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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term measurements of carbonaceous aerosols in the eastern Mediterranean: evidence of long-range transport of biomass burning" *by* J. Sciare et al.

J. Sciare et al.

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Anonymous Referee #1 Received and published: 31 May 2008

We would like to thank the reviewer 1 for his/her comments that have helped us to prepare this final version. Most of the suggestions have been taken into account and all raised issues are answered one by one. Minor comments have been also taken into account. Below is a point by point answer to the reviewer comments (by Italics).

The authors use the term BC to describe the non-organic, non-carbonated, part of the carbonaceous aerosol. The terms BC (Black Carbon) and EC (Elemental Carbon) are used frequently to specify this fraction ; usually the term BC is employed when pure optical methods are used in the analytical determination and quantification (such as

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the aethalometer) and the term EC is employed more frequently when measurement is done by thermal methods (or thermo-optical methods). Here in the paper three (four) different methodologies are used. I would like that the subject would be addressed and referred, and that one or two sentences would be added explaining the causes for the choice of nomenclature applied.

Following reviewers suggestion the following sentences have been added in the MS. Soot is determined either optically or chemically. The optical method relies on light absorption; the corresponding operational definition for soot is black carbon (BC). The chemical (thermal and thermo-optical) measurements measure the mass concentration of total carbon, in which the fraction that is refractory and does not volatilize below 400°C in air is defined as elemental carbon (EC) (Birch and Cary, 1996). Distinction is done in the following between EC and BC since they refer to somewhat different fractions of light absorbing carbon.

The sampling of the aerosol is performed with two lines in parallel, with a filter holder having a quartz filter for carbon analysis and a SFU using Nuclepore filters for ions and other constituents. Sampling seems to be done with one week extension periods. Taking into account the long sampling extension, the atmospheric concentrations of particles at the site and the characteristics of Nuclepore filters I wonder if the cutting size characteristics of the Nuclepore filter are maintained during the extended sampling events. Clogging of filter pores are probable in these seven days sampling extensions.

Sequential filter sampling (15min of sampling every 1 hour) was adopted for both SFUs and QMA filters in order to minimize the risk of clogging the SFUs and consequently alter the distribution between fine and coarse mode. Flowrate was also checked at the beginning and the end of each filter sampling. Information on the sampling strategy was added in the MS.

It is not clear from the paper but it seems that sampling over the quartz filter is also done during one week periods in parallel with SFU. Please add information concerning

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the expected size collection (TSP?) and sampling flow rate of the quartz filter line.

TSP QMA filters were sampled at approximately flow rate of 2.8m3/h following the same sampling strategy with SFU. Information was added in the revised MS.

Page 6954 lines 5-10 - It is not clear the advantage of heating the filters with the sample at 60°C for 20 minutes, prior to the analysis, to minimize artifacts. By doing so what is achieved is the evaporation of any semi-volatiles, either the ones adsorbed on the filter surface or those collected as particles. Furthermore if the reaction of volatiles (VOCs) with active sites in the filter result in a strong chemi-adsorption the heating of the filter may remove the particulate semivolatiles without desorbing the volatiles (VOCs) from the filter surface, introducing then a higher artifact.

We do agree with the reviewers concerns. Note the analytical protocol adapted for the OC/EC analysis was that reported by Cachier et al. (1989). Interestingly this pre-heating step also occurs during almost all the analysis performed using the Sunset lab instrument. Indeed the instruction ;safe to put a new sample; given by the instrument is activated when the front oven temperature is below 70°C. Most of the people running analyses with the Sunset lab instrument do not wait the front oven to be at room temperature (it may take 1h) and they run samples with a front oven temperature typically in the range of 50-60°C. Thus, the higher artefact proposed by the reviewer to occur in our samples is likely to be observed for each sample routinely; analysed by the Sunset Lab instrument (unless a special care is taken regarding the front oven temperature). Note also that under such long exposure time (1 week) applied to our QMA filters collection, it is not possible to address in a quantitative way the role of SVOC due to important changes in thermodynamic equilibrium and which may occur in the course of the sampling. So the best compromise might me to remove them (SVOC) from the filter prior to the analysis (as done here with our pre-heating step).

Page 6955, equation 1 - Adopting of a R value of 1, considering that the filter deposit is low, is questionable and should be explained. Although the flow rate of aerosol

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sampling is not known, the fact that samples extend for one week, presumably will accumulate too much material to maintain the R value as 1.

As mentioned previously, the weekly QMA samples correspond to a period of less than 2 days of continuous sampling which given the character of the sampling station (natural background) is considered as normal;. Note also that under similar conditions Weingartner et al. (2003) also applied an R value of 1. Thus our choice of R seems to be realistic.

Page 6958, lines 1-10 - A mean difference of 0.7 μg/m3 between PM and PM-CMB is reported. From Table 1, a value of 8.88-8.47= 0.41 can be estimated. Clarify!

As mentioned in the MS ; Monthly mean concentrations of the major aerosol species, PM and PMCMC are given for the fine mode in Table 1 ;. This means that PMCMC reported in Table 1 (like PM and other species) is monthly mean calculated for each individual filter sample. In other words, PMCMC values reported in this table are not obtained from the sum of the monthly means of each chemical species. That is the reason why i) the reviewer could not recalculate by himself PMCMC and ii) PMCMC is presented with standard deviation in the table. We have made this clearer in the manuscript.

Page 6960, lines 18-22 - The fact that light transmission increases during the analytical step at 850°C, under helium, in the NIOSH protocol is not the theoretical cause for the lower BC values under the NIOSH protocol, by comparison with the IMPROVE methodology. If the BC reacts in these NIOSH conditions with oxygen from oxides, for example, this would only reflect on the calculated levels of Pyrolitic Carbon. The filter light transmittance control during heating has precisely the objective of compensating for phenomena of carbonization and decarbonisation processes during the evaporation of organic carbon. If the initial transmission level of the filter is used for separation between BC and OC, then any previous pyrolisis and oxidation of BC are compensated (presuming that all the OC has evaporated, previously to regaining the initial transmission, and that the light absorbity of initial BC and pyrolysis formed BC are equal). But if the colour of inorganic compounds absorbing light change irreversibly during the heating step at 850C under helium, in reducing conditions, (as it was described in Sciare, 2003b) then this heating step under NIOSH protocol could introduce errors in the calculation of BC. It is interesting to notice that the average relative differences between absorption coefficients of the aethalometer with and without inclusion of Fe2O3 in Figure 2 seem to be of the order of 15%, value similar to the differences in BC calculations by NIOSH and IMPROVE type methods.

We do agree with the reviewer comments and we have removed the sentence which is obviously incorrect and included by mistake. One should mention that the hypothesis assuming an equal light absorbity for initial BC and BC formed from pyrolysis is used for all the thermo-optical instruments. On the other hand, these instruments have been designed to avoid the release of OC together with whitening of the filter since one cannot be sure that all the OC has been analysed before the split point. This is a first reason why one should mind about the release of O2 from metal oxides at the last He plateau of the NIOSH protocol. A second reason is that proposed by the reviewer on the role of dust deposit on absorption measurements and their possible change at the last He plateau.

Page 6961, equation 4 - Equation 4 seems to be a kind of moving average and I could not understand neither what it represents nor its objective in the paper. If I understood, Ci-1, Ci and Ci+1 are the monthly averages corresponding to month i minus one, month i and month i plus one. Therefore Ci_bar is not a weighted monthly mean concentration. If I understood the meaning of equation 4 then the result of the equation would smooth the monthly mean results resulting in not so high maxima and not so low minima. However this is not shown in Figure 5.

It is true that equation 4 (equation 5 in the revised MS) is a smoothing and this section of the MS has been re-written accordingly. This equation has been used on monthly mean data covering the whole period when C measurements were available. For instance, the smoothed concentration of EC(IMPROVE) for August will be the combination of 3 monthly mean (July, August, September) with different weights for each month (1, 2, 1, respectively). These last 3 monthly means are calculated from all the available months of July, August, and September of the 5 year dataset. The smoothed dataset is then representative of the 5-yr measurements. This dataset has been put in Figure 5 (seasonalised data) and thus cannot show any year-to-year variation. That is the reason why the reviewer cannot see correspondence between monthly mean and seasonalised data in this Figure 5. The aim of this figure is to show the important intensity and time variability of the maxima/minima in our EC and OC dataset. For instance, a peak of EC that is expected in August from the seasonalised dataset will be observed some years in September. This can be understood intuitively for agriculture waste burning peaks which timing will critically depend on weather conditions driving the harvests that can be easily shifted of few weeks for one year to another. Air mass origin variability can also explain partly this time shift sometimes observed in our dataset. Smoothing the dataset by taking into account the previous & next months for each monthly mean will allow us to take partly into account this temporal variability in the timing of the maxima/minima. Few sentences has been added in the revised MS accordingly.

Page 6963, line 10 - substitute "poorly" with "less".

It has been corrected in the revised version.

Page 6964, lines 5-10, The monthly mean nssK taken from figure 4 is around 55 ng/m3 and not 50 ng/m3. So it is more correct to say that this is a round average using May and June months (there are several of these inaccuracies in the paper, as referred by referee 2, that should be avoided.)

Correction in the direction proposed by the reviewer was done in the text

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 6949, 2008.