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Atmospheric
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Discussions

Interactive comment on “Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols” *by* M. O. Andreae and A. Gelencsér

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General comments

This paper is a good review of current understanding of aerosol that absorbs light. It touches on many important points, and is very timely. The abstract is a very nice summary. I suggest that it be expanded somewhat, because not all the discussion in the paper relates to the distinction between Csoot and Cbrown.

I encourage the authors to be more conclusive when possible. They raise several valid points, particularly regarding analytical difficulties. The reader might like to know if, after their examination, they feel that correction is possible, or whether the present analytical methods are partially unsuited for the analytical task at hand, or whether these methods can never be made suitable. Such an analysis, and the addition of recommendations, would make the paper more practical.

The paper is well written except, as I suggest in specific comments, in some places it could be reorganized somewhat.

Specific comments

Page and line numbers refer to the print version.

Page 3420, Background, line 19. It is interesting that you make the identification of soot as black material in the smoke from wood and coal fires, since these are the sources most likely to produce Cbrown!

Page 3421, lines 20-22. "Soot particles are the only physically existing and observable particle types that can be readily recognized by their special morphology..." First, what do you mean by "physically existing and observable"– what sorts of particles are not physically existing or observable? Second, does this sentence mean that the aggregate nature of soot particles identifies them as combustion-generated, and that other spherical or crystalline particles cannot be so uniquely identified? This could be stated more concisely.

Page 3421, line 25. "...aggregates are... their most stable form." It is true that the spherules usually do not exist on their own, because they coagulate quickly at the high concentrations in and around flames. But the statement that an aggregate is a stable form is puzzling to me. It implies that there are other, less-stable forms.

Page 3422, lines 3-4 "...soot of which 50% by mass is organic matter." Since you are later going to call the highly graphitized material Csoot, I suggest that you not use "soot" to mean "all particles," as you are doing here.

Page 3422, lines 8-9. "...only one third of a double bond character, unlike a strictly aromatic or olefinic linkage." First, I think you mean aliphatic, not aromatic. The graphitic bonds are aromatic. Second, I find "one third of a double bond" confusing. I think one-half would be closer to accurate, but why not just use the standard hybridization terminology (sp, sp^2, sp^3)?

Page 3422, lines 9-10. "The resonance of the pi-electrons among various configurations accounts for..." This is misleading. The structures that exhibit the standard (chemical) definition of resonance aren't the ones that participate in conductivity. My understanding is that resonance occurs among the sp2 bonded orbitals, and the conductivity occurs in the pi-electrons. The high density of states of the pi-electrons allows absorption of low-energy (long-wavelength) photons, but this isn't related to the resonance.

Page 3422, lines 28-29. "At longer annealing times..." I would not use the word "annealing" here, because the order may result from formation kinetics rather than transformation of already-formed solid. I also think that ordered structures can occur far more quickly than seconds. Diesel soot is reasonably well ordered, and must be formed in less than 0.1 second (the time of a power stroke at 3000 rev per minute). Annealing times of minutes are probably found in association with amorphous carbon literature, but there the carbon is already formed and has to change its structure.

Page 3423, lines 6-7. Please give a reference for this composition, which is very specific. As you have pointed out earlier, the composition depends on formation, so any composition cited should be traceable to the processes which produced the material.

Page 3423, paragraph beginning line 21, proposal of "Csoot" as terminology. To me this is quite acceptable, but as you have nicely discussed, there is quite a range of combustion-produced particles. It would be helpful to the reader if you summarize in this paragraph what is and is not to be considered Csoot. Will you include rapidly-formed amorphous soot, which has a lower absorption cross-section than more ordered soot (Schnaiter et al., 2003, ref cited in paper)? I am not certain that even Raman spectroscopy would identify this material as Csoot.

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Pages 3423-3424, long paragraph. I think you are implying that range of material classified as "BC" and "EC" has different responses to the varying techniques, and that this variation in response leads to different results. You should say this directly. The example of graphite is useful but not pointed enough.

Page 3424, lines 24-25, "light absorbing carbon" used to refer to all forms of light absorbing carbonaceous aerosols. We (Bond and Bergstrom 2006) did not use "light absorbing carbon" to refer to all light absorbing aerosols, but specifically to the material you are calling Csoot. I do not have a problem with a change in terminology, but I request that you cite our use of "light absorbing carbon" properly– I am mainly concerned that readers will think that conclusions in our paper refer to all light absorbing carbonaceous materials, when we explicitly exclude some of these materials.

Page 3425, lines 22-23, "...thermally reactive and colorless organic substances, such as hydrocarbons." I suggest that you be more specific; perhaps you mean "aliphatic hydrocarbons" (as many aromatic hydrocarbons do absorb light).

Page 3425, lines 29-30, discussion of Cbrown. Again, I think it would be a great service to the reader if you provide some definitions for Cbrown. Perhaps it eludes precise characterization because it has a wide range, but can you at least tell us what it is not? Analytically, how would one tell the difference between Cbrown and Csoot?

Page 3426, first paragraph. Forgive the picky comment, but the yellow particles in initial combustion were not seen at the industrial lignite plant, but rather in residential coal combustion (Bond 2001, cited in your paper). Further, the 2001 paper is the source of the remainder of the speculation you discuss.

Page 3427, lines 3-4, "...properties closely resembling those of natural humic/fulvic substances." Please list some of the properties that were compared: absorption? chemical composition? solubility?

Page 3427, lines 10-11, discussion of Figure 2. How much fulvic or humic acid is on the filters? Is this comparable to an atmospheric sample?

Page 3428, lines 17-19, discussions of operational definition. Your point that a single reference material is unlikely to represent Cbrown is well taken. Can you comment on whether Cbrown might be bounded by judicious selection of one or more reference materials?

Pages 3428-3429. Definitions as stated, especially the introduction of the terms "apparent" and "equivalent", will be very useful.

Page 3429, lines 21-22. I think that "black carbon" is only prevalent in climate pollutant inventories. It may not be so in inventories developed for air quality purposes.

Page 3430, lines 11-12. Wasn't EGA developed in part for occupational situations, like mines? I wonder how they dealt with coal dust, which might also be considered "brown carbon."

Page 3431, paragraph beginning line 5. I think you have two different theses here, and they should be divided. First, Cbrown has a wide range of volatilities, and thus could confound thermochemical analysis. Second, EC itself may be affected by the analysis, including catalysis of coexisting chemical components.

Page 3432, lines 20-25. This seems largely speculative to me, and perhaps it is intended to be so. Perhaps a statement at the beginning of this discussion could clarify this, e.g. "It is not known whether brown carbon is prone to charring."

Page 3433, paragraph beginning line 11. This paragraph would be more usefully located before the discussion on page 3432. It details the correction for and implications of charring during thermochemical analysis, which is good background for understanding the discussion of whether Cbrown chars.

Page 3434, line 20. "This is supported by the studies of Wittmaack..." I didn't understand how Wittmaack determined that their atmospheric aerosol came only from diesels. True, it looked like diesel soot, but was there unambiguous identification? If, as you propose, Csoot has a wide range of properties, do you feel comfortable extrapolating the Wittmaack results to all Csoot?

Pages 3434 -3435, paragraph beginning line 17. It sounds like you are proposing that diesel soot (or perhaps Csoot) volatilizes below 510 C, and material volatilizing above that temperature is some other type of carbon. However, I may have gotten an incorrect impression. A one-sentence summary of what authors do believe, based on this literature review, would be welcome.

Page 3435, paragraph beginning line 11. I agree that Cbrown and Csoot may confound the thermal analysis but I do not understand how from the arguments laid out here. First, if Cbrown absorbs very little at the instrument wavelength, then it probably does not affect the optical correction much. Second, you identify an assumption that char and LAC have the same optical properties, and say that this leads to a bias. Are you inferring that Cbrown has the same optical properties or wavelength as char? If so, please provide some evidence or reasoning.

Section 2.2, Light absorption measurements. This section summarizes some of the vagaries involved with inferring mass from optical measurements. Much discussion (over 3 of these print pages) is given to issues which have been raised previously, and which do not directly relate to the distinction between Csoot and Cbrown. I think that it is useful to present these issues, but perhaps some background should be given: it is difficult to determine Csoot from optical measurements in the first place. Also, the abstract should be expanded to reflect your review of analytical techniques in addition to distinctions between different substances.

Page 3437, paragraph beginning line 26. Again, I think that this paragraph contains two separable discussions. There is a difference between the filter response to absorption and the absorption cross-section per mass, and both discussions are woven into this paragraph. They should be separated throughout the section, perhaps with sub-headings. In addition, avoidable and unavoidable problems are entangled. For

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example, most installations run only dry air through filter-based techniques just because of the wetting problems discussed here. These problems are preventable, but variations in absorption cross-section are not.

Page 3439, paragraph beginning on lines 7. I suggest that the beginning of the paragraph on line 29 (same page) should be incorporated into the paragraph on line 7. It is not known how much of this variation is due to thermochemical measurements, and this is an important distinction.

Page 3440, lines 9-11. This sounds like the aethalometer and PSAP are fundamentally different; they aren't. I would guess that only the interpretation (i.e. use of attenuation coefficient) is different.

Page 3440, lines 18-21. Please give sizes for "accumulation" and "Aitken" mode. For absorption, there is a big difference between even 100 and 300 nm particles (for 550 nm light). You may also want to point out that a 200-nm particle of Csoot is an aggregate and may have higher absorption than a 200-nm spherical particle.

Section 3, general comment. This section raises two important points–the potential effect of Cbrown on UV photolysis and on cloud water–which should appear in the abstract.

Page 3441, general discussion. I agree that the properties of Cbrown may not be constant, and that there may not be a relationship between light absorption and “black carbon” or Csoot. However, this statement relies on two assumptions: (1) the wavelength dependence is so variable that it cannot be reliably estimated, even in regions dominated by particular sources; and (2) brown carbon absorbs at all wavelengths, and thus no chosen wavelength is free from its artefact. Without tabulated data to support these assumptions, it is difficult to confirm how broadly these statements apply to atmospheric aerosol. In the next section (3. Wavelength dependence), you do provide some data on wavelength dependence. You could also refer to the tabulation by Kirchstetter et al (2004, paper which you cite). In some work (e.g. Kirchstetter), an assumed wavelength dependence, along with absorption at a long visible wavelength, have been used to attribute extinction to Cbrown and Csoot. Can you comment on these procedures, and quantitative estimates of likely errors? Because of the review nature of this paper, it would be nice if some firmer conclusions were given.

Page 3444, line 4. Bond and Bergstrom (2006) didn't make any comments about the wavelength dependence of Cbrown.

Page 3444, line 19. I would be reluctant to call this a "discovery." You have cited literature that goes back 20 years.

Page 3445, lines 7-11. I think this is an unfair statement. I believe that many modelers are aware that analytical techniques for Csoot, BCe, ECa, and so on are open to question. For example, Bond et al. (2004) discuss these analytical issues and account for the uncertainties in "BC" fraction in the inventory. To turn the tables, it isn't really the duty of climate modelers or inventory developers to resolve this problem! Rather, the measurement community needs to provide some guidance.

Also, no models use the optical properties of graphite, which are quite different than those of Csoot.

Editorial comments

Page 3427, line 10, "humid" should be "humic"

Page 3444, line 26. Sentence should end after "overlooked."

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 3419, 2006.

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