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Interactive comment on "Seasonal variations of the Water Soluble Organic Carbon massfraction of aerosol in two valleys of the French Alps" *by* J.-L. Jaffrezo et al.

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Answers to the reviewer's comments for MS ACPD-2005-0065

Overall, the authors would like to thank the referees for their dedicated work and constructive comments that led to large improvements of the paper.

Anonymous referee #1 :

1 - Opportunity of the closing and reopening of the TMB It is true that this point is not introduced in the discussion. Indeed, the traffic in the Chamonix Valley did not recovered totally during the period after the reopening of the TMB, with an intensity about

1/3 only of that before the closing during the last few months of the continuous sampling. Therefore, the conditions were not that expected, and it was not really possible to follow the evolution of concentrations and properties according to the traffic (cf change p 4003, line 3). However, the results indicate that the differences are not really large in the WSOC fractions between the two valleys, despite large differences in the sources inside the valleys (particularly the number of heavy duty trucks). This observation is reinforced in the text, with the addition of a new table (now table 4) and the associated text (page 4010; line 8).

2 - Details about the experimental method of WSOC determination We felt that the method was already largely described, compared to what can generally be found in many other publications on the topic. There are several aspects that could be further considered in this method, the acidification of the samples being one of them. It should be noted that the acidification is only mild, in order to drive off the CO2. The final pH of the solution is in the order of 2, and therefore semi volatile weak acids like acetic and formic acids are certainly driven off. However, since the original samples are aerosols, these acids represent a low percentage of the mass : concentrations are generally up to 100 ng/m3 as a maximum in urban environment (Meng et al., 1995), representing at most a few % altogether of the WSOC fraction. This is mentioned in the revised version of the text (page 4004, lines 18 and following).

Meng Z, Seinfeld JH, and Saxena P (1995) gass / aerosol distribution of formic and acetic acids. Aer. Sci. Technol., 23, 561-578.

3 - Selection of the filters All of the filters from the Saint Jean series were analyzed, as mentioned in the text, and the samples were gathered by 2 or 3 depending on the OC concentrations. Not all the series from Chamonix was analyzed because it was too labour intensive. The selection for this last series was only based on the period of sampling: series of samples from the two winters and from one summer were analyzed in order to be representative of the most extreme atmospheric conditions. Please, note that the number of results from the Chamonix series already represents a much larger

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number of samples than in any previously published study.

4 - Figure of the annual cycle of the WSOC concentrations. This new figure is added in the new version of the paper.

5 - Temperature at the Jungfraujoch : No information is given on the temperature during the sampling for this experiment, neither in Krivacsy et al. (2001a) Atmos. Envir., 35, 6531-6544, nor in Krivascy et al. (2001b), J. Atmos. Chem., 39, 235-259. However, one of the authors of our paper is now working at that site and can confirm that the mean summer temperature is on the order of 0°C. The text was therefore changed to mention that our data are “some of the first few ones at low temperature”.

6 - Discussion on the concentrations of the dicarboxylic acids This is partly discussed in the PhD thesis of G Aymoz, available at http://tel.ccsd.cnrs.fr/documents/archives0/00/00/89/18/index_fr.html (cf additions in the list of references). It will also be discussed in part in the paper Jaffrezo et al. 2005b (quoted page 4002, footnote 1).

7 - Definition of the warm / cold conditions Samples from “warm or cold conditions” were defined in the same way as in (old) figures 9 and 10: Warm : daily average temperature above 7°C in Saint Jean and above 3°C in Chamonix Cold : daily average temperature below 7°C in Saint Jean and below 3°C in Chamonix. This is now explained in the text, page 4013, line 29).

8 - Differences between the text and the figures, for WSOC vs. DCA: This allows to show both types of correlations and of regression equations.

Anonymous referee #2 :

1 - Comments about section 2.4 (experimental section) We totally agree with the referee that filtration is needed for a correct determination of WSOC in filter extract. One of the first method we tested (for tentatively using the TOT method for the determination of the WINSOC) is indeed including filtration on the same quartz filter used for

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the atmospheric collection, to recollect insoluble particles suspended during the washing part. Further, we totally agree with the referee that the drying of the filter after the washing step may introduce some contamination due to atmospheric gases in the laboratory : this was the reason why it was performed in a nitrogen atmosphere in our case. Finally, we agree with the referee that the distinction between EC and OC may be changed between washed and non-washed samples, and that it can be an important drawback of the methods using TOT (or TOR) determination of WINSOC. (cf comment #3 of referee #3, and change in the text, page 4006, line 19). However, we strongly feel that this short paragraph (about 24 lines altogether) showing two methods that are apparently not working should not be removed from our paper. A standardized procedure for measurement of WSOC is not existing still, and many different protocols are used in the litterature, sometimes with no assessment of their performance. Very few papers are published, that present detailed protocols in order to make progresses towards a standardized method (eg, Yang et al., Atmos. Env., 37, 865-870, 2003). It should be noted that one of the methods we tested (the "washing method") is used in several recent studies (Hoffer et al., ACPD, 5, 8027-8054, 2005; Kryvacsy et al., Atmos. Env., 6231-6244, 2001). Some other papers present results obtained with methods that do not seem to include a filtration of the water extract before the determination of the WSOC in the liquid phase (Zappoli et al., Atmos. Env., 33, 2733-2743, 1999, for exemple). Therefore, we really feel that a discussion on the comparison of protocols is needed, and could be usefull towards the definition of a unified method for the measurement of the WSOC content of aerosols.

2 - Further details on the method The low concentrations of OC (hence of WSOC) in our summer samples led us to use the maximum volume possible (i.e. 10 ml) for the determination of WSOC concentrations with our machine. In turn, taking into account all of the loses during sample processing (rinsing of the sample loop, rinsing of the syringe used for filtration, etc), we had to use 17 ml for the extraction of the samples. Only one determination is possible for each actual sample with this extraction volume of 17 ml. However, we performed tests on the repoducibility, as indicated in the text

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(page 4007, lines 16-18) ising some larger samples collected on purpose. These tests indicate that a coefficient of variation (standard deviation over mean) below 2% can readily be achived.

3 - Comments on the paper by Decesari et al. The referee is confusing between a) WSOC concentrations for which there are seasonal cycles, both in our data set (cf the new figure requested by referee #1 and the new associated text) and in that of Decesari et al., b) and WSOC mass fraction to OC, for which we do see seasonal variations that are not apparent in the data of Decesari et al. (see their table 1, page 3694).

4 - Comment on autocorrelation of DCA and WSOC Part of the comment is missing. It is clear that DCA are a part of WSOC (albeit a non dominant part), and that it induces a certain degree of autocorrelation. However, figure 8 is indeed showing that the relation between the two concentrations is evolving and that one of the major factor at play in this evolution is (or is linked to) the temperature.

5 - Units of DCA for calculation of DCA fraction of WSOC The reviewer is totally right and new figures are now presented with units of μgC/m3 for both DCA and WSOC (figures 8, 9, and 10). The text is modified accordingly (page 4012, lines 18 and 21, page 4013, lines 27 and 28 (equations)).

6 - Correlation between WSOC and OC It is clear that WSOC and OC are strongly correlated, as WSOC is the major part of OC and the ratio WSOC/OC is always in the range 45 - 80 %, as exemplified in our data and in most other studies (cf our table 3). This lead to correlations and regressions as presented in the figure below, with slopes very close to 2.3, as mentioned by the reviewer. However, it is also clear that there is some remaining variability in this ratio, and that the slopes are not the same for the high and low OC concentrations (cf figure below). Our investigations presented in the paper are an effort to better understand this variability, and it shows that part of it is linked with the evolution of the atmospheric temperature at our sites (as a proxy of processes or of changes of sources). It was our choice not to present the correlation between OC

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and WSOC in the original paper, since the really good correlations can be misleading in introducing the idea of a “constant WSOC / OC ratio”, as suggested by the reviewer, while it is not the case. We are now presenting it (figure 7, see also new text page 4009, line 21).

7 - Separate papers for the presentation of the sources and concentration changes of EC / OC and WSOC We fully acknowledge that the discussions on the evolutions and sources of EC / OC and of WSOC are strongly linked, and that it may be interesting to discuss them jointly. However, it is also the case for the DCA (see remark from reviewer #1), for the size distribution of OC (that give information on formation processes), for molecular tracers, etc. All of these information are strongly connected and relate to each other, and it is clearly not possible to present all of them in a single paper. We felt that it was possible to discuss about the evolution of WSOC in a separate paper without dealing in detail of the evolutions of OC, since the main points detailed in the present paper are the links with temperature and DCA concentrations. The paper presenting EC and OC evolutions (referenced Jaffrezo et al., 2005b) is introducing discussions on NO/NO2, ozone, meteorology, traffic counting, etc, it is already quite large in itself, and it cannot be merged with the present paper.

8 - Minor comments All were taken into account.

Anonymous referee #3 :

1 - No discussion on the link between concentrations and changes in traffic See answer to question #1 of referee #1.

2 - Emission inventory Yes, we performed emission inventories in the valleys [see paper G. Brulfert, J.P. Chollet, B. Jouve, H. Villard (2005) Atmospheric emission inventory of the Maurienne valley for an atmospheric numerical model. Science of the Total Environment, in press (now referenced in our paper)]. However, these inventories so far take into account some gaseous emissions and that of total suspended particles only, as it is really difficult to assess speciated particulate emissions. Therefore, a

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detailed discussion on the link between the evolution of WSOC and that of specific particulate emissions is not really possible. Note that part of the discussion (pages 4015 and 4016) is indicating that the change of sources between summer and winter probably have to be taken into account to explain the evolution in WSOC concentations and its fractions to OC. Further, a discussion between the emission sources of OC and the concentrations of WSOC would have to take into account the processes involved into the formation of secondary OC, and the state of the art with this respect is probably not advanced enough to make firm connections.

3 - Loss of EC during washing We fully agree with that. Correction is made in the text, page 4006, line 14.

4 - Change in temperature between the two winters, and seasonal variations in Chamonix. The temperatures were quite different between the two winters. For exemple, in Chamonix, the average temperature for the period December 1st to January 15th is -6.3°C for winter 01-02 while it is only -1.4°C for winter 02-03. In our paper, we suggested that this may introduce differences both in the frequency of the inversion layers and in the emissions sources. We changed the text to make the sentence more explicit and supported. We aggree with the reviewer that the number of samples for Chamonix (even if it is already much larger than any other data set presented in the literature) may be to small to be fully conclusive on a clear seasonal variation of the WSOC fraction. The text was changed accordingly.

5 - Impact of transported air masses in the valleys We understand the request from the referee for a definite answer on how much OC is from local sources and how much is transported from outside of the valley, in order to better understand the evolution of the concentrations of DCA (as a proxy for the secondary fraction of OC). However, we cannot currently answer this question without performing 3D modelling of the particulate phase (which requires both a precise inventory of the sources of OC in the valleys, a correct assessment of the regional background, and a realistic module of secondary OC formation). All of this is both out of the scope of this paper and partly currently un-

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der progress. As for the information given from the ozone concentrations in the study by Brulfert et al. (ACP, 5, 2341-2355, 2005), it is also extremely difficult to assess the exact fraction due respectively to transport vs local production / destruction. It is variable according to time, to the location in the valley, and to the season. There is no "magic number", and none is given in this last study. It only states that the influence of transported air masses on the evolution of the ozone concentrations in the Chamonix valley in summer, is probably dominant, taking into account the high correlation between the daily maximum of the ozone concentrations at these sites and at remote sites. However, we do not think that determining quantitatively the fractions of OC (even less that of ozone) respectively transported and emitted in the valley will bring direct information on the question addressed in this paragraph (ie, "are the characteristic of relations between DCA and WSOC similar between the two valleys in summer because a predominant share of these classes of species are coming from the same areas outside of the valley ?"). Our current knowledge of the relations between OC, WSOC and DCA are so scant that is would be premature to make any equivalence between the fractions produced/transported for OC and that for WSOC or DCA. In our original text, we only suggested as "a likely hypothesis", that the transported fractions of WSOC and DCA are dominant in both valleys in summer. This paragraph is now changed sligthly in order to make it clearer, to better present the results by Brulfert et al., and to put less emphazis on the potential implications of this "likely hypothesis".

6 - Quantification of wood burning and traffic as sources of OC Indirect evidences (Aymoz, 2004; Jaffrezo et al., 2005b) tend to indicate that Heavy Duty Traffic represents about 30 % of the source of EC in both valley on average, while it amounts for a lower fraction (about 10-15 %) for OC. It is more difficult to assess the impact of residential wood burning and the share it takes to local OC concentrations. There is no real good information on the actual mass of wood burnt the the valleys, since most of it is coming from cutting of privately owned woodlands, and not from an organized market. Based on a Chemical Mass Balance using PAH, a preliminary assessment indicated that wood burning can contribute between 25 - 55 % of PAH concentrations in a sub urban area

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of the Chamonix valley in winter, up to 60 - 75 % for a rural site further away from sources of traffic (Marchand, 2004). Further investigations are conducted, using more specific wood burning tracers (Marchand et al., 2005). The text is modified to give some indication on the potential importance of the wood burning source in the valleys.

7 - Formation through clouds processing The text was modified to make it clearer and to add a couple of sentences on propositions of experiments to test this hypothesis.

8 - Additional sources of potassium We have currently no proposition for the identification of an additional source of K that would explain the differencies in the average K+ / EC ratios observed between Chamonix and Saint Jean de Maurienne. Potential candidates includes traffic emissions or emission from industrial processes, both being more intense in the Maurienne valley. However, it should be mentionned that a change of the type of wood burnt could also produce a large change in the K/OC ratio, as already mentionned in the paper. The text was slightly modified (page 4016, line 19), to indicate that we cannot propose any convincing hypothesis so far.

Comment by C. Chan

There are many papers in the open litterature that mention the production of dicarboxylic acids during cloud processing and formation of a droplet mode of the aerosol size distribution, including papers dealing with field measurements and papers dealing with modelling. We believe that quoting the paper by Erven et al. (2004) is enough to make the case.

Comments by J. Yu

1) Changes in our table 3 : These additions are now performed in the new version of the paper.

2) Correlations between WSOC and sulfate, and between oxalate and sulfate, as an indication of secondary production of all these species during cloud processing in winter We believe that we do not need to further develop the section dealing with the hy-

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pothesis of a production of WSOC through cloud processing during winter conditions in the valleys (see comments above). This is kept as an hypothesis in our text, and the new addition (after the comment by Chan, above, and the answer to comment #7 of reviewer 3) clearly mentions that further measurements of the speciated chemical composition are needed. Further, we do not believe that the correlation between the concentrations of WSOC, oxalate, and sulfate can lead in our case to an unambigous demonstration of such an in cloud production. The evolutions of concentrations in the valleys in winter are strongly influenced by the local meteorology (particularly the daily change in the elevation of the inversion layer), that can easily masks the role of sources and production processes.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 3999, 2005.