

## ***Interactive comment on “On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols” by A. Karanasiou et al.***

### **Anonymous Referee #1**

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#### General Comments:

This manuscript deals with a fairly important topic (the possible interference of carbonate in organic carbon and elemental carbon determination) in view of the new European Directive 2008/50/EC, which states that PM<sub>2.5</sub> chemical speciation should be performed at regional background sites by the EU member states from 2010 onwards. However, it fails in showing how well atmospheric carbonate carbon (CC) can be quantified using different thermal / optical analysis protocols for the following main reasons:

1- The manuscript does not provide the method for determining CC when using the NIOSH-840 protocol. The thermogram obtained with this protocol after sample fumigation indeed suggests that not all C evolving between 120 and 250 s is CC, and no

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clear indication is given on how to distinguish CC from OC on the thermogram of an actual atmospheric sample.

2- The amounts of carbonate used by the authors for testing the various protocols was much too large compared to what can be expected to be found in a vast majority of atmospheric samples (and what was actually measured by the authors). Furthermore, the behaviour of the “chemical” CaCO<sub>3</sub> they used could well be very different from the one of natural calcite, which is expected to account for a large fraction of atmospheric carbonate. The grain size (not specified in the MS) of CaCO<sub>3</sub> purchased as a chemical could as well be much larger than atmospheric particle diameters.

3- The authors did not account for the information regarding the behaviour of carbonate in thermal/optical analyses recently published in AMT by Cavalli et al. (2010), which are not in agreement with some of their conclusions. They are also advised to consider the comments to their MS by Cavalli, and perhaps to merge these results with their own to obtain a more exact, precise, and comprehensive description of the possibility to determine CC using thermal/optical carbon analysers. It is advised to thoroughly improve the MS before considering submitting it again to AMT.

Specific comments:

p. 5377, line 5: “Seinfeld and Pandis, 1998” is not specific enough. Please consider e.g. Putaud et al., 2004, Yttri et al., 2007; Putaud et al., 2010.

p. 5377, line 26: Carbonate carbon and inorganic carbon are not strictly equivalent. E.g. carbides are species contributing to the latter, not to the former.

p. 5378, line 18: was the temperature of 800°C confirmed by experiments for any variety of carbonate ?

p. 5378, line 20: “during thermal-optical analyses of samples from [specify] with the NIOSH protocol”

p. 5378, line 25: spell out BC

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p. 5379, line 2: applied “to”

p. 5379, line 17: please specify grain size

p. 5379, line 19: “differing by its form” is unclear

p. 5380, lines 24-25: first, 0.03-0.25 mg are not concentrations but masses. Second, they correspond to CC surface concentrations (in  $\text{g}/\text{cm}^2$ ) which are > 20 times as large as what would have been obtained from sampling (for 24h with a flow rate of 16.7 l / min) on a 40 mm diam. filter during the experiments described by Silanpää et al., 2005, quoted by the authors to describe the concentrations of CC that can be expected in Europe.

p. 5381, lines 16: as the NIOSH protocol 5040 does not indicate the temperature program, a more correct sentence would be “ A NIOSH protocol (NIOSH, 1999). . . .”

p. 5381, line 27: Is the statement “carbonate to appear as a unique peak in the analysis.” taken from the articles cited earlier?

p. 5382, line 11: “during THE fumigation”

p. 5383, line 1: “close to 1”, rather = 0.99. Furthermore, the lowest mass analysed (about 30  $\mu\text{g}$ ) is still far bigger than the highest amount of CC expected based on Silanpää et al. (2005) data (12  $\mu\text{g}$ ).

p. 5383, line 1: for CC standards, the whole C peak in CC, and there should not be any uncertainty associated with the manual integration. Furthermore, it is very unlikely that manual integration would systematically underestimate CC by 10%.

p. 5383, line 5: the low CC recovery with NIOSH-700 and EUSAAR-2 protocols comes from the consideration by the authors of the C evolved in the He mode only to determine “measured CC”, as can be understood from Fig. 5 and 6. However, Fig. 2 and 3 clearly show that for reasonably low CC amounts (about 30  $\mu\text{g}$ ), CC recovery is close to 100% for both NIOSH-700 and EUSAAR-2 protocols. Let’s keep in mind that collecting 30  $\mu\text{g}$

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CC or more on a filter surface area to be analyzed with a Sunset lab or field instrument is very unlikely.

p. 5383, line 23: “for filter with higher loadings”, that will actually never occur while sampling atmospheric aerosol.

p. 5384, line 24: it is not demonstrated at this point of the MS that “CC can be reliably quantified [ . . . ] and subtracted from OC” in case of an actual ambient sample.

p. 5384, line 5-10: it would be interesting to see if this statements still apply to “reasonable” amounts of CC.

p. 5385, parag. 2: this comparison looks little rigorous. CC was subtracted from OC when detected with the NIOSH-840, but not from the C evolved with EUSAAR-2 (probably because the authors did not know how to do it). However, CC will of course be evolved from the sample analyzed with the EUSAAR-2 protocol. Then, the comparison does not make sense The authors do not show how they cut out the CC contribution from the OC peak in the thermogram of an actual atmospheric sample. It is interesting to note that the highest CC concentration they observed ( $1.3 \mu\text{g}/\text{m}^3$  in Barcelona PM10, see Table 2) correspond to a CC mass of  $20 \mu\text{g}$  on a  $1.5 \text{ cm}^2$  punch (max. size of the punch that can be analyzed in a Sunset Lab instrument), assuming that the High Vol sampler was operated at its maximum flow rate ( $80 \text{ m}^3/\text{hr}$ ) with 15 cm diam. filters (which is not specified). This is well below the smallest CC mass used for validating the NIOSH-840 protocol, as well as for discrediting the NIOSH-700 and EUSAAR-2 protocols.

p. 5386, lines 6-8: again, are the observations based on Fig. 6 applicable to the amount of CC present in actual atmospheric samples ?

p. 5386: Section 3.4 is out of place and should come as a support of Section 3.5 when comparing the results obtained at these 2 sites.

p. 5388, line 5: again, readers would surely appreciate seeing how well the analyst

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can distinguish OC and CC when performing the manual integration.

p. 5388, line 23: Fig. 12 reveals a significant intercept in the regression between Ca and CO<sub>3</sub>, which could for instance be due to the fact that the thermal method systematically overestimates CO<sub>3</sub>, probably because its far from obvious to distinguish between OC and CC on a thermogram.

p. 5389, line 27: this might be a sound estimate for the lower limit of the precision, but the accuracy is probably much worse.

p. 5390: the whole first and fourth paragraphs of the conclusion should be reconsidered in light of the previous comments.

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Interactive comment on Atmos. Meas. Tech. Discuss., 3, 5375, 2010.

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