

Interactive comment on “Comparison of the levels of organic, elemental and inorganic carbon in particulate matter in six urban environments in Europe” by M. Sillanpää et al.

M. Sillanpää et al.

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We thank for the critical comments of the Referee #2 that have led to a thorough revision of the manuscript with addition of new data. Our responses and text revisions have been made according to the general comments and specific comments as detailed below. The comments are numbered and each of them is followed by a response from the authors (AR). We have paid special attention to a more concise presentation of the results and their analytical discussion. Therefore, we also suggest a more concise title of the manuscript, i.e. ‘Organic, elemental and inorganic carbon in particulate matter of six urban environments in Europe’.

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GENERAL COMMENTS FROM THE REFEREE: The work by M. Sillanpää et al. presents an interesting “monitoring” strategy: sampling on periods in which severe PM pollution events have been observed in various cities and focusing analyses on the carbonaceous fractions, which are likely to have major contributions to the PM health effects and are the most difficult to quantify, due to various sampling and analytical artifacts. A large set of elements have also been quantified, which might give information on possible aerosol sources. However, the level of the discussion is very disappointing, as it remains very much too speculative. Full paragraphs indeed start with “most likely explained by”, “most likely due to”, “suggesting that”, “could be explained by e.g. ...” and actually present commonly accepted concepts, without using the data acquired in this work to give evidence of what is stated. This manuscript, as such, only presents and compares data, without any further step to explain the observed differences and similarities. The same applies to more technical considerations (OC found on back filters) or to comparisons with other studies or measurements: no conclusion is derived from the observations. One can wonder if this work represents a significant enough contribution to the atmospheric chemistry research for constituting a stand-alone article.

Response from the authors (AR): We agree with the Referee that our discussion in the original manuscript was too speculative and that there were no clear conclusions from the data. In our thoroughly revised manuscript, we have taken a full advantage of our new data on inorganic and organic tracers analysed from the PM_{2.5} samples in order to establish firm grounds for a more objective discussion on the likely sources of EC and POM during the six sampling campaigns. In addition, we present clear conclusions both in the Abstract and section 4 Conclusions and implications.

Responses to specific comments:

1) p. 2724, line 25: the fact that the deliquescence point was not reached does not mean that the contribution of water to the filter mass was negligible.

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AR: The PM masses were measured from the PTFE filters that have, due to a small surface area, a much lower capacity to adsorb water than e.g. quartz fibre filters or glass fibre filters (Turpin et al., 1994). Our mass closure study (submitted to Atmospheric Environment) written on the basis of all the chemical analyses results from the same samples of six European cities showed that the contribution of water was less than 10 % to PM_{2.5} and much less than that to PM_{2.5-10}.

2) p. 2725, line 22: please specify how the increasing of OC solubility from left to right (i.e. I guess from OC1 to OC4) was established. Is this rule valid for OCP also?

AR: This sentence had been deleted from the manuscript because the water-solubility of the OC thermal fractions depends much on the origin of the particulate sample (e.g. Yang H.Y. and Yu J.Z. Environ. Sci. Technol. 2002, 36: 5199-5204 (Figure 1a)). The water-soluble and insoluble OC fractions were not separated in this study.

3) p. 2726, line 2: according to last paragraph in page 2725, XRF measured the total Ca concentration. So why does Ca²⁺ appears in page 2726, line 2?

AR: The abbreviation of total calcium has been changed from Ca²⁺ to Ca.

4) p. 2726, line 9: integrating thermograms to get CO₃ concentrations might be an interesting approach. However, readers would certainly like to know and understand how it has been established that (1) CO₃ contributes to OC₄ only, (2) CO₃ peak starts at 210-225 s and ends at 250-275s, and (3) how the CO₃ peak start and end times are determined for each thermogram.

AR: Carbonate causes a narrow peak during the OC₄ temperature step, which was confirmed by analyzing a piece of same filter sample that was earlier decarbonated by HCl fumes. The decarbonation method has been described by Cachier et al. (Tellus 1989, 41B, 379-390). A typical OC₄ peak without CO₃²⁻ is broad and, therefore, the narrow peak of carbonate can be identified and integrated when the CO₃²⁻ concentration is high like it was in all the PM_{2.5-10} samples from Athens. Each thermogram was

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manually integrated: the narrow CO₃₂- peak started at 210-225 and ended at 250-275 s. This issue is now explained in an additional sentence after the integral definitions: “The C(CO₃) peak was initially localised by comparing the analysis results of the original Athens sample to its duplicate that was decarbonated in HCl fumes as described by Cachier et al. (1989).”

5) p. 2728, line 7-9: it is not clear whether the back filter OC amounts were used to correct the front filter data. Such a correction relies on assumptions that should be specified. If back filter OC data were not used for correcting front filter, it should also be clearly stated and explained. Positive artifacts are believed to depend - among other parameters - on face velocities. Isn't it surprising that the OC back / OC front filter ratio are similar in the coarse and fine fractions, whereas the minor and main flow rates usually differ by 1 order of magnitude in a virtual impactor?

AR: The OC correction method was briefly described on p. 2724, lines 9-11: “In the latter VI, a tandem filter collection method (two quartz fibre filters from the same lot in series) was applied to estimate and correct for the positive sampling artefacts, i.e. the absorption of organic gases.” Now the sentences “In practice, the OC value of backup filter was subtracted from that of front filter. The positive artefact correction has been performed to all the POM results presented in this study.” has been added to the end of this paragraph.

In the virtual impactors used in our study, the flow rate through the filter for PM_{2.5-10} was one tenth of that for PM_{2.5} like the Referee anticipated. Indeed, the backup to front filter OC concentration ratios are similar for PM_{2.5} and PM_{2.5-10}. This observation can be explained to a small part by the generally lower OC concentrations in PM_{2.5-10}, but it probably implies that the backup filter for PM_{2.5} saturated with organic gases during the 3- or 4-day collections and could not adsorb additional vapour. A saturation of backup filters for PM_{2.5-10} was not likely to occur during these collection periods because of the lower flow rate.

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6) p. 2728, line 24-26 and p. 2729 line 14-19: what does the comparison with the works by Querol et al. and Putaud et al. bring to the discussion? Are the observed differences due to the various sampling and analytical techniques employed, or due to seasonal variations, or meteorology-linked variations?

AR: We would like to keep this comparison of the ambient air total carbon (TC) concentrations (Querol et al 2004) or the BC/EC and POM concentrations (Putaud et al 2004) between our study and these recent multicentre studies but remove all the speculation on differences in PM sources, as this is replaced by a thorough analysis of EC and POM sources with the help of selected tracers (see our responses to general comments and the new section “3.3 Assessment of EC and POM sources”). A sentence has been added to the end of paragraph in p. 2729 line 20: “Despite the differences in sample collection and analysis techniques between our study and the other European studies, this finding suggests that the selected campaign periods of public health concern in several cities (e.g., Prague, Athens, Helsinki) were associated with a relatively high POM content.”

7) p. 2728, line 28 - page 2729, line 6: the discussion about method-dependent OC/EC split should be moved up to the “Experimental” section, or down after discussions of EC concentrations.

AR: The paragraph regarding the discussion about method-dependent OC/EC split has been moved to follow the paragraph on the BC/EC and POM contributions to PM_{2.5} and PM_{2.5-10} and the additional sentence given in point 6).

8) p. 2729, from line 21: this section compares PM_{2.5} / PM₁₀ ratios for EC and OC, whereas parag. 2 page 2727 compares PM_{2.5} / PM_{2.5-10}. More consistency is recommended.

AR: The ratios for particulate matter, POM and EC have been calculated so that the presentation is more consistent. All the ratios are now given in PM_{2.5-10}/PM_{2.5}. Now the sentence on page 2729 (lines 21-28) has been revised as follows: “The mean

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PM_{2.5-10} to PM_{2.5} ratio of the EC ranged between 0.17 and 0.29. These low ratios indicate that the EC existed mainly in PM_{2.5}, which has been observed in many European urban environments (Viidanoja et al., 2002; Salma et al., 2004). The mean PM_{2.5-10} to PM_{2.5} ratio of POM had a much larger range than that of the EC, being 0.094 for Prague, 0.24 for Amsterdam, 0.45 for Duisburg, 0.50 for Helsinki, 0.56 for Barcelona and 0.59 for Athens. The ratios were lower for sampling campaigns with a lower mean ambient temperature and a higher precipitation (see section 2.1).”

9) p 2729, line 23-24: there is no logical link between “EC existed mainly in the fine particulate fraction” and “EC is produced only in combustion processes” if a statement about the size of combustion particles is not included.

AR: The sentence has been changed to “These low ratios indicate that the EC existed mainly in PM_{2.5}, which has been observed in many European urban environments (Viidanoja et al., 2002; Salma et al., 2004).”

10) p. 2729, line 25 - page 2730, line 2, in line with the general comments: some reasons for explaining the OC size distribution could be confirmed or ruled out by looking at other data. E.g. decreases in fossil fuel combustion for heating should be confirmed by decreases in EC. Can shifts in OC sampling artifacts at least partially explain the observed differences?

AR: A new section “3.3 Assessment of EC and POM sources in PM_{2.5}” is started from p. 2730 line 3. The revised two paragraphs on OC to EC ratios and correlations in PM_{2.5} (lines 3-21) are followed by a new paragraph on a more specific source assessment with the help of selected inorganic and organic tracers measured in this study.

11) p. 2730, line 18: the OC vs. EC correlation and the OC/EC ratio are also consistent with carbonaceous species coming mainly from (light or heavy duty?) Diesel engines. Ships’ fuel is very rich in S compared with road vehicles’ fuel. Can SO₄ concentrations be used to demonstrate the role of ship emissions?

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AR: See response to specific comment 10. We have used Ni and V as tracers of heavy fuel oil combustion in ship engines at city harbours.

12) p. 2730, line 26: again, a clear explanation on how CO₃ is distinguished from other OC₄ components is missing.

AR: See response to specific comment 4.

13) p. 2731, line 6-15: would this discussion still hold considering that XRF leads to Ca and not Ca²⁺ concentrations?

AR: See response to specific comment 3.

14) p. 2731, line 21-24: the reason why the distribution of Ca among the fine (PM_{2.5}) and coarse (PM_{2.5-10}) fractions could not be derived from XRF analyses of the VI samples should be clarified.

AR: The use of BLPI data is unnecessary in this case. The sentence “In addition, based on the mass size distribution measurements by Berner low pressure impactor and on the IC analysis (data not shown), the PM₁₀ calcium existed almost exclusively in PM_{2.5-10} in both Barcelona (93.54%) and Athens (89.52%) as well as in other cities (75-86%).” is replaced by the sentence “In addition, the fine-to-coarse ratio of total Ca was lower in Barcelona (0.064) and Athens (0.068) than in the other four cities (0.086-0.183), indicating a strong coarse particle dominance in Ca distribution.”.

15) p. 2732, line 16-18: can the effect of the filter loads be ruled out to explain the differences in the contribution of the various OC fractions?

AR: As seen in Fig. 7, the different thermal fractions (OC₁-OC₄ and OCP) had actually quite similar contributions to the total OC of the six sampling campaigns. This is likely to be due to the methodological default explained on p. 2732 lines 21-27.

16) p. 2732, line 19-20: is the 33% OC₁ fraction observed for Barcelona and Athens significantly higher than the 26-29% observed at the other sites?

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AR: The percentage differences of OC1 thermal fraction between the cities varied between 26-33%. Significant differences were not found and, therefore, the sentence “In addition, the OC1 fraction (at 310 °C) was 33% for both Barcelona and Athens while it was somewhat lower (26-29%) for the other cities.” was deleted.

17) p. 2732, 2nd paragraph: these observations simply suggest that as such, the thermal program does not lead to any valuable data regarding the various OC_i fractions. This could prevent from seeing any relationship between OC1 (front) and OC1 (back). Such a relationship (if any) could be a useful tool for a crude correction of the OC positive sampling artifact.

AR: In our study, the temperature steps of the slightly modified NIOSH program were too short in relation to the present sampling duration in order to reliably determine the thermal fractions of OC. On the other hand, Kirchstetter et al. (2001) have concluded that the accuracy of the tandem quartz filter subtraction method, i.e. positive artifact correction, improves with longer sampling duration. In 2001, Mader et al. (Environ. Sci. Technol. 35, 4857-4867) have reported a study in which they collected urban air particles with a particle trap impactor / denuder system that was placed side-by-side with an open-face filter pack sampler and the samples collected on quartz filters were analysed by the TOA method using a temperature program very similar to that of NIOSH. They concluded that the positive artefact from ambient gaseous OC was much more important than the negative artefact from evaporation of the OC from collected particles on front filter. However, in their modelling both the positive and negative artefact appeared to vary depending on several factors related to the sampling conditions (P/G partition coefficients of the compounds comprising the particulate OC, temperature etc.). Thus, the use of back filter in impactors seems necessary for correction of the positive artefact.

18) p. 2734, paragraph 1: the most striking observation re. PM mass concentrations is certainly the very different PM_{2.5}/PM₁₀ ratios observed at the various sites. Other statements are not clearly demonstrated from data.

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AR: Chapter 4 title has been changed to “4 Conclusions and implications” and the text has been thoroughly rewritten to avoid unnecessary repetition of results but instead to include clear conclusions on all the main results.

19) p. 2734, paragraph 3: as already commented, the thermal program does not seem to lead to valuable data regarding the 5 OC fractions, which should therefore not be quoted again in the conclusion.

AR: This paragraph of conclusions has been deleted. We agree with the Referee that the OC thermal program did not lead to valuable data regarding the five OC thermal fractions due to too short-lasting temperature steps.

[Interactive comment on Atmos. Chem. Phys. Discuss., 5, 2719, 2005.](#)

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