Atmos. Chem. Phys. Discuss., 10, C7592–C7601, 2010
www.atmos-chem-phys-discuss.net/10/C7592/2010/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources of light-absorbing aerosol in arctic snow and their seasonal variation" *by* D. A. Hegg et al.

D. A. Hegg et al.

deanhegg@atmos.washington.edu

Received and published: 16 September 2010

1. Reviewer #1

1.1 Calculation of the error matrix.

The equation-based approach to construction of the uncertainty file was used (Norris et al, U.S. EPA report 600/R-08/108, July 2008; available at www.epa.gov). Uncertainty estimates and detection limits were based on analysis of replicate standards with the uncertainty calculated as twice the standard error of the mean for each analyte species. We now note this in the text.

1.2 Justification of the four-source solution.

The reviewer raises an important point here, the number of sources in the preferred PMF solution. We had cited only the Q analysis to justify our choice, this being, in our view, the single most widespread criterion in use. However, as the reviewer points out, a number of other considerations commonly go into the choice of factor/source number that is, in any case, not an entirely objective process. We now discuss this process more fully (and will cite the Ulbrich et al study suggested by the reviewer as an example of how complex the process can be for pathological data sets). First, we note that we used the model in robust mode (Paatero, Chemom. Intell. Lab. Syst., 37, 23-35,1997). This, in itself, tends to stabilize the solutions. We also ran a set of six random seeds for each data set, finding no appreciable difference in the results. To test for rotational ambiguity, we did in fact vary the FPEAK parameter for each data set. The minimum in the Q versus FPEAK plot is rather well defined and the variation in the solutions over the FPEAK range is slight. We now include as an example of this a plot of Q vs. FPEAK for the 2008 data set in a supplementary information file – as suggested by the reviewer. We also show the associated variation in the factor loading of several key chemical species as a function of FPEAK for both data sets. Perhaps most tellingly, we also employed the EPA UNMIX 6.0 model in a preliminary assessment of the data. We did this to take advantage of the NUMFACT algorithm (cf., Henry et al, Chemom. Intell. Lab. Syst., 48, 91-97, 1999), included in this model, to give a more objective determination of the optimal number of sources/factors to include in the model. For the Canadian data set (2009), the NUMFACT algorithm found only a four-factor solution, with factors quite similar to those found by PMF. For the 2008 data set, with precisely the same variables as were used in PMF, the model offered no feasible solutions. However, UNMIX is relatively sensitive to the input species used (cf., Maykut et al, Environ. Sci. Technol., 37, 5135-5142, 2003). Upon examination of the data, we decided to remove the NSS K from the model due to the large number of zeros and substitute P instead (we had not used P in the PMF analysis because the uncertainties were very large for this analyte). With this change, UNMIX did yield a four factor solution but rejected 3 and 5 factor solutions. Again, for the key analytes (e.g., the LAA's, levoglucosan and vanillin), the source profiles resembled those for the PMF solution. Hence, we feel that the four-source solution has reasonable support. We now summarize this discussion in the text.

1.3 Citation of Doherty et al and Grenfell et al.

Given that the Doherty et al and Grenfell et al studies are still in review, we agree that more information on them must be included in the current text, perhaps not so much for the Doherty et al work which is simply a report of measurements which we do in fact summarize in Table 1 (and in any case has actually been posted in ACPD and is thus available for review), but certainly for the Grenfell et al study. To address this, we now include the number of measurements for each geographic region in Table 1 from Doherty et al. For Grenfell et al, we more fully describe the technique for differentiating non –BC and BC LAA, pointing out that the maximum possible BC concentrations are based on the assumption that all of the aerosol light absorption in the wavelength interval from 650 to 700 nm is due to BC (with a mass absorption crossection – MAC - of 6.0 $m^2\ g^{-1}$ – note that our citation of 6.5 $m^2\ g^{-1}$ in the text was incorrect). We also provide some support for our choice of Angstrom coefficients for the BC and non-BC absorption and discuss the impact of variation of these choices on the results.

1.4 Wavelength range for the cited mass absorption crossection.

As per our above response, the wavelength interval for the cited MAC is 650-700 nm and is now given in the text.

1.5 Transport patterns for transport of LAA to the arctic.

We presume that the reviewer is referring here to the fact that transport of aerosol into the arctic is favored in the spring (e.g., Stohl, J. Geophys. Res., 111, doi:10.1029/2005JD006888, 2006) and that any observed enhanced springtime impact of biomass burning is likely due to a convolution of favorable transport with seasonally high emissions. We now allude to this in the text.

1.6 Initial altitude for back trajectories.

Back trajectories were tested for initial altitudes of 300, 400 and 700 m as well as 500 m. The 400 and 700 m altitudes produced no significant change in trajectory. The 300 m altitude yielded somewhat different trajectories (generally shorter, for example) but still essentially the same. A few tests of an initial altitude of 1500 m did yield rather different trajectories but this is above the likely altitude for incorporation of LAA into precipitation. We now refer to these tests in the text.

1.7 Citations on the use of the Angstrom coefficient.

We have added additional references to the discussion on (current) page 13760 of the use of the Angstrom coefficient to differentiate between BC and non-BC, as suggested by the reviewer. Indeed, in response to both a previous comment of this reviewer and comments by reviewer 2, this discussion has been expanded substantially.

2. Reviewer #2 (R. Subramanian).

2.1 Discussion of Grenfell et al.

We agree that, in light of the fact that Grenfell et al is still in review, substantially more discussion of the methodology for BC and non-BC LAA partitioning is in order. Addressing the reviewer's first explicit concern, that the problem is ill-posed, with insufficient information for a unique solution, we note that we make three assumption: (1) that all of the absorption at 650-700 nm is due to BC, (2) the Angstrom coefficient for BC is 1.0, (3) the Angstrom coefficient for non-BC is 5.0. With these assumptions, the problem is not ill posed and there is a unique solution. The issue is how good the assumptions are. The assumption of all absorption being due to BC at 650-700 nm is reasonable given the much weaker wave-length dependence of BC absorption as compared to OC or iron oxides but will certainly lead to an overestimate of BC absorption. However, this assumption can be tested once estimates of the non- BC absorption fraction are in hand (again assuming the Angstrom coefficient values for BC and non-

BC) and the error is found to be second order. This is in accord with previous work on aerosol absorption from predominantly biomass combustion aerosols (e.g., Favez et al, Aerosol Sci., 40, 613-620, 2009).

The reviewer next raises the important issue of how valid our choices of BC mass absorption cross-section (MAC) and non-BC Angstrom coefficient really are, and, still more fundamentally, whether they can reasonably be treated as constant over different combustion types. Addressing first the issue of the Angstrom coefficient of the non-BC LAA, certainly there is variability in this value (see Doherty et al, ACPD, 10, 18807-18878, 2010) but the value of 5 is a reasonable choice. For example, contrary to the assertion of the reviewer, the Kirchstetter et al (2004) study is in accord with this. The value of $\sim$ 2 which the reviewer cites is for the TOTAL aerosol Angstrom coefficient, not that for non-BC LAA. These total values range from 2.2 to 2.5 for SAFARI data. If one uses the directly measured BC mass fraction from Kirchstetter et al for the SAFARI measurements together with a value of 2.3 for the total coefficient and a value of 1.1 for that of BC, one gets a non-BC light-absorption Angstrom coefficient of 5.1, in agreement with our value. The dependence of the partitioning of absorption between BC and non-BC LAA on the non-BC Angstrom coefficient is complex. However, if one uses a value of 2.2 for the total angstrom coefficient (the mean of all our data as per Doherty et al) and a value for the BC Angstrom coefficient of 1.0, a linear regression of the partition fraction onto the assumed non-BC Angstrom coefficient over the range from 3-6 (encompassing most reported values) yields an R^2 of 0.93 with a slope of 0.12 $\pm$0.02 and an intercept of 0.08 $\pm$ 0.11, i.e., the dependence is essentially linear. There will thus be no effect whatsoever on the PMF analysis if the non-BC Angstrom coefficient is constant. As for the MAC, we use a value of 6.0 m^2 g^{-1} at 550 nm (note that the value of 6.5 cited in the text was a mistake and has been corrected) as in our 2009 study (Hegg et al, ES&T, 43, 4016-4021). This value of the MAC is that of the BC aerosol used to calibrate the spectrophotometer. To the extent that the actual MAC of the LAA differs from this value, the LAA concentrations will differ linearly from those we derive so long as the MAC is constant. Again, this will have little impact on the PMF

analysis: the relative apportionment of BC to different sources will remain the same; just the absolute amount of BC from each source will change.

There then remains the daunting issue of variability in the MAC and non-BC Angstrom coefficient for different combustion conditions, as for example between fossil fuel combustion and biomass burning. However, this is less of a problem than might first appear to be the case. First, there is little evidence that such inter-source variability exits. After correction for various errors, Bond and Bergstrom, in their recent detailed review (Aerosol Sci. Technol., 40, 27-67,2006), find a rather constant value for the BC MAC of 7.5 $\pm$ 1.2 m^2g^{-1}. This is for near-source BC, where systematic differences between sources should be most evident. Furthermore, some part of the variance in this mean value may be due to uncertainties in the thermo-optical method commonly used to derive the BC mass used in determining the MAC. For the non-BC Angstrom exponent, much fewer data are available but what are do not suggest any difference between the coefficients for fossil fuel and biomass burning (cf., Sun et al, Geophys. Res. Lett, 34, doi: 10.1029/2007GL029797, 2007; Kirchstetter et al, J. Geophys. Res., 109, D21208, doi: 10.1029/2004JD004999, 2004). Secondly, and most fundamentally, the precise nature of the source allocation we are doing must be kept in mind. Our basic goal is the source attribution of the light absorption by LAA in arctic snow. The application of a MAC to this data is, essentially, to convert the values to units (mass concentration) compatible with the other species used in the input data matrix (i.e., a homogeneous matrix is necessary for proper scaling). Taken no further, the PMF inversion then yields the sources of the light absorption due to LAA. This attribution is completely independent of any assumptions as to the MAC or Angstrom coefficients used in our analysis. We noted this explicitly in our 2009 study but were remiss in not reiterating it in this study and we now do so. Over and above this fundamental attribution, with the assumption of constant MAC, we can attribute the LAA mass, or more precisely the mass of LAA equivalent to that with a MAC of 6.0 m^2g^{-1}, to various sources. Finally, assuming a constant non-BC Angstrom coefficient, we can do a source attribution of both BC and non-BC LAA equivalent to that with a MAC of 6.0 m^2g^{-1}. Since the BC and non-BC LAA turn out to have the same source attribution (both coming predominantly from the two biomass burning sources), we dwell mostly on the source attribution of LAA in toto, as we note in the text. We will revise the text to make clear this hierarchy of attribution and the assumptions necessary to implement it.

2.2 Assumption of biomass burning source for BC

The reviewer asserts here that we assume that the major source of BC (and non-BC LAA) in Arctic snow is biomass burning. This is incorrect and we are puzzled by it since the attribution of most LAA to biomass burning is a major RESULT of the PMF model. Unlike, for example, chemical mass balance modeling, the factors/sources are generated based on what produces the best fit to the data, they are not pre-assigned. If one looks at the PMF source profiles in Figure 2, it can be seen that both BC and non-BC LAA are loaded mostly on the two biomass burning sources. Furthermore, as illustrated in Figures 3 and 7, the biomass burning sources are the most important contributors to the LAA in most of the geographic areas examined. These are model results, not assumptions. As to the findings of numerical models used in general assessments, while we acknowledge that they typically show a larger impact from fossil fuels than from biomass, this is not always the case and there is no categorical exclusion of biomass burning as an important and sometimes dominant source of LAA's in arctic snow (e.g., Stohl, J. Geophys. Res., 111, D11306, doi: 10.1029/2005JD006888, 2006; Generoso et al, J. Geophys. Res., 112, D15302, doi: 10.1029/2006JD008344). Finally, we agree that the co-mingling of sources during long-range transport can render the deconvolution of sources difficult, but that is the very purpose of multivariate statistical models such as PMF. For example, if the BC at a given site/region was 50% from biomass burning and 50% from fossil fuel burning, the BC and non-BC LAA should be about equally loaded onto the biomass and fossil fuel factors. For our samples, they are mostly loaded onto the biomass factors, which is a fundamental conclusion of our analysis. Remember too that we are using the model on a spatial as well as temporal matrix and this enhances the ability of the model to deconvolute sources that become

mixed during transport.

2.3 Vanillin to levoglucosan ratios

The reviewer notes that the vanillin to levoglucosan ratios (v/l) we see are much higher than those found in the studies we cite and suggests that this may be due to another source of vanillin, or at least a source with much higher v/l than either boreal biomass or crop and grass burning. We disagree. First, it is unclear what the source of unusually high vanillin might be if not biomass burning. Vanillin has no other appreciable sources. Second, and more fundamentally, the difference in vanillin concentrations – and it is the vanillin concentrations that are high – are likely simply due to different sensitivities of the analytical techniques employed. All of the studies we cited – and indeed very nearly all in the literature – use derivatization followed by GC-MS to get the vanillin and levoglucosan concentrations. We, on the other hand, use IC-PAD, which we have found much more sensitive, for vanillin (and electrospray LC-MS for levoglucosan). For the 2008 data set, we in fact initially employed GC-MS to measure vanillin in selected samples (essentially to test the approach) but found few samples above our detection limit. When similar samples were analyzed by IC-PAD, appreciable (though low) concentrations of vanillin were found on most of the samples. The key point we make in our analysis is that the v/l ratio is much higher for the presumed boreal burning than it is for the crop and grass burning. Such a comparison of ratios avoids differential sensitivities over different analytical techniques. Our ratio of v/l ratios between boreal burning and crop and grass burning is $\sim$ 160. The mean ratio for the studies we cite is $\sim$ 50 but can be as high as 266 depending on specific fuels types (the 266 is associated with the ratios in wheat straw as compared to pine – a quite plausible boreal to crop and grass burning contrast, especially for Siberia). Hence, we feel that our interpretation of the differences in v/l is reasonable. However, we will modify the text to clarify that it is a comparison of RATIOS that is important.

2.4 Interpretation of non-BC LAA as Brown Carbon (BrC)

The reviewer here expresses skepticism about our attribution of non-BC LAA as BrC. Two points are raised. First, our argument concerning the implausibility of high covariance of dust and biomass smoke is suspect because dust could be entrained into fire plumes and thus be essentially co-emitted from fires. We would agree that this is possible, even probable, for large fires with distinct fire columns and thus substantial surface wind generation. However, crop burning, residential heating of boreal biomass, and a good deal of open boreal burning do not involve such columns. For the very large geographic areas of biomass burning which appear to be the sources of much of the LAA, we would argue that saltation is very unlikely to contribute anywhere near as much aerosol mass or LAA as the burning itself. It is also important to note that such dust is not mineral dust but rather, essentially, “dirt” and any absorption associated with it is likely due to humic species, i.e., BrC. The predominant areas of MINERAL dust emission (where the absorption is NOT due to BrC) are far removed from those of biomass burning (cf., Chen et al, Annales Geophysicae, 27, 3439-3464, 2009) and Fe-containing mineral dust (as distinct from dust in general) does not deposit very much in our receptor areas (Mahowald et al, Annual Rev. Mar. Sci, 1, 245-278, 2009). Hence, we feel our argument has some validity though certainly we agree that it is a plausibility argument, not a categorical imperative and will revise the text to make sure this is clear. Next, the reviewer appears to accept our argument concerning the low contribution of Fe to absorption based on the Fe concentrations, but raises again the point about discrimination of BC and non-BC LAA. We are not entirely sure what the reviewer is getting at here and so simply point to our arguments in our response 2.1. However, we feel that perhaps some confusion has arisen due to our neglect to specify that the only plausible alternative to BrC absorption is that due to MINERAL dust and we will revise the text to clarify this, explicitly stating that non-mineral dust may have made some slight contribution to LAA associated with the biomass sources.

2.5 Use of PMF to distinguish combustion sources and use of organic combustion markers.

The author first raises the point that we have not included any organic fossil fuel combustion tracers in our analysis, explicitly invoking hopanes and steranes as possibilities as per the pioneering work of Schauer and his colleagues. We agree that if appropriate markers could be found they would very much enhance our analysis – or at least future analyses. However, this is very difficult. For example the hopanes and steranes suggested by the reviewer do not typically survive long range transport on the scale necessary to reach our receptor area. Indeed, they are almost always invoked to identify sources close to the receptor sites (e.g., Schauer et al as cited by the reviewer; Schauer and Cass, Environ. Sci. Technol., 34, 1821-1832, 2000; Zheng et al, Environ. Sci. Technol., 36, 2361-2371, 2002). We are aware of no utilization of such markers as tracers for long range aerosol transport in the Arctic. On the other hand, such tracers as we have used, e.g., levoglucosan, are quite suitable for long range transport studies (e.g., Simoneit, Atmos. Environ., 33, 173-182, 1999). The reviewer has also suggested PAH’s as possible markers. We in fact used these in our earlier work (Hegg et al, Environ. Sci. Technol., 43, 4016-4021, 2009) but feel that their discriminatory power is limited since the major (and detectable in arctic snow) species are emitted by a number of combustion sources including biomass burning and industrial. Conversely, we disagree with the reviewer as to the utility of metals as tracers. These species have a long and distinguished history as industrial emission markers in the arctic (e.g., Rahn et al, Nature, 306, 459-461, 1983; Maenhaut et al, Atmos. Environ., 23, 2551-2570, 1989; Davidson et al, Atmos. Environ., 27, 2709-2722, 1993; Douglas and Sturm, Atmos. Environ., 38, 805-820, 2004). Finally, as to the numerical model alternative explanation, we have already addressed this in our response 2.2.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 13755, 2010.