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Comment

Interactive comment on “On the effect of water-soluble compounds removal on EC quantification by TOT analysis in aerosol samples” by A. Piazzalunga et al.

A. Piazzalunga et al.

andrea.piazzalunga@unimib.it

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Answers to referee 1

» QUESTION: The authors identify weakly light-absorbing and resilient organics as the cause for the differences between protocols, but how frequently are these species found in other regions? They state that these organic possibly originate from biomass burning, therefore should they also be found in other central and northern EU regions, or are these organics specific to the Po valley? And what about rural sites (instead of urban)?

» ANSWER: Unfortunately, at the state of the art, insoluble organics (WINSOC) in
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aerosol samples are still poorly characterised and, in general, there is very scarce information about insoluble organics at different locations. As an example, Mayol-Bracero et al. (2002) analysed WINSOC in biomass burning aerosol over Amazonia. They report that this fraction probably includes significant amounts of incompletely combusted products and biogenic detritus such as wax esters, aliphatic hydrocarbons, triglycerides, long-chain ketones, alkanols, and polycyclic aromatic hydrocarbons. Moreover, WINSOC can be also make up of water insoluble humic-like substances (Salma et al. 2007; Cachier, ICCPA 2011). The ultimate origin of HULIS is still being debated, but there are evidences that they are omnipresent in rural, urban, and biomass burning aerosol (Graber and Rudich, 2006). All these water insoluble components might be considered among possible contributors to the observed He4 peak. According to the authors' opinion, it is unlikely that the presence of resilient organics affecting the EC/OC determination is peculiar of the Po valley. More likely, these organics could be found also in other areas impacted by a mixture of sources including biomass burning and/or by poor atmospheric dispersion but further research is needed to clarify this point.

» QUESTION: In addition, a very important question which arises from reading this MS refers to a potential artefact whereby EC is overestimated by low temperature protocols: do the authors believe that EC and OC measured by what they call lower temperature protocols are systematically biased in the EU regions where these protocols are applied (for urban aerosols)? And in rural sites, do the authors believe that the low temperature protocols should be used for the analysis of samples collected at rural sites?

» ANSWER: The interest in testing our methodology on samples collected at an urban site was twofold: - many monitoring campaigns are still performed at urban locations and EC/OC concentrations are often determined by different methods/protocols; - the EUSAAR community already tested high vs. low temperature protocols on a large number of samples collected at many different European background sites as reported in

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Cavalli et al., (2010). The washing procedure performed on our samples evidenced that high T protocols are more suitable for urban samples impacted by a complex mixture of sources. Our opinion is that high T protocols on washed samples should minimise errors in EC determination at urban sites. It would be interesting to extend our procedure also on background/rural samples to verify the effect of water soluble compounds removal on filter differently loaded and/or with a totally different composition. Indeed, in the work by Cavalli et al. (2010) no systematic tests on washed samples were carried out. Therefore, at the moment we have not enough information to decide which protocol (high or low T) would be the most suitable for rural samples as it depends on how much is the refractory organic component in a site. In conclusion, it is likely that low T protocols are the most suitable if the refractory organic carbon in rural samples is low compared to the EC content while high T protocols should be chosen in the opposite case.

» Answers to specific comments

According to the referee's comments we changed the title as follows: "On the effect of water-soluble compounds removal on EC quantification by TOT analysis in urban aerosol samples"

» QUESTION: Pag. 19853, line 7: "a twofold difference", do the authors mean "between protocols"?

» ANSWER: The sentence refers to differences concerning both temperature steps and light corrections for pyrolysis (i.e. optical transmittance or reflectance)

» QUESTION: Pag. 19855, line 21: why did the authors not use the original NIOSH and IMPROVE protocols, and instead use similar ones? What was the purpose of using proxy protocols?

» ANSWER: The original IMPROVE protocol prescribes the use of reflectance to correct pyrolysis effects. We used a TOT instrument; therefore, we applied the same tem-

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perature steps as in IMPROVE_A but the optical correction could not be by reflectance. As for the NIOSH protocol, we preferred to test the QUARTZ.par protocol (here defined NIOSH-like) installed on the SUNSET instrument. Indeed, it is widely used in Europe by many research groups and it has been also recently reported in the CEN/TC 264 “Guide for the measurement of elemental and organic carbon deposited on filters”.

» QUESTION: Pag.19856, line 10: how many replicates were analysed of each type?

» ANSWER: 26 untreated and 26 parallel washed samples were analysed using the three protocols. For each sample, only a 1 cm² punch was analysed for each protocol. This information will be added in the next version of the text.

» QUESTION: Pag 19856, line 21: I assume that the minimum amount of water was used in order to minimise dilution of the WSOC concentration, correct? Please add a sort sentence to clarify this.

» ANSWER: The amount of water used for the filter washing was mainly chosen to “preserve” the sample integrity. In fact, the higher was the quantity used for washing, the more brittle became the filter and more inhomogeneous the sample deposit. Therefore, our goal was to ensure a good WSOC removal without affecting the possibility to carry out reliable TOT analyses. Moreover, the “minimum” water quantity limited the dilution of WSOC, which are highly diluted indeed with the water quantities needed for their complete removal. The word “minimum” has been cancelled in the revised text because it causes confusion.

» QUESTION: Pag. 19858, line 15: "EC>15", this is also a specific characteristic of the EUSAAR protocol, which was designed for regional background aerosols and not for urban ones. How different would the authors expect their results to be if their study had been carried out with rural background aerosols? What would the impact of lower EC loadings be on the washing procedure and on EC and TC determinations? And what about the different types of organics found in regional background aerosols when compared with urban (and heavily polluted) aerosols? It would be interesting for the

authors to include a new paragraph/section on the impact of having selected urban aerosols instead of regional background ones for their study, what differences would be expected?

» ANSWER: As reported in Subramanian et al. (2006), 15 $\mu\text{g}/\text{cm}^2$ as the EC loading on a filter is a limit for assessing a good performance of the TOT instrument. It does not depend on the type of samples (urban or rural), but it is due to the SUNSET instrumentation set-up. Indeed, the laser signal is so low that no signal modulation for higher EC loadings can be detected during the He phase, and no correction for pyrolysis can therefore be performed. However, as rural samples are expected to be generally less loaded than urban ones (for comparable air volume sampled) it is possible that longer samplings can be performed at rural sites than at urban ones without affecting the possibility to perform a reliable EC determination by a TOT measurement. On the contrary, it is possible that the different sample composition affects the thermal behaviour of organics as well as the WSOC content in the sample. Therefore, we think that big differences in samples characteristics (and not in the EC content only) might require the modification of the washing procedure set-up to ensure the complete WSOC removal. As for the site selection, please refer also to the answer reported at the beginning.

» QUESTION: Pag. 19859, line 1: page 19859, line 1: the differences were unfortunately not much lower, $y=1.12x$ to $1.42x$ for washed samples, vs. $y=1.06x$ to $1.59x$ for untreated samples. Please rephrase and possibly discuss further, also on page 19861, lines 20-23.

» ANSWER: There was probably a misunderstanding. Our comment referred mainly to figure 2a and figure 2b, where EUSAAR_2 and He-580 EC results (y-axis) are compared to He-870 (x-axis). According to the referee's suggestion, we decided to rephrase the original sentence: "However, significant differences (slope >1.48) in absolute EC concentrations were detected on untreated filters when comparing the results obtained by the He-870 protocol to those by other protocols (Fig. 2). Differences were lower in the results obtained on water-washed filters" as follows: "It is noteworthy that

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the disagreement between EUSAAR_2 and He-870 reduces from 1.49 to 1.24 (-17%) after filter washing. As for He-580, the reduction is lower (from 1.59 to 1.42, -11%, after filter washing) probably because He-580 protocol allows the complete carbon evolution before changing the temperature, thus reducing pyrolysis even in untreated samples and limiting the advantages of washing the filters". Moreover, figure 2c was removed in the revised paper because it may be confounding. In the text we added the sentence "agreement in EC determination by the low temperature protocols was found (He-580 vs. EUSAAR_2 slope was 1.06 and 1.12 for untreated and washed samples, respectively)".

» QUESTION: page 19861, line 27: all samples were mixed, to obtain 1 single sample? This is what I understand from the text, but cannot be sure. Please clarify.

» ANSWER: The referee is right. The text will be modified to clarify this point.

» QUESTION: Pag. 19862, line 22: once again, the analysis is too interesting to be limited to the Milan aerosols: how would results differ at a rural site, or at an urban area outside the Po valley? How frequent are these weakly light-absorbing and resilient organics in other EU regions? If they possibly derive from biomass burning as stated by the authors, are they specific of this region, or of these pollution levels? Would the authors expect to obtain the same results if their methodology had been applied to samples from Switzerland, or from Spain? In addition, as stated by the authors, the presence of organics in the He870 temperature step has a large influence on OCEC determinations and results in an artefact whereby EC is overestimated (using low temp protocols): it would be useful to know the authors' opinion on the geographical extent of this artefact. Do they think EC is being systematically overestimated in EU, where low temperature protocols are currently being applied?

» ANSWER: Please, refer to the general comments reported at the beginning.

» QUESTION: Pag. 19863, line 12: what is the equivalent of these surface concentrations in microg/m³?

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» ANSWER: The reported concentrations correspond to 0.3-2.3 ug/m³

» QUESTION: Pag. 19864, line 15: what about refractory OC? Can we consider that it is fully independent of the protocol?

» ANSWER: In principle, we can not be completely sure that this fraction is not dependent on the protocol. Indeed, one problem can arise due to the differences among the highest temperature of the He step for the two low temperature protocols and the temperature of the third step of He-870 protocol. However, in the He-870 protocol the third T step is at 615 °C, which is only 35 °C far from the highest temperatures in the He step of both the other two protocols (580°C and 650°C for He-580 and EUSAAR_2, respectively). There is also another possibility for the refractory carbon not to be independent from the protocol: some compounds could undergo to partial pyrolysis at the lowest temperature step in different way depending on heating ramps. Indeed, if the pyrolysis is not complete, they could change into refractory forms of organics but it is very difficult to verify this possibility. However, it was demonstrated in par.3.3 that a good agreement was found in our measurements when the EC measured by the low temperature protocols was compared to EC+C_He4870. Therefore, the refractory carbon fraction (i.e. C_He4870) seems to be not so much influenced by the above mentioned effects, at least in this kind of samples.

» QUESTION: Pag. 19865, line 16: "in untreated samples", please add "in urban samples from the Po valley". Otherwise this statement does not apply to all types of sites (e.g., rural) and it cannot be generalised.

» ANSWER: The referee is right, the sentence will be modified.

» QUESTION: Pag. 19865, line 25: "was ascribed to the carbon fraction" please substitute with "was ascribed to a fraction of the carbon fraction" (not to the entire fraction).

» ANSWER: We referred to the He4 fraction and we think that – in the analysed samples - the whole He4 carbon component is the responsible of the observed effects.

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» QUESTION: Table 1: the authors could add "NIOSH-like" and "IMPROVE-like" as a footnote for columns He870 and He580.

» ANSWER: It will be modified accordingly

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