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Interactive comment on “Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol” by F. Cavalli et al.

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R: This discussion paper is an important work towards a better understanding of the historical EC/OC controversy. Its main benefits are the meticulously systematic optimization of the most critical experimental parameters, and in particular the use of artificial proxy samples to mimic the conditions likely relevant in atmospheric samples.

R: On page 2325 the authors state that they have optimized their protocol to regional background samples: however, this remains an ill-defined category.



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A: According to the European Environment Agency (Larssen et al., 1999), regional background stations are defined as located in rural/agricultural areas, with a distance of 10-50 km from built-up areas and other major pollution sources.

R: It is well-known from recent source apportionment studies that sources of regional aerosols can be very much different in different times of the year: in winter biomass burning is predominant, whereas in summer the photochemical reactions between biogenic VOCs and anthropogenic pollutants can produce large concentrations of SOA which can be further aged in the conditions of photochemical smog. Therefore I miss from the test matrices listed on page 2325 biomass smoke obtained under controlled conditions, both in the flaming and smoldering phases. This would be particularly important since from the surrogate matrices inorganic salts are completely missing in spite of the fact that they had been conclusively proven to introduce substantial biases into thermo-optical EC/OC measurements.

A: The EUSAAR_2 protocol has been developed and validated also with samples collected in winter at Ispra (IT) and Birkenes (NO). Studies using light absorption measurements and macro tracers (i.e. levoglucosan, potassium and C14) performed on one year samples collected in Ispra indicate that in winter more than 80% of the TC is due to biomass burning (two manuscripts are in preparation). In Birkenes, about 40% of the TC is produced by biomass burning in winter. We think it is more important to validate the protocol against wood burning-rich aerosol samples, than against samples collected directly close to sources.

R: Additionally, as WSOC was shown to be mainly responsible for charring, a filter loaded with aqueous extract of ambient aerosol would have been very useful (also containing inorganic species but hopefully no EC).

A: A. Gelencsér suggests that using WSOC-rich and EC-free samples, we could demonstrate that EUSAAR_2 can accurately split PC and EC. Five samples collected in Ispra in different seasons of year 2009 were subjected to water extraction, filtration

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to remove EC residuals, and concentration of the extract to a suitable volume for filter spiking. Punches spiked with the water extracts were then analysed using the EU-SAAR_2 protocol. Results show that the EU-SAAR_2 protocol detect as pure OC the carbon content of samples actually containing only a mixture of WSOC and inorganics and therefore it can properly correct for pyrolytic carbon formation. The carbon range tested is from 1 to 7 $\mu\text{g cm}^{-2}$.

R: I have two additional problems when any standard measurement protocol is declared to be restricted in use: first, this restriction is often overlooked in subsequent applications (see, for example, what happened with Cachier's 1989 paper, their protocol was declared to be valid only for EC/TC ratio of 0.24, but applied widely without care); second, I miss the discussion of limitations of its extension in use (i.e. what happens if the protocol is to be used for kerbside aerosol and/or biomass smoke?). I understand that such a comprehensive approach may be outside the scope of an optimization paper, but certainly further tests should be carried out before the suggested protocol can become a standardized procedure at least in Europe. I also appreciate that a fixed measurement protocol (even with limitations) is much better than having as many protocols as laboratories and therefore a mess of EC data (which are then readily used without any concern for their comparability and origin).

A: As previously mentioned, the protocol has been specifically defined for rural background aerosol in line with the recent EU-directive 2008/50/EC. The use of a thermal-optical protocol "free" of biases would guarantee the determination of comparable OC and EC data from any site. As shown in our paper, biases occur over a range of temperatures depending on sample load and chemical composition. Specifying a single thermal protocol for which all biases would disappear is impossible. Our study indeed demonstrates the need to adopt a compromise that minimizes biases. The thermal protocol EU-SAAR_2 has been developed on the basis of daily samples collected in Ispra (IT) over several years. This site can be impacted by background clean air from the Alps, polluted air from the urban/industrial/farming area of the Po Valley, and inten-

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sive domestic wood burning emissions, according to the season and the meteorological conditions. It was validated against samples collected in Birkenes (NO), K-Puszta (HU), and Montseny (ES), i.e. under different pollution and weather climates. Comparing PC determined from the thermal-optical method, and from the laser transmission variations only, we showed that EUSAAR_2 is robust for TC concentrations lower than $20 \mu\text{g m}^{-2}$. The EUSAAR_2 protocol (together with others) is currently under evaluation by a dedicated working group of the European Standardisation Committee (CEN), which will also strictly define the field of application of the finally selected European standard protocol.

R: On page 2330, the authors state (based on references) that pyrolytic carbon (PC) has much higher sigma than native EC. If so, it would also imply higher degree of graphite like structures, which may also affect its refractory character. To put it differently, is there any guarantee that PC fully evolves before native EC in the thermogram?

A: No, as stated in the manuscript (abstract, line 15; page 2327, line 11-112), PC and EC have been found to co-evolve. We have confirmed by the analysis of paired water-extracted and untreated punches from the same filters that PC and EC co-evolve for the analysed samples: in fact, i) the He/O₂-mode carbon remaining after the water extraction (i.e. EC) evolves not just at the end of the He/O₂-mode but throughout the entire mode and, furthermore, ii) He/O₂-mode carbon removed by water extraction (i.e. PC) does not just evolve at the beginning of the He/O₂-mode but also up to 65% after the split point. For more details please see also answer to the referee #1 comment on lines 131-134. As the second assumption for charring correction (PC formed during the analysis has the same specific attenuation cross section as native EC) does not hold either, charring should be limited as much as possible.

R: The authors have done the experiments and observed significant charring then the evolution of LAC in the high final temperature He experiments (750 and 850 C). Were in these experiments the formation and oxidation rate of LAC comparable (particularly in surrogate samples which did not contain inorganic constituents, therefore premature

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oxidation of EC is not expected)?

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A: A. Gelencsér requires comparing the formation rate of PC with the evolution rate of LAC (ie. PC+EC) to possibly deduce the nature of the LAC species evolving. In the experiments where a LAC-only sample is generated, OC of the ambient aerosol is completely converted into PC. The resulting LAC-only sample is a mixture of PC and EC. This sample is then analysed using a thermal protocol with varying maximum temperature in the He-mode. A fraction of LAC is observed to evolve in the He-mode at temperature $\geq 650^{\circ}\text{C}$. This fraction can be PC or EC or a combination of PC and EC but it is not possible to determine the nature of the species evolving. We believe that this comparison will not help much further. During LAC formation: $dA/dt = \sigma_{\text{PC}} (d\text{CPC}/dt)_{\text{form}}$

where A is the laser attenuation, and σ_{PC} and CPC are the specific attenuation coefficient and the mass per filter area unit of PC, respectively.

During LAC oxidation: $dA/dt = \sigma_{\text{PC}} (d\text{CPC}/dt)_{\text{oxid}} + \sigma_{\text{EC}} d\text{CEC}/dt$

where σ_{EC} and CEC are the specific attenuation coefficient and the mass per filter area unit of EC, respectively.

In case the two rates are comparable (i.e. the variation in the laser attenuation A is the same in absolute value but opposite in sign during the formation and oxidation of LAC):

$$\sigma_{\text{PC}} (d\text{CPC}/dt)_{\text{oxid}} + \sigma_{\text{EC}} d\text{CEC}/dt = - \sigma_{\text{PC}} (d\text{CPC}/dt)_{\text{form}} \quad (\text{Eq.1})$$

To conclude that just PC evolves at this time, we should show that:

$$d\text{CEC}/dt = 0$$

We also know from the variation in the FID signal (dF/dt):

$$d\text{CTC}/dt = dF/dt = (d\text{CPC}/dt)_{\text{oxid}} + d\text{CEC}/dt$$

assuming there's no OC evolving at this time of the analysis.

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Then, as soon as σ PC \approx σ EC, the conditions:

$$(dCPC/dt)_{oxid} = - [\sigma EC \, dF/dt + \sigma PC \, (dCPC/dt)_{form}] / [\sigma PC - \sigma EC]$$

or

$$dCEC/dt = \sigma PC [dF/dt + (dCPC/dt)_{form}] / [\sigma PC - \sigma EC]$$

are sufficient to ensure that Eq. 1 is verified. Therefore, the evolution rate of LAC can equal the formation rate of PC even when EC or PC+EC evolve if one of the two equivalent relationships are verified.

R: The paper has important retrospective implications for the most commonly used EC/OC protocols, implying potentially substantial biases to EC determinations. This should be treated with caution until they are confirmed with analyses of more realistic surrogate samples (i.e. those containing inorganic species).

A: Most of the protocol development and validation work was performed using ambient PM samples collected daily in Ispra (IT) for several years and from 3 other sites across Europe, with quite different chemical compositions. Therefore, our observations are valid for real ambient samples, also containing inorganic species. A systematic comparison between EUSAAR_2 and the other most commonly used OC/EC protocols is envisaged for possibly make use of the OC/EC data obtained in the past, in case EUSAAR_2 is adopted as a reference method in Europe.

Minor comments: R: page 2328: "accordingly" - check grammar

A: The additional step at 200 °C and longer times favour the release of organic carbon prior to the more aggressive heating steps where pyrolysis occurs accordingly to thermograms... In the revised manuscript we have removed the sentence accordingly to thermograms.

R: p. 2332 line 10 "ca. 80 % only" check grammar

A: Conversely, ca. 80% only of the carbon from fulvic acid evolves and/or pyrolyses by

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the end of the 650_C step. In the revised manuscript we have replace the Conversely with On the contrary.

R: Fig 2. no temperature scale, no indications (a: : :d) on thermograms

A: The red line on the thermograms is the temperature profile. Values divided by 100 are reported on the left side y-axis, as indicated in the plot legend. The authors will ask to the Copernicus Production Office to clearly indicate a:b:c:d on the thermograms reported in Figure 2.

References

Larssen, S., Sluyter, R. and Helmis, C. Criteria for EUROAIRNET - The EEA Air Quality Monitoring and Information Network, <http://www.eea.europa.eu/publications/TEC12>

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