Atmos. Chem. Phys. Discuss., 7, S5001–S5010, 2007
www.atmos-chem-phys-discuss.net/7/S5001/2007/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP" *by* K. E. Yttri et al.

K. E. Yttri et al.

Received and published: 17 September 2007

General comments made by reviewer:

This manuscript deals with the measurement of carbonaceous particulate matter in aerosols collected at 12 rural/background sites and 2 sub-urban sites across Europe, using, mainly, the EMEP measuring network. Taking into account the relative importance of carbonaceous material in continental atmospheric aerosols and the lack of extensive measurements of carbonaceous aerosol characteristics in rural areas in Europe, across the seasons, this work and its conclusions are important for the understanding of the behaviour, formation processes and origins of the European continental aerosol.

The conclusions taken from this experimental campaign are very much in agreement with another recent rural carbonaceous aerosol study across Europe (CARBOSOL) and the observed levels of EC, OC and tracers, such as levoglucosan, are quite similar, although different analytical methodologies were employed in each study. This permits to have confidence on the representativeness of the results and conclusions. In general I agree with the interpretation of the concentration data and the conclusions/suggestions of possible causes for the observed concentrations behaviour across Europe and from winter to Summer, in the manuscript. In my opinion the manuscript is written mostly in a clear manner but, in the tentative of explaining thoroughly each detail and parameter, there is a repetition of similar arguments when dealing in different sections with the aspects of EC, OC and TC; EM, OM and TCM; etc., which makes the reading somehow tiresome. I think that by reorganizing the manuscript it would be possible to make it shorter, without loosing any important information and interpretation. Generally most of the discussion about TC gives very similar results than when discussing OC and should happen only in cases when the results are exceptionally divergent. Also average annual values can be obtained directly from the averages of winter and summer averages.

General comments to be answered:

First of all, we would like to thank the reviewer for the positive comments made to our manuscript and for the effort made to clarify and improve its content.

1.In my opinion the manuscript is written mostly in a clear manner but, in the tentative of explaining thoroughly each detail and parameter, there is a repetition of similar arguments when dealing in different sections with the aspects of EC, OC and TC; EM, OM and TCM; etc., which makes the reading somehow tiresome. I think that by reorganizing the manuscript it would be possible to make it shorter, without loosing any important information and interpretation. Generally most of the discussion about TC gives very similar results than when discussing OC and should happen only in cases when the results are exceptionally divergent. Also average annual values can be obtained directly

ACPD

7, S5001–S5010, 2007

from the averages of winter and summer averages.

Reply: We recognize the argument raised by the referee, and initially we tried to organize it as suggested by the referee. However, we found the manuscript more difficult to read then, because there are not every aspect of EC and OC that are similar, which made it necessary to explain any deviation from a common pattern. These explanations provided breaks in the text, which made it less fluent to read. Further, EC and OC are different parameters, and when looking up in such a descriptive manuscript, one should expect to find the various subfractions discussed separately. Indeed we have tried to avoid tiresome repetition e.g. by providing only a short paragraph (8 lines on page 3871) on TC. People which read the manuscript before this section on TC was added, strongly argued that it had to be included for the reasons mentioned in the text, namely that "The aerosol content of TC is not subject to uncertainties related to the split between EC and OC. Hence, it is a more robust parameter and can be used to confirm some of the findings deduced from the EC and OC data." Thus, we have not discussed TC in detail, as is the case with OC and EC.

The referee argues that the annual levels of EC, OC and TC could be obtained from that of winter and summer mean averages. In the text we discuss the annual levels for the various carbonaceous fractions and we don't find it suitable to refer the reader to calculate these levels him or her selves based on the summer and winter averages. In addition, annual concentrations are typically the parameter used when describing the concentration levels at various sites, and is therefore commonly used for comparison.

2.As an example I think that there are too many Tables with too much information that could be reorganized and condensed. For example Table 7 has too many Pearson correlation coefficients columns. Also information in Table 4 can be directly calculated from Tables 5 and 6.

Reply: The referee argues that there are too many tables with too much information, pointing towards Table 7 as an example, arguing that it has too many Pearson correla-

ACPD
7, S5001–S5010, 2007

tion coefficients. We agree with the statement made by the referee regarding Table 7 as we only discuss the Pearson correlation coefficient obtained for EC vs OC. Thus we will remove the columns providing the correlation coefficients for EC vs PM10, OC vs PM10 and TC vs PM10.

With respect to the argument raised that the information in Table 4 could be directly calculated from Tables 5 and 6, please see comment made under bullet point 1.

3.The referee has concerns regarding the decisions taken by the authors with respect to how we are dealing with the interferences from organic blanks.

Reply: This "general question" has been merged with the specific comment concerning Page 3865 lines 7-12.

The discussion concerning importance of blank concentrations and interferences is included to underline the importance of these. Although the annual levels are presented uncorrected, this does not mean that we are not aware of the uncertainties in the current dataset. Chapter 3.1 is dedicated to the uncertainties and the field blank levels and their relative importance are presented in Figure 2 and Figure 3, respectively.

The referee states that the more correct option would be to subtract the blank values. In general, the authors agree to this statement of how to use a field blank, and we would indeed have done so if the field blanks had been inserted into the sampling train and run for an appreciable period of time. Only this way could the field blanks have been true field blanks.

Field blanks are collected and analysed to assess the amount of material (e.g. OC) found in samples, which does not come from the atmosphere, but instead from the sampling substrate itself (e.g. filters) or from contaminations (e.g. during handling or storage). We have observed that the amount of C found in filters through which particle-free denuded air has been sampled (dynamic blanks) may be twice smaller than in field blanks, which experienced exactly the same history, except that no air had

ACPD
7, S5001–S5010, 2007

EGU

been sampled through. Considering field blank levels, we would have calculated that the C concentration in particle-free denuded air was negative, which can of course not be true. The C concentration in dynamic blanks is indeed expected to be significantly positive as soon as the denuder efficiency is not 100% for VOCs that can be trapped by quartz fibre filters. This demonstrates that the amount of C found in field blanks is not suitable for determining the amount of C detected in a quartz fibre filter through which air has been sampled through, that comes from other sources but the atmosphere. This result can obviously be demonstrated sampling "zero" air only. Sampling particle-free air through a quartz fibre filter can obviously lead to enhanced C levels in these filter, when ab- and/or ad-sorbtion of atmospheric VOCs are predominant with respect to the volatilisation of VOC present in blank filters. This is the often-observed positive sampling artefact. However, this amount of carbon really comes from the atmosphere. It cannot be attributed to blank levels.

The referee wonders whether this is a phenomenon observed all across Europe or just at one site. So far we only have data from one site, Ispra.

Specific comments made by the reviewer:

4.Collection of PM10 particles may contain important contribution of soil, principally in dusty environments. Carbonates may be then an important carbon contributor to the aerosol. Nothing is referred in relation to this in the manuscript. Is the filter decarbonated before OC and EC analysis? If not, in this NIOSH methodology carbonates will be measured (at least partially) as OC. If this is the case, the higher levels of OC in PM2.5-10 during summer, in Figure 7, may also be resultant from carbonates in the soil.

Reply: Regardless of how a dusty environment is defined, Birkenes is not likely to be defined as a site particularly influenced by mineral/soil dust. Further, soil/mineral dust originating from the earths crust in Norway is not likely to have a content of CO32-, as it is mostly made up of granite and no limestone at all. Any CO32- containing mineral dust

ACPD
7, S5001–S5010, 2007

EGU

detected in Norway is likely to have its origin outside the Norwegian borders. Given the fact that mineral dust tends to be present in the coarse mode of PM10 its residence time in the atmosphere is rather low compared to fine aerosols, thus long range transport of CO32- containing mineral dust is not likely to be a major source in Norway. As carbonate typically is present in the form of CaCO3, addressing the aerosols content of Calcium could indicate something about the presence of carbonates. At Birkenes, the concentrations of Ca are very low, and there is no sign of increased levels of Ca in summer. Thus we don't find it likely that the increase in coarse OC seen during summer is attributed to CO32-.

Further, the referee asks whether the filters were acidified before being analyzed. This was not the case. However, based on the WSOC analysis, performed using the Schimadzu TOC liquid analyzer (Model TC 5000 A) it was found that the concentrations of inorganic carbon was negligible most of the time. This statement is meant to describe the entire dataset, including samples collected in Southern Europe where carbonate is likely to be more abundant in the soil/mineral dust.

5.Page 3864, lines 1-10 - The determination of WSOC uses an analytical methodology that may result in interferences, as result of suspension of particulate EC or insoluble organic particles, during the extensive sonication. Filtration of the extract through a 0.2 um Teflon filter should reduce this probable interference. The subject should be discussed in the manuscript.

Reply: The water extracts was filtered using PTFE-membrane single-use syringe filters (Sartorius Minisart SRP 15). Unfortunately this was left out from the original manuscript. This part of the sample preparation has no been added to section 2.2.1. (See below).

"A total of 71 samples were subjected to WSOC (Water-soluble organic carbon) analysis. Before analysis, parts of each filter were soaked in Milli-Q water (7 ml for low volume filters and 20 ml for high volume filters) and subjected to sonication (30 min)

ACPD
7, S5001–S5010, 2007

EGU

for extraction of the WSOC. The water extracts were filtered using PTFE-membrane single-use syringe filters (Sartorius Minisart SRP 15). The dissolved organic material was then quantified using a Shimadzu TOC liquid analyzer (model TC5000A). This instrument also allows for determination of inorganic (carbonate) carbon following acidification. The inorganic carbon was subtracted from the dissolved organic carbon in order to obtain the WSOC fraction. However, the concentrations of inorganic carbon were negligible most of the time. The water-insoluble organic carbon (WINSOC) was quantified by subtracting WSOC from OC. The WSOC analysis was performed at the Institute of Atmospheric Sciences and Climate of the Italian National Research Council (ISAC-CNR)."

6.Page 3865, lines 7-12- It seems from this paragraph that in all samples the analysed and measured filter blanks were not subtracted from the exposed filter measurements. This decision seems a bit incongruent with all extensive discussion in the paper about the importance of blank contamination and interferences. It seems that the decision is based in a non clear and scarcely described experiment (?) showing that in a QBQ evaluation the value of the blank decreased to half. The decrease of blank values in a second quartz filter on a QBQ set up, although not impossible, does not seem to be common. So it is important that this point needs to be discussed and clarified. Where these QBQ experiments done extensively, at all sites across Europe, during different seasons? Or were they only limited at one location and one period of the year? Anyway, even if the experiments are generally observable and the blanks decrease to half values during QBQ sampling, the more correct option should be to subtract this half value.

Reply: See bullet point 3.

7.Page 3866, 10-17- the interpretation of results and explanations given for bank values in this paragraph are not clear to me. Why possible lower values of particulate OC during summer are the explanation for higher positive artefacts of OC (related mostly with absorption of gases on filter substrate)?. Also, lower concentrations of VOCs in

ACPD
7, S5001–S5010, 2007

EGU

winter, if they result in lower adsorption in the filter substrate will give a lower positive artefact (but will not underestimate it). Furthermore, lower VOC values in winter are counter-balanced by lower temperatures and easier adsorption of these VOCs.

Reply: Lower levels of particulate OC in summer would give a higher relative contribution of the positive artifact given that the absolute concentration of the positive artifact was maintained. Given a maintained or higher adsorption of VOC in summer compared to winter, but a lower particulate OC in summer, then the relative contribution of the positive artifact would be greater compared to winter.

We state that if a lower level of VOC in winter causes less adsorption to the filter substrate, i.e. fails to saturate the backup filter, then the positive artifact would be underestimated, because we succeed in saturating the front filter, but not the back up filter. According to the theory behind QBQ, an equal adsorption on both front filter and back up filter is necessary to make this approach work properly.

We agree with the statement made by the referee that the lower levels of VOC in winter might be contradicted by increased condensation, but we can only speculate whether it will be balanced.

Originally we included the last paragraph in section 3.1 to provide a basis of understanding for how the positive artifact, as measured by QBQ and QBT, might vary according to season. However based on the argument raised by referee 1 that we don't use this text to explain our results, we will remove it from the manuscript.

8.Page 3870, lines 11-16 - increase of coarse OC in summer could not also result from an increase in plant debris and pollen in summer? (besides the possible increase in carbonates - if decarbonation is not done previous to EC/OC analysis).

Reply: We argue that coarse OC seen at Birkenes could be attributed to Primary Biological Aerosol Particles (PBAP). According to the definition of Sabine Matthias-Maser pollen and plant debris belongs to this group of particulate matter. The reason that we

ACPD
7, S5001–S5010, 2007

EGU

state that resuspension might be a driving force is that we see almost no coarse OC when snow is covering the ground. However, the evaluation of coarse OC throughout the season also closely resembles the vegetative season. This topic is also discussed in the recent paper by Yttri et al. Atmos. Chem. Phys., 7, 4267-8211;4279, 2007.

9.Page 3870, lines 25-26 - I don't understand this sentence. Why the coarse OC is not subject to positive artefacts? If I understood correctly, on lines 2-4 of the same page it is said that the same sampling methodology is used for both size fractions in order to have identical positive artefacts. It seems to me that the artefacts are related mostly with the filter substrate and not with coarse or fine particles deposited in it. Anyway this discussion seems to be irrelevant when the authors decided to forget anything about artefacts in their blank corrections (by not correcting blanks).

Reply: Given that the same type of sampler and sampling methodology is used for OC in PM10 and PM2.5, then the same magnitude of the positive artifact could be expected on the filters loaded in the two samplers regardless of the inlet cut off. That means that the positive artifact for OC in PM10-2.5, which is obtained by subtracting OC in PM2.5 from OC in PM10, will be cancelled.

Based on the request made by referee 1 we have stated this more clearly in the text.

"It is likely that the relative contribution is even higher, as OC in PM10 might be subject to positive artefacts, while this is not the case for coarse OC, as the artifact from PM2.5 and PM10 cancel each other".

We do not forget about the artifacts, neither about our field blanks. Section 3.1, Figure 2 and Figure 3 are indeed dedicated to the field blanks and the artifacts. We have just decided to present the magnitude (Figure 2) and the relative importance of the field blanks (Figure 3) in another way.

10. Page 3876, lines 1-5 - In my opinion to use the values of the RM 8785 of EC/OC between the NIOSH and the IMPROVE methodologies to calculate the EC levels in

ACPD
7, S5001–S5010, 2007

Europe, if the IMPROVE method was employed, has to be done with caution because the EC/OC relation between the two methods is dependent from the type of samples and seems to vary strongly from urban kerbside to rural samples. The RM 8785 is made with urban particles and most of the measured aerosol in this study is rural.

Reply: The statement raised by the referee is sound, and we agree that the best alternative would be to make such a comparison based on a standard reference material that was collected on an European rural site rather than at an US urban site. However, RM8785 is the only reference material for EC/OC available that we are aware of. To optimize such a comparison, samples from each of the 14 sites, collected at various seasons should have been subjected to both the Quartz.par protocol, used in the present study, and the IMPROVE protocol. However this would have required a large additional number of analyses (1 sample pr season pr site, provides 1 x 4 x 14 = 56 samples) by an instrument/protocol that we don't have access to (IMPROVE/TOR).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 3859, 2007.