

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 are very pleased with the constructive comments of the Reviewer 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 remarks and specific comments as detailed below. The comments are summaries and numbered (4 general comments and 8 specific comments), 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’.

GENERAL COMMENTS FROM THE REFEREE:

The manuscript is very timely because of quite a lack of data on OC/EC in Europe, specifically of data obtained with a minimum quality check. However, this said I dearly miss reference to recent work performed with filterpacks, in which even denuders were used. This refers to work by the groups of Maenhaut in urban settings and reported in J. Aerosol Science and Putaud for a site in the polluted PO-Valley (in frame of Eurotrac-II). The analysis of inorganic carbonate is possibly the most important addition because it is often raised as an issue in conjunction with the specific method for analysis of OC/EC used here. Normally acidification is used or suggested as the proper tool to remove carbonate but actual measurement of the contribution of carbonate is even better for a proper closure of the mass of PM-coarse.

There is a lack a general conclusion, which may be related to the different seasons in which the sampling was performed; but this should also be realised in the coamariosn of data from different cities in the main text. In this sense the abstract contains too many data. This also applies for the main text. For instance the SD's should not be mentioned with every data point in the main text, rather a general statement on the vairance should be made and actual SD's appear in the tables to make paper more accessible.

RESPONSE FROM THE AUTHORS (AR): We have reduced the amount of data given in the Abstract and the main text to improve reading. Moreover, we have added clear conclusions both to the Abstract and to section 4 Conclusions and implications. Section 4 is also shortened to avoid unnecessary repetition of results.

1. Is earlier work adequately recognized and credited? No, see above.

AR: Several new references on carbon analysis techniques as well as on inorganic and organic tracers of sources of the EC and POM have been added into the text and reference list as requested by the Referee.

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2. Is the paper well organized and clearly presented? Yes though there is a repetition for EC.

AR: The repetition related to the sentences “The variations were most likely explained by differences in season, local emission sources and geographical location.” (p. 2727) and “The differences are most likely due to variable contributions of local emission sources and seasonal factors such as residential heating with solid fuels, vehicle exhausts and photochemical reactions.” (p. 2729). The former sentence has been presented in connection to the discussion on the fine and coarse PM ratios (chapter 3.1) and we have kept that. The latter sentence was mentioned in the discussion on carbonaceous components (chapter 3.2) but it has now been replaced by new data (Fig. 3) and text (section 3.3) on the EC and POM sources assessed with the help of inorganic and organic tracers that were measured in our study.

3. Can any of the illustrations be clarified, reduced, combined or eliminated? Yes map with the well-known cities is redundant.

AR: The map (Figure 1) has been deleted since the cities are well-known.

4. Is the standard of English usage satisfactory? There are quite some instances that (in translation) wording has been chosen that is not the standard jargon to the extent that the meaning of a sentence is not really clear. Instances provided in the specific comments

AR: The English language has been thoroughly revised throughout the manuscript including the instances pointed out by the Referee.

Responses to specific comments:

1) The adsorption artefact is a function of the amount of air drawn through unit filter surface (Turpin). In this study the amount of air sampled is more than in standard sampling of one day. This, in turn, could also mean that the evaporation artefact can be higher because there is more time and more variation in the filter condition than in

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shorter-term sampling. The authors are asked whether they compared their long-term sampling artefact with that of 4 times one day sampling. Examples of such a test are given in Turpin et al.

AR: In our study, the sampling durations were consecutively 3 or 4 days and the sampling flow rates through the filters of fine and coarse particles were 15 l/min and 1.7 l/min, respectively. On one hand, the long sampling time may cause a substantial negative artifact, i.e. evaporation of semivolatile organic compounds from the collected particulate matter. We did not compare the influence of sampling duration on the negative artifact since any 1-day sampling was not performed in parallel with the 3- or 4-day samplings. This comparison would have needed to be done in all six cities, since according to the literature many variables, such as sample volume, filter face velocity, ambient air temperature, and the chemical composition of the PM sample should be considered (Van Vaeck et al., 1984; McDow and Huntzicker, 1990; Turpin et al., 1994). On the other hand, Kirchstetter et al. (2001) have concluded that the accuracy of the tandem quartz filter subtraction method, i.e. the positive artifact correction, improves with increased sampling time. We had to compromise between the different views and we chose the tandem quartz filter subtraction method. Moreover, the general protocol of the PAMCHAR field campaign necessitated 3- or 4-day sampling durations due to a parallel sampling of large, size-fractionated PM samples for toxicological cell and animal studies, using a high-volume cascade impactor (Sillanpää et al. 2003).

2) A major problem is the data on crustal material in table 6. The standard ratio of Al to Si is 0.3 in all publications I have seen for W-Europe. It is also noted that there is no reference to these studies in this paper.

AR: The Al to Si ratio has been published in many papers. As the Referee mentioned, the standard ratio of Al to Si is 0.3 for Western Europe. This is in good agreement with our present results, as we measured a mean ratio of 0.27 for Duisburg PM_{2.5-10} and 0.29 for Amsterdam PM_{2.5-10}, and only slightly higher (0.32-0.40) ratios for the other four cities. The ratios have not been added into the text because they do not belong to

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the scope of this paper.

3) Abstract: Carbon should be mentioned first because this paper is on carbon and not on crustal (the only crustal compound, CaCO_3 is also carbon and should be prominently mentioned here.

AR: We agree with the Referee that the instruments need to be written in a different order. We have also added which constituents have been measured with the different instruments. The revised sentence is: “From the collected filter samples, elemental (EC) and organic (OC) carbon contents were analysed with a thermal-optical carbon analyser (TOA); total Ca, Ti, Fe, Si, Al and K by energy dispersive X-ray fluorescence (ED-XRF); As, Cu, Ni, V, and Zn by inductively coupled plasma mass spectrometry (ICP/MS); Ca^{2+} , succinate, malonate and oxalate by ion chromatography (IC); and the sum of levoglucosan+galactosan+mannosan (∑MA) by liquid chromatography mass spectrometry (LC/MS).”

4) last sentence of Abstract: portion = contribution?

AR: The latter part of the Abstract has been totally rewritten due to a summary and conclusions of the new data. The word “portion” has been replaced with “contribution” in the Abstract and elsewhere in the manuscript.

5) Introduction: 2d 3d sentence should read: urban aerosol contains a substantial amount of carbonaceous material.

AR: The 2nd to 4th sentences of Introduction have been revised and joined. The new sentence is: “Urban aerosol contains a substantial amount of carbonaceous material (20-80%; Rogge et al., 1993 and Nunes and Pio, 1993) that is composed of two main fractions: 1) elemental carbon (EC; sometimes referred to as black carbon or graphitic carbon) is a primary pollutant formed in combustion processes, and 2) particulate organic matter (POM) is a complex mixture of different groups of compounds originating from a large variety of processes (Seinfeld and Pandis, 1998).”

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6) pg 2723 line 26: alternation=consecutively?

AR: The sentence “The sampling durations were 3 or 4 days in alternation, Ě” was replaced with the sentence “The sampling duration was 3 + 4 days per week, Ě”.

7) 2724 line 26: can there be hysteresis in the water release from the molten samples?

AR: The filter weighing procedure has been described in chapter 2.3. Our chemical mass closure study (submitted to Atmospheric Environment) conducted from the same samples of six European cities shows that the contribution of water is less than 10 % to PM_{2.5} and much less to PM_{2.5-10}.

8) page 2728: discussion on EC is literally repeated on page 2729

AR: See the General comment 2.

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