

Interactive comment on “Seasonal variation of PM₁₀ main constituents in two valleys of the French Alps. I: EC/OC fractions” by G. Aymoz et al.

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Author's answers to reviewers #1 and #2.

First, the authors would like to thank the reviewers for their comments on this manuscript.

As a general comment, we would like to point out that the respective opinions of the two reviewers are really diverging. Reviewer #1 thinks that the paper could be considerably reduce, when reviewer #2 have no substantial criticism on this point. The main arguments developed by reviewer #1 is that conclusions of the paper do not need so much text and figures to be supported, and that local emissions of EC and OC could be quantified. We feel, in agreement with reviewer #2, that each step of the discussion

is useful and necessary in order to support the conclusions..

Answers to comments from Referee #1

General comments In my opinion the main novelty is the possibility to quantify local OC emissions by way of relating OC to K. A possibility to relate EC to HDV is not fully examined. The authors do not make it clear from the start what the interest of the data is for the general public. In my opinion the MS should focus on the local EC and OC emissions and quantify these better. Then the MS is of interest to a broader audience; as it is now it is a databank. It should be a short technical note, meaning brought back to a size about half of the current. Also six of the figures are redundant because they are not necessary to provide insight.

We totally agree with reviewer #1 on the fact that the data set concerns a site with a specific typology. However, we see this as an advantage: meteorological conditions in winter considerably limit the dispersion and the mixing of the air masses. This is illustrated by the very strong relation between EC, OC, and NO. So, in winter-time conditions, we can observe a quasi-isolated system, with the implication of a limited number of emission sources. This simplified system makes it easier to point out to relation (or lack of) between EC, OC, and some specific tracers of traffic or biomass burning. This could help to elucidate relations that should be studied in more complex situations in order to better constrain the sources of carbonaceous species in aerosols, what is actually a challenging problem.

1) Artefacts Another issue is the absence of the use of a filterpack for assessing the artefacts in OC sampling. Since the last author is one of the TWO experts on these artefacts in Europe I give it the benefit of the doubt. It is well-known by now that artifacts during collection are possible for OC when sampling with quartz fibre filters [e.g., Turpin et al., 2000; Mader et al., 2003]. Both positive artifacts (i.e., adsorption of volatile organic compounds (VOCs) onto the filter) and negative artifacts (loss of semi-volatile organic compounds from the collected aerosol on the filter) do exist. Several

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approaches to assess and/or to correct for the artifacts have been proposed and are now commonly used. Among the simpler approaches are the use of a denuder (to collect VOCs) upstream of the filter sampler and the use of a tandem filter set-up (with front and back filters). In the approach with the denuder, a tandem filter set-up can also be used. It is generally believed that positive artifacts (for the front filter) prevail in the undenuded set-up and negative artifacts in the denuded set-up. If this is really the case, then artifact-free particulate OC data can be obtained in (a) the denuded set-up by adding the OC data from the back filter to those of the front filter and in (b) the undenuded set-up by subtracting the OC data for the back filter from those for the front filter. Moreover, if the assumptions about the prevailing artifacts do hold, then the corrected data OC from collections with denuded and undenuded tandem filter set-ups should be identical [Mader et al., 2003]. This has been tested in various European environments by the group of the last author, and it seems often to be the case, though not always [e.g., Maenhaut et al., 2005]. Thus, a simple pragmatic approach for our study would have been to make use of an undenuded tandem filter set-up and to subtract the back filter OC data from the front filter OC data. This approach is now commonly used by several research groups in Europe and elsewhere [e.g., Decesari et al., 2006; Viana et al., 2006a, 2006b]. However, at the time of the start of our study, such approach was not common at all in Europe. With the information that is available now (and thus several years after the start of our samplings), we admit that it would have been better to try to assess the extent of the artifacts for OC during sampling. Since this was not done, we can give a reasonable estimate for the extent of the artifacts. Based on previous experiments by the group of the last author [Chi and Maenhaut, 2004, and unpublished results], we estimate that the use of an undenuded tandem filter set-up would probably have provided OC percentages on the back filter (relative to the front filter) of between 5 and 20%, so that applying the subtraction in this case would have given corrected OC data that would be 5% to 20% lower than the uncorrected data that are given in our manuscript. Chi and Maenhaut [2004; and unpublished results] used the undenuded tandem filter set-up at different locations in Europe and they found that

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the percentages on the back filter are higher in summer than in winter. This was also found by Viana et al. [2006b] in Barcelona and would likely also be the case in our study.

References

Chi, X. and W. Maenhaut, Organic carbon, elemental carbon and water-soluble organic carbon in the PM_{2.5} aerosol at different sampling sites, Eighth International Conference on Carbonaceous Particles in the Atmosphere, September 14-16, 2004, Vienna, Austria, Abstract Book, p. 113.

Decesari, S., S. Fuzzi, M.C. Facchini, M. Mircea, L. Emblico, F. Cavalli, W. Maenhaut, X. Chi, G. Schkolnik, A. Falkovich, Y. Rudich, M. Claeys, V. Pashynska, G. Vas, I. Kourtchev, R. Vermeylen, A. Hoffer, M.O. Andreae, E. Tagliavini, F. Moretti and P. Artaxo, Characterization of the organic composition of aerosols from Rondônia, Brazil, during the LBA-SMOCC 2002 experiment and its representation through model compounds, *Atmos. Chem. Physics*, 6 (2006) 375-402.

Maenhaut, W., X. Chi, M. Viana, J. Cafmeyer, P. Mikužka and Z. Veřeš, Investigations during summer field campaigns in Ghent and Barcelona on the performance of a diffusion denuder for the elimination of sampling artifacts for carbonaceous aerosols, Abstracts of the European Aerosol Conference 2005 (EAC 2005), 28 August - 2 September 2005, Ghent, Belgium, Editor: W. Maenhaut, 2005, Abstract no. 572. (ISBN: 9080915939).

Mader, B.T., J.J. Schauer, J.H. Seinfeld, R.C. Flagan, J.Z. Yu, H. Yang, H.J. Lim, B.J. Turpin, T.J. Deminter, G. Heidemann, M.S. Bae, P. Quinn, T. Bates, D.J. Eatough, B.J. Huebert, T. Bertram and S. Howell, Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia, *Atmos. Environ.*, 37 (2003) 1435-1449.

Turpin, B.J., P. Saxena and E. Andrews, Measuring and simulating particulate organics

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in the atmosphere: problems and prospects, *Atmos. Environ.*, 34 (2000) 2983-3013.

Viana, M., X. Chi, W. Maenhaut, J. Cafmeyer, X. Querol, A. Alastuey, P. Mikužka and Z. Veřeřa, Influence of sampling artefacts on PM, OC and EC levels in carbonaceous aerosols in an urban area, *Aerosol Sci. Technol.*, 40 (2006a) 107-117.

Viana, M., X. Chi, W. Maenhaut, X. Querol, A. Alastuey, P. Mikužka and Z. Veřeřa, Organic and elemental carbon concentrations in carbonaceous aerosols during summer and winter sampling campaigns in Barcelona, Spain, *Atmos. Environ.*, 40 (2006b) 2180-2193.

2) Blanks There is no indication of the blanks of the filters, which I like to see mentioned in a next version. Indications about filter blanks are well mentioned in the reviewed ms (number of field blanks are indicated pp 6216 In14 and Table 1, field blank concentrations for EC and OC : pp6217 In 25)

3) About table 2 and 4 Table 2: omit Table 4: redundant The reviewer probably means a potential redundancy between tables 3 and 4. Indeed, despite the fact that a limited number of the data appears in both tables, we feel that table 3 is necessary in order to give a much more precise statistical description of our data set.

4) Relations between HD-traffic and EC as well as K and OC Also in a next version a more quantitative relation between HD-traffic and EC as well as K and OC should be provided. This latter issue is very worthwhile because there is very little knowledge on this relation in Europe. As explained in the text (p 6225, In 19), the direct relation between HD number and EC or OC is not developed here because there is no such direct relation. We feel that illustrating this part would have overloaded the text, but one can found a more detailed discussion on this part in Aymoz (2006), as indicated in the text. See below for the relation between OC and K+.

5) Abstract While the conclusion section is vague on these both issues, the abstract does not provide any quantitative data, only subjective formulation like significant (?).

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Hence my suggestion/demand to use the conclusion section as abstract because it is a summary of the study. Actual conclusions are missing and should be given in two to three quantitative sentences. In the first version of the MS submitted to ACPD, the abstract and the conclusion were very similar, as suggested by the reviewer. Then, it was requested by the editor not to use the conclusion as an abstract. We were asked to rewrite the abstract “in a more focused manner”, and notably to exclude from it the maximum of quantitative data.

6) Smaller issues Pg 6213, In 5: “under” the Mont Blanc Tunnel” should be “in”. Pg 6219, line 9/ table 4 when indeed a different sampler is used, and one not sampling the smaller aerosol, why do the data from Bologna still appear in the table These were performed.

I rather see K as the marker than K+ because what is actually meant here is that K stands for potassium as the marker for biomass source The question of the pertinence of K+ (K+ being the soluble fraction of potassium measured in aerosol) as a tracer for biomass burning emissions is also developed by reviewer #2. So, we bring a global response below. However, it is important to distinguish here between K (the total potassium), and K+ (the soluble fraction of K). As developed in the text, the literature indicates that K+ concentrations can be considered as a good tracer for biomass burning emissions in areas influenced by anthropogenic activities. This is not the case for K concentrations that can be strongly influenced by soils emissions, for example.

Pg 6225, In 20 I do not understand/accept the term any and the reference to unpublished data for this See answer to comment 4) above.

Anonymous Referee #2

General Comment: This paper presents the results of a large data set of measurements of carbonaceous matter in PM10 aerosols collected in two French Alp valleys subject to important road traffic contamination. This large amount of data on the carbonaceous content of the atmospheric aerosol, taken along the various seasons of the

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year, was used to infer about the origins of the carbonaceous fraction of particulates. The relationships of the EC and OC contents and of the EC/OC ratio were used together with variation in temperature, weekend / working-day traffic and concentrations of NO and K to assess the origins of the carbonaceous aerosol. Based on these assumptions the authors concluded that an important fraction of the OC is resulting from biomass burning for home heating, principally in winter low temperature conditions. EC seems to have a more distributed origin and heavy road traffic seems to contribute also significantly to the carbonaceous aerosol load. The significant presence of SOA was not clearly demonstrated from the data evaluation, even in summer conditions. For a discussion on the presence of SOA, see: Jaffrezo JL, Aymoz G, Delaval C, and Cozic J (2005) Seasonal evolution of the soluble fraction of particulate organic carbon in Alpine Valleys. *Atmos. Chem. Phys.*, 5, 2809-2821.

I have to say that in general I agree with the various degrees of discussion and interpretation that the authors have developed in this paper and I have no substantial criticism to present or alteration to propose to the text. In my opinion the paper is well written and the experimental data is well explored. The conclusions about the importance of biomass burning in the regional atmospheric aerosol loading are well based and in agreement with other recent information that indicates or even demonstrates the presence of a large and predominant source of carbonaceous aerosol as result of biomass burning from home heating across Europe, at least during more colder months of winter.

1) General comments : about soluble potassium as a tracer for biomass burning emissions Fine water soluble potassium is a good tracer for biomass burning, although in PM10 there is always contamination from other sources, such as soil and road dust (can desalting of snow be a source of potassium in road dust during subfreezing periods?). Contamination from dust is possibly one of the causes for the higher K/OC ratios at higher temperatures as shown in Figure 9. Therefore potassium is not a perfect tracer for biomass burning and the quite different ratios between K/OC for the two

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measuring sites, tentatively explained in the paper as result of burning different types of wood in different conditions, has to be taken with precaution. A more specific tracer for biomass burning, such as levoglucosan, would help in a more clear and quantitative interpretation of the data, if it was measured. However it is possible to filter the potassium data for contaminations from sea salt, or from soil, by considering sodium or/and magnesium as tracers of salt and calcium as a tracer for soil dust, using for example Ca/K ratio envelopes during periods of previsible low biomass burning.

What we show in the first paragraph of the section 3.5 is that, according to the literature, potassium (K) in aerosol has several sources, but soluble potassium seems to be a good tracer for biomass burning emission in areas influenced by anthropogenic emissions. We agree on the fact that we did not consider the problem of the contamination of the fine water soluble fraction of potassium in PM10 by other sources, like soil, road dust, or sea salt. However, size segregated measurements of the ionic fraction of aerosols were performed during both winter and summer periods (Jaffrezo et al., 2005), and showed that size distributions of soluble potassium, especially in winter, are monomodal with mass median diameters centred in the interval 0.40 to 0.65 μm . This sub-micronic mode is a very strong indication that soluble potassium originate from combustion and not from soils or re-suspension of dust. We changed the text to add this important precision. Also, levoglucosan was measured during intensive sampling campaigns and results are presented in Marchand (2003) and Marchand et al., in prep. In this last manuscript, these results are discussed in relation with EC, OC, and PAH concentrations.

Jaffrezo J.L., Aymoz G., and Cozic J. Size distribution of EC and OC in Alpine valleys during summer and winter. *Atmos. Chem. Phys.*, 5, 2915-2925, 2005.

Marchand N. (2003) Etude de la composante organique l'aérosol atmosphérique : cas de deux vallées alpines (Chamonix et Maurienne) et développement analytique. PhD thesis, in french, 339pp, available at http://tel.archives-ouvertes.fr/index.php?halsid=e5b517a217faf4d886142f4c26415572&view_this_doc=tel-

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Marchand N., Aymoz G., Jaffrezo JL. and Besombes JL. Biomass burning indicators in the aerosol of Alpine Valleys. In prep for Atmospheric chemistry and Physics.

2) Specific comments: EC/OC and OC/EC: In some sections of the paper the ratio EC/OC is used for data interpretation. In other sections it is the inverse ratio OC/EC that is discussed. For a matter of consistence it would be preferable to present the relative concentration values of OC and EC in only one manner. Changes were performed accordingly in the text.

Sampling artefacts: In Section 3.2, end of Paragraph 3 - “A last hypothesis is related to sampling artifacts”. In my opinion, sample artifacts by more intense semivolatile adsorption at lower temperatures (not detected in PM10 total mass as result of constant heating at 50 °C of the mass analyzer) would give the opposite effect, that is - an increase in the OC/PM10 ratio with decreasing temperatures. This sentence was deleted.

Semi-volatile fraction of OC: In Section 3.2 paragraph 5, referring to the discussion of the EC/OC ratios decrease at higher ambient temperatures: This paragraph also discusses the possible interferences of organic semivolatiles. A way of having an insight into the presence of more volatile organic components at lower sampling temperatures is to observe-inspect the first fraction of OC that evolves during measurement in the beginning of the analysis at low heating temperatures. The justification of lower EC/OC at low ambient temperatures as result of the semivolatile organics is in contradiction with the EC/OC ratios observed at the highest ambient temperature range.

We agree with the last remark, and the precedent one about sampling artefacts. The manuscript was changed to take these in account. About the first fraction of OC (the “peak 1”) evolving during the measurement, we think that this could be difficult to consider the “peak 1” as a real semivolatile fraction of OC, and this for many reasons: ¶ to the best of our knowledge, there is no publication that really demonstrate this, ¶

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the “peak 1”, in our case, is a part of the carbon evolving in helium at 250°C. Can we consider the carbon evolving to a temperature of 250°C as representative, or at least proportional to the “semi-volatile” fraction at ambient temperature? † the separation between peaks is totally artificial and depending on the duration of the stage (in our case, 60 seconds at 250°C). Moreover, and according to our experience, this peak, and more generally the distribution of OC between each peak, is also dependant on the load of the sample. Thus, it would be difficult to compare directly samples from winter (with high loadings) and from summer (with weaker loadings). Finally, if we agree that as a very first approach we can take this fraction of OC as an indication for the semi-volatile fraction of OC, we feel that it is in reality something to check in an accurate manner before using it as a real and reliable argument.

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