding the

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contribution of plant fragments to PBA, we note that Pan et al (2007) found, at urban and rural sites in the United States, between 1% and 3% of particles having laser-induced-fluorescence spectra characteristic of cellulose. It seems appropriate for the authors to cite recent papers which discuss the contribution of PBAs to the atmospheric aerosol loading, e.g., Deguillaume et al, 2008; Winiwarter et al, 2009; Bauer et al, 2008 and Heald et al, 2009.

It is unclear to us whether the combined use of all the parameters measured by the WIBS-3 (both fluorescence channels, and the measurements of the Asymmetry Factor), could be used to differentiate PBA from non-PBA organic carbon particles, as suggested in other work by Gabey et al 2009 (submitted to Biotropica). However, in this paper the authors do not indicate that they tried to use these other features for additional discrimination.

We think it may be more clear for Gabey et al. to refer to their particles as fluorescent aerosol, normalized by elastic scattering, or possibly by volume, instead of presenting the concentration data in terms of PBA, which appears speculative. It might be convenient for the authors to assume that the fluorescent particles above a certain threshold are primarily PBA; but the authors go too far in determining concentrations and size distributions of PBA as if that assumption were true.

Finally, we note that Fig 3 of the present paper is identical to the second part of Fig. 1 of Gabey et al 2009 (submitted to Biotropica) not referenced in the paper under review.

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