

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

M. O. Andreae and A. Gelencsér

Received and published: 20 July 2006

Authors' responses are in italics after the reviewer's comments.

Page and line numbers refer to the original 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 *C_{brown}*!

Terminology is almost everything in this business. We are using “soot” here in the sense defined in Webster: “a black substance formed by combustion or separated from fuel during combustion, rising in fine particles, and adhering to the sides of the chimney or pipe conveying the smoke”, and we are actually providing an abbreviated

form of this definition in the first sentence. Since we are making a historical statement, we are bound to use this term. Note that “soot” is different from “soot carbon”, C_{soot} , which we introduce and define later. We are now introducing this distinction in para 2, page 2.

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.

The statement has been changed to “one of the few particle types”, since the same could be said for some primary biogenic particles, for example.

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.

We have changed the sentence to make clear that the primary spherules do exist, but not in ambient air.

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 C_{soot} , I suggest that you not use "soot" to mean "all particles," as you are doing here.

It is extremely difficult to find a satisfactory solution to this terminological nightmare. We had initially put the definitions at the end of the Introduction, so the reader would have been given all of the explanations before encountering the concise definitions. But maybe it is better to put the definitions up front, and ask the reader for some patience

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Interactive
Comment

with getting the details. This way the reader is more alert to the quagmire he is getting into. We have thus restructured the Introduction. Still, the reader will have to distinguish between “soot” and “C_{soot}”. To make things easier, we have nearly eliminated the use of “soot” as a noun, or annotated it where it was unavoidable.

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, sp², sp³)? 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.

The resonance formulation is an equivalent (older) treatment for the more modern hybridization approach. One can treat benzene as either two structures that “resonate” with each other, or as one structure in which the bonds are hybridized. In graphite, each carbon has three bonds, “made up” from two single bonds and one double bond, thus 1/3 double-bond character. In hybridization terminology, three electrons (one s, two p) are hybridized to sp² and connect the atoms in the plane. The fourth unhybridized p electron has an orbital perpendicular to the plane. These orbitals overlap sideways and produce delocalized pi bonds. The pi electrons form an “electron gas” that can move along the graphite planes. This produces a metal-like character (with conductivity along, but not across the planes) and light absorption with an infinity of adjacent orbital energy levels. The text has been reformulated in hybridization terminology.

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 transforma-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

tion 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.

The problem here is that the experimental work has often been done in lab experiments where lower temperatures and longer annealing times were chosen to make the experiments more controllable. Five lines earlier we already point out that the chemical and thermal environments also play a key role. We replaced the “and” with “or” in the present version, to read: “At longer annealing times (seconds to minutes) or higher temperatures, more highly ordered carbon structures develop.”

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.

The composition values have been replaced by a more generally applicable range, and references included.

Page 3423, paragraph beginning line 21, proposal of " C_{soot} " 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 C_{soot} . 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 C_{soot} .

A very specific definition is now given in the definition paragraphs near the beginning of the Background section.

Pages 3423-3424, long paragraph. I think you are implying that range of material

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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.

We have made the text more explicit. Also, this issue is belabored in the rest of the text.

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 C_{soot} . 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.

We have specified the difference in definition in the definition section, and have removed the reference to Bond and Bergstrom 2006 in the present paragraph.

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).

We've added "most" in front of "hydrocarbons". There's really no reasonable way to be very specific here. The "prototype" aromatic compound, benzene, does not absorb visible light, neither does toluene, xylene, naphthalene, etc.

Page 3425, lines 29-30, discussion of C_{brown} . Again, I think it would be a great service to the reader if you provide some definitions for C_{brown} . 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 C_{brown} and C_{soot} ?

Defined in the definitions section, which now has been moved up.

Page 3426, first paragraph. Forgive the picky comment, but the yellow particles in initial

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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.

Reference and text corrected.

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?

Done.

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?

We did not measure the loading, as these samples were meant for qualitative illustration only. They would be comparable to very heavily loaded urban samples. This has been indicated in the caption.

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

We don't think there is a reasonable candidate at this time. There is some more discussion on this issue at the end of the paper.

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

The definitions have been moved up.

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.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

OK. We now specify “climate-science community”.

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."

The present paper focuses on ambient aerosols, and applications like coal dust are beyond the scope of our paper. The sentence was changed to “Thermochemical analysis was originally applied to urban aerosols...”.

Page 3431, paragraph beginning line 5. I think you have two different theses here, and they should be divided. First, C_{brown} 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.

This is what we meant to indicate by “Firstly” (line 7) and “Furthermore” (line 10). We have substituted “First” and “Second”.

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."

This paragraph was a little confusing, because we mixed up the more general issue of charring with the more specific one of charring of C_{brown} . We have tried to straighten this out by rewriting the paragraph.

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 C_{brown} chars.

We disagree, because this paragraph addresses only one subset of the problems and one technique, while the previous paragraph is more general. This should be clearer now after changing a few of the sentences.

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, C_{soot} has a wide range of properties, do you feel comfortable extrapolating the Wittmaack results to all C_{soot} ?

Wittmaack basically did it by inference. Given the high fraction of diesel vehicles (LD and HD) on German roads, the low emissions from current gasoline vehicles, and the presumably low incidence of biomass burning in May in Germany, I think one can believe him. But no, there was no unambiguous identification. We have made the sentence a bit more cautious. And no, we do not want to extrapolate to all particles. This is precisely the point here: we say things agree well for diesel exhaust (accepting Wittmaack's inference), but they are a mess for other LAC-containing aerosols.

Pages 3434 -3435, paragraph beginning line 17. It sounds like you are proposing that diesel soot (or perhaps C_{soot}) 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.

A summary sentence was added to the end of this paragraph.

Page 3435, paragraph beginning line 11. I agree that C_{brown} and C_{soot} may confound the thermal analysis but I do not understand how from the arguments laid out here. First, if C_{brown} 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 C_{brown} has the same optical properties or wavelength as char? If so, please provide some evidence or reasoning.

This is a really messy issue, that's why we have used words like "complication" and "bias". We think the reviewer is correct here by saying that C_{brown} does not affect the

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

optical correction significantly. As long as the laser never sees C_{brown} because of its low absorption in the red, the instrument will interpret the fraction of C_{brown} combusted before the EC cutpoint as OC, the more refractory part as EC. Thus, part of C_{brown} will be counted as OC, part as EC_a . Since the optical properties of C_{brown} are different from those of C_{soot} , EC_a is then not a good proxy for LAC any more. We have changed the text to make this clearer.

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 C_{soot} and C_{brown} . I think that it is useful to present these issues, but perhaps some background should be given: it is difficult to determine C_{soot} 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.

Because optical methods are very widely used to measure BC_e , and this is interpreted generally as C_{soot} , BC , or LAC , a thorough treatment of these issues is essential. We have added a couple of introductory sentences to end of the first paragraph of section 2.2, and we have expanded the abstract.

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 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.

We have tried to improve the structure of the discussion by introducing subheadings.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

A complete restructuring along logical lines is not realistic, since much of the literature also uses terms that involve the effects of filter bias and absorption cross-section (α_{ATN}). Trying to deconvolute this discussion does not seem possible. Going into a discussion of what is avoidable and what is not would lengthen an already long paper.

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.

The discussion has been restructured as suggested.

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.

We agree and have modified the sentence.

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 C_{soot} is an aggregate and may have higher absorption than a 200-nm spherical particle.

Sizes have been added. We feel that it is better not to crowd in more information here.

Section 3, general comment. This section raises two important points—the potential effect of C_{brown} on UV photolysis and on cloud water—which should appear in the abstract.

Done.

Page 3441, general discussion. I agree that the properties of C_{brown} may not be constant, and that there may not be a relationship between light absorption and “black carbon” or C_{soot} . However, this statement relies on two assumptions: (1) the wave-

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

length 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 C_{brown} and C_{soot} . 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.

This paragraph refers to all the sources of error discussed in this section: Instrumental issues related to the aerosol/filter interactions, errors related to the determination of the absorption cross section, and problems related to different spectral properties of C_{brown} . That is why there is the word “especially” in line 12. The error in the C_{soot} measurement can be reduced by choosing a higher wavelength, where C_{brown} absorption is minimal. The problem comes back when the data are used for climate studies. If “BC” is measured using a technique that only sees C_{soot} , thereby ignoring C_{brown} , and if the BC data thus obtained are used to calculate atmospheric absorption using the spectral properties of C_{soot} , the contribution by C_{brown} is lost. We tried to bring out these issues in the revision by adding/changing text in sections 2, 3, and 4.

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

Reference deleted.

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

Reworded to “The recent discovery of the widespread abundance of brown carbon in

Interactive
Comment

atmospheric aerosol...". Before 2000, nobody really was aware of this issue, except a very small number of specialists.

Page 3445, lines 7-11. I think this is an unfair statement. I believe that many modelers are aware that analytical techniques for C_{soot} , BC_e , EC_a , 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 C_{soot} .

This paper originated from my frustration of the uncritical use of "BC" in the climate modeling community. Its original purpose was exactly to provide this sort of guidance to the modeling community. We hope that it will serve this purpose.

We admit that it was unfair to include Bond et al. in this statement. Nevertheless, we stand by our view that the climate modeling community in general accepts the "BC" concept in a very uncritical fashion (maybe some awareness is now developing), and that many in the inventory community also show little concern regarding the difficulties of measuring and defining "BC". We have looked over the papers cited in the current version, and none of them even bother to define BC. Exceptions have been mentioned in the revised version.

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

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)