We would like to thank the reviewer for the helpful and constructive comments. The answers addressing the reviewer's comments are given below (referee comments first, followed by our response in italics).

Anonymous Referee #1
Received and published: 18 January 2011
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 PM2.5 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 clear indication is given on how to distinguish CC from OC on the thermogram of an actual atmospheric sample.

Response:
Indeed there are limitations regarding the quantification of CC. For example, as mentioned in the manuscript, the calculation of CC content is performed manually by the analyst, introducing thus an uncertainty which is difficult to estimate. Nevertheless, for areas where there are frequent events of significant CC concentrations, it is important to be able to estimate CC easily and rapidly. NIOSH-840 protocol offers this possibility, producing accurate results within a level of acceptable uncertainty, compared to the uncertainty of the other two carbon fractions. As stated in the manuscript page 5389, lines 7-15:"the uncertainty of the offline thermal optical transmittance method analyzer is typically in the range of 5–20% depending on carbon concentration, with higher uncertainty at lower concentrations (Peltier et al., 2007)… estimated the overall uncertainty in the semi-continuous Sunset analyzer at ±20%."
In this work results are presented for this uncertainty to lie on average around 15 % or higher of the determined CC concentration. As we demonstrated after the fumigation 90% of the peak attributed to CC disappear and only 10% of the peak area remained. This could be because of a fraction of OC appearing at the same temperature with CC or because the fumigation was not sufficient to remove all CC.

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" CaCO3 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 CaCO3 purchased as a chemical could as well be much larger than atmospheric particle diameters.

Response:

The quantities of CaCO$_3$ added on standard samples (filter punch of Ø16 mm) were in the range 0.24 – 1.84 mg while the concentration of the deposited CC was in the range 15 -110 µg /cm.^{2} The standard of calcium carbonate was weighted using a certified analytical balance (Sartorius) according to EN12341 standard. The precision of the balance is 0.01 mg, which allowed us to weight accurately the selected quantities of CaCO$_3$. As the purpose was to quantify CC by different protocols the deposited mass of CC on the filter punches should be accurate and sufficient so to identify any changes in the thermograms. These concentrations correspond to higher levels than the average concentrations reported for the urban aerosol. However the objective of the paper is to quantify CC in a simple and rapid way during dust events common for Southern Europe and Asia where PM$_{10}$ concentrations exceed the average "normal" values and the contribution of carbonates might be up to 40% (Querol et al., 2009). In the conclusions the recommendation given, clearly refers to dust episodes. For example in Athens during an intense dust event the maximum observed PM10 daily average concentration, as reported by the Greek Ministry of the Environment was 441 µgm^{-3} while the hourly PM$_{10}$ mass concentrations peaked at 2384 µgm^{-3} (Athanassiadou et al., 2006). In Eastern Mediterrenean (Crete Island) several dust events have been reported were the PM$_{10}$ daily (24h average) concentration exceed 200 µg m^{-3} and reached 400 µg m^{-3} (Gerasopoulos et al., 2006). In Eastern Mediterreanean Kocak et al., (2007) measured maximum PM10 concentration equal to 326 µg m^{-3} while for the Mediterranean Tunisian coasts Bouchlaghem et al., (2009) report daily PM$_{10}$ levels up to 700 µg m^{-3}. We should also refer to the intense events during dust storms in Asia. Draxler et al., (2001) report PM$_{10}$ (24h average) values in the range 200-1000 µg m^{-3} during dust events. Xie et al., (2005) and Lee et al., (2006) report average PM$_{10}$ value >300 µg m^{-3} during dust storms, while a 4h PM$_{10}$ concentration reached 1510 µg m^{-3}.

For the quantification of CC we used commercial CaCO$_3$ as in the previous work of Jankowski et al., 2008. We agree with the reviewer that the physico-chemical properties of natural calcite might be different of those of commercial CaCO$_3$ and all together quite different from the form of CaCO$_3$ in aerosol particles. However, as demonstrated by Fabrizia Cavalli in her short comment, the thermal decomposition of both natural calcite and CaCO$_3$ occurred at 650 ^{0}C with EUSAAR-2 protocol. For this reason we believe that the thermal decomposition properties of standard CaCO$_3$ would not be so different of those of CaCO$_3$ present in aerosol particles.

In the manuscript we have included the following text in the "Methodology" section to clarify the procedure of the standards preparation, page 5380, line 16:

"A number of 32 standard samples containing CC were prepared in the laboratory by depositing known amounts of powdered calcium carbonate (Merck, CaCO$_3$) on preweighted filter punches (PALLFLEX, Tissuquartz). Although commercial powdered calcium carbonate may differ from atmospheric carbonate particles this technique was found to be simple and efficient to quantify CaCO$_3$. Previously, Jankowski et al. (2008) used powdered calcium carbonate as a standard for carbonate carbon. The average atmospheric CaCO$_3$ concentrations as reported in Sillanpaa et al. (2005) in the areas of Athens and Barcelona, CaCO$_3$ determined in PM$_{2.5–10}$ ranged from 0.3 to 29 µgm^{-3}. Converting this concentration into mass (for a 24h sampling with a flow rate of 16.7 lmin^{-1}), approximately 0.007–0.7mg of CaCO$_3$ were collected on the filter (Ø47 mm). The quantities of deposited CaCO$_3$ in the prepared filter punches (Ø16 mm) were in the range of 0.24–1.84 mg resulting in CC surface concentration 15-125 µg/cm^2. All weighing was conducted with a Sartorius microbalance after 48 h of equilibration in a room maintained at 20±1 ^{0}C and 50±5% RH (according to EN12341, 1998). These concentrations are higher than the average concentrations reported for the urban aerosol (Sillanpaa et al., 2005).

However, the objective of the paper is to quantify CC during dust events common for some regions (Southern Europe and Asia) where the atmospheric aerosol concentrations are much higher than the average and carbonates constitute a high fraction of the particle mass (up to 40%, Querol et al., 2009). For example in Athens during an intense dust event the maximum observed PM_{10} daily average concentration, as reported by the Greek Ministry of the Environment was 441 $\mu g m^{-3}$ while the hourly PM_{10} mass concentrations peaked at 2384 $\mu g m^{-3}$ (Athanassiadou et al., 2006). In Eastern Mediterranean (Crete Island) several dust events have been reported were the PM_{10} daily (24h average) concentration exceeded 200 $\mu g m^{-3}$ (Gerasopoulos et al., 2006). Again for Eastern Mediterranean Kocak et al., (2007) measured maximum PM_{10} concentration equal to 326 μg m^{-3} while for the Mediterranean Tunisian coasts Bouchlaghem et al., (2009) report daily PM_{10} levels up to 700 μg m^{-3}. Moreover during intense events in Asia Draxler et al., (2001) report PM_{10} (24h average) values in the range 200-1000 μg m^{-3}. Xie et al., (2005) and Lee et al., (2006) report average PM_{10} value >300 μg m^{-3}, while a 4h PM_{10} concentration might reach 1510 μg m^{-3}.

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.

Response:
It is true that when we applied the EUSAAR-2 protocol we obtained different thermograms from that of natural calcite (Cavalli et al. 2010) and to the thermogram of $CaCO_3$ provided by Fabrizia Cavalli in the short comment. The dissimilarity may be associated among others with the mass of natural calcite and chemical $CaCO_3$, deposited on the filter as mentioned by the reviewer in comment #2. We found the contribution of Fabrizia Cavalli valuable as it has urged new experiments to investigate the reason of this discrepancy. We propose to merge her contribution with our results and include Fabrizia Cavalli as co-author to the revised manuscript. The experiments conducted by Fabrizia Cavalli with the lab analyser and our additional experiments with the semi continuous analyzer will form a section in the article where the performance of the thermal protocols will be examined with regards to the levels of carbonate carbon.

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.

Response:
The recommended references have been included in the manuscript.

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.
Response:

We agree with the reviewer, we have deleted the term inorganic carbon from the manuscript.

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

Response:
The temperature of 800 ^{0}C was based on the literature. Chow and Watson (2002) report that calcium carbonate cannot be measured by thermal methods with temperatures <800 °C. In the study of Miyazaki et al., (2007) carbonate carbon when it was present in aerosol samples peaked sharply at 870 ^{0}C in the He mode during thermal/optical analysis. In the study of Birch and Cary (1996) CC peaks at 820 ^{0}C during thermal/optical analysis in the inert mode.

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

Response:
The information has been included, the text has changed to: "Koulouri et al. (2008) found that during thermal/optical analysis of samples of Finokalia monitoring station (Crete, Greece) with the NIOSH protocol a significant part of OC (up to 20%) originates from carbonates, and subsequently particulate organic matter concentrations are overestimated without a subtraction of CC."

p. 5378, line 25: spell out BC p. 5379, line 2: applied "to"
Response:
The changes have been made.

p. 5379, line 17: please specify grain size
Response:
The size fraction of the aerosol samples has been included: "The latter is primarily used for the analysis of PM_{10}, $PM_{2.5}$ and PM_1 samples previously collected at a Barcelona urban site, belonging to the local air quality monitoring network and PM_{10} and $PM_{2.5}$ samples collected at the EUSAAR regional background site, Montseny (MSY,http://www.eusaar.net/files/overview/infrastructures-descript.cfm).

p. 5379, line 19: "differing by its form" is unclear
Response:
The text has changed to: "Although commercial powdered calcium carbonate may differ from atmospheric carbonate particles this technique was found to be simple and efficient to quantify $CaCO_3$."

p. 5380, lines 24-25: first, 0.03-0.25 mg are not concentrations but masses. Second, they correspond to CC surface concentrations (in g/cm2) 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.

Response:
The text in page 5380 has been updated, please see answer 2.

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): : :."

Response:
The comment will be taken into account.

p. 5381, line 27: Is the statement "carbonate to appear as a unique peak in the analysis." taken from the articles cited earlier?
Response:
To support this statement we have been included the following references in page 5381, line 27: Miyazaki et al., 2007; Birch and Cary, 1996. In that studies CC appeared as a sharp peak in the inert mode of the analysis.

p. 5382, line 11: "during THE fumigation"
Response:
The comment will be taken into account.

p. 5383, line 1: "close to 1", rather = 0.99. Furthermore, the lowest mass analysed (about 30 µg) is still far bigger than the highest amount of CC expected based on Silanpää et al. (2005) data (12 µg).
Response:
The omission has been corrected. Please see answer 2.

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%.

Response:
There is always an uncertainty related to manual integration. Nevertheless, we do not claim that the systematic underestimation of CC by 10% is due to manual integration uncertainty. It is a result associated mainly with the analysis method used.

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 µg), CC recovery is close to 100% for both NIOSH-700 and EUSAAR-2 protocols. Let's keep in mind that collecting 30 µg CC or more on a filter surface area to be analyzed with a Sunset lab or field instrument is very unlikely.

Response:
For low concentrations of CC all three thermal protocols gave good recovery but the problem exists in the shape of the thermogram. As we demonstrated in Figure 6 when using the EUSAAR-

2 thermogram we obtained 2 peaks, one in the inert mode and a second one in the He-O$_2$ mode for two different concentrations of CC 30 μg/cm^2 and 75 μg/cm^2. In the case of NIOSH-700 we obtained one peak (in the He mode) for 20 μg/cm^2 of CC and two peaks for high concentration of CC equal to 100 μg /cm^2.

Taking into account the reviewers comment we have changed figures 2 and 3 as we calculated CC recovered concentrations by including the peak appearing in the He mode and also when it was present the second peak in the He-O$_2$ mode. The text in page 5383, lines 5-12 has been replaced by: "The other two thermal protocols also provide high recovery concerning CC but the obtained thermograms had a different pattern."

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

Quoting from text, page 5383, line 23: "Moreover, for filters with high CC loadings, the thermograms presented a very wide peak at around 150–195 s, quantified as CC, and a sharper one at 360–370 s, in the He/O$_2$-mode.." It is true that the higher concentration of CC shown in Figure 5 (100μg/cm^2) is too high compared to the average values of CC in urban aerosol. We agree with the reviewer that these concentrations will probably never occur in regions like Central and Northern Europe. However, since in Southern Europe dust events are quite frequent (Querol et al., 2009; Mitsakou et al., 2008; Meloni et al., 2007) we should not exclude the case of high CC levels. Please see answer in comment 2 where we provide PM$_{10}$ levels during dust events. So it is possible to get a second peak for CC in the He-O$_2$ mode. In the conclusions section we refer only to dust events where the contribution of CC to PM is expected to be high.

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.
Response:
To avoid any confusion we changed this phrase so to point out that we are referring to high amounts of CC e.g: during African dust intrusions. "During dust events that the CC content might exceed its average concentrations it would be interesting to estimate CC easily and rapidly with thermal analysis. Using NIOSH-700 or EUSAAR-2 protocol, a fraction of CC may decompose in the He-O$_2$ mode so a separate analysis would be necessary to quantify 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 μg/m^3 in Barcelona PM10, see Table 2) correspond to a CC mass of 20 μg on a 1.5 cm2 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 m^3/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.

Response:
We agree with the reviewer that the comparison in page 5385 creates confusion to the readers. As the purpose was to identify the differences between these two protocols with regards to the EC and OC content, with the possible occurrence of CC we decided not to exclude the CC content (when detected).
CC concentration was estimated only when a sharp peak was observed around 130-165 s of the analysis. An example of an atmospheric sample analysis is shown in Figure 7, where the presence of CC was verified since after the fumigation 90% of the peak area attributed to CC disappeared.
The smallest amount that we used was 30 μg on a filter punch (2 cm^2, punch of the semi-continuous analyzer) in the same range with the concentration used by Cavalli et al., (2010). However we have conducted new experiments with lower concentrations (please see response to the comment of Fabrizia Cavalli) where we produce similar results with Fabrizia Cavalli and they will be included in the revised manuscript.
The information about PM samples has been included in the manuscript, page 5387, line 23: "Carbonate was determined in PM_{10}, $PM_{2.5}$ and PM_1 24 h filter samples (∅15 cm) collected by high volume samplers (MCV, flow rate: 30 m^3h^{-1}), at the urban monitoring site in Barcelona (IDAEA-CSIC) during February–August 2008. CC was also determined during field measurements during November 2009–February 2010, by the semi-continuous Sunset instrument, in Athens urban background site (GAW-DEM, 2007). Sampling was conducted on a 3-h basis with a flow rate of 8 L min^{-1} using PALLFLEX, Tissuquartz filters (∅ 47mm). A $PM_{2.5}$ cut-off cyclone impactor was employed along with the semi-continuous OCEC analyzer."

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

Response:
As shown in Figure 6 the two peaks were also obtained when 60 μg of CC (30μg/cm^2) were deposited in the filter punch. In our previous answer in comment 2 we report ambient PM_{10} concentrations (during dust events) that could justify these high CC concentrations. We should keep in mind that we are referring to dust events and not to the average atmospheric mass concentrations.

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.

Response:
We agree with the reviewer, Section 3.4 has been combined with section 3.5.

p. 5388, line 5: again, readers would surely appreciate seeing how well the analyst can distinguish OC and CC when performing the manual integration.

Response:

In figure 7 where we provide the analysis of a real sample, the CC peak is shown before and after fumigation so is clearly distinguished from the OC peak. However we can include an example (please see following figure) of how the integration is done in real samples (during dust events) with the calculation program of the Sunset analyzers.
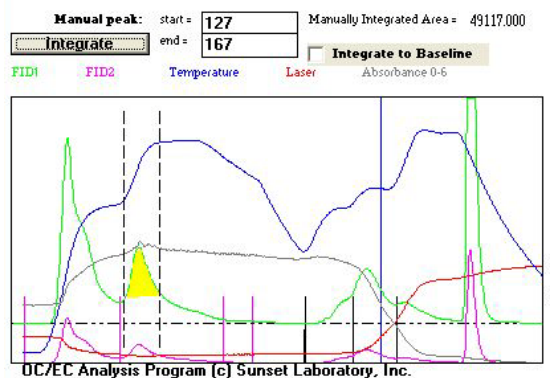

Figure. Thermogram of an atmospheric sample during dust event

p. 5388, line 23: Fig. 12 reveals a significant intercept in the regression between Ca and CO3, which could for instance be due to the fact that the thermal method systematically overestimates CO3, probably because its far from obvious to distinguish between OC and CC on a thermogram.

Response:
In real atmospheric samples we detected CC when the thermogram showed a peak at 130-165 s. Two of these samples (with the highest peak at this point of the thermal analysis) were subjected to fumigation with HCl. The peak initially attributed to CC disappeared and only 10% of the peak area remained. So we believe that we have not overestimated CC. This intercept might also reveal that some carbonate could be associated with other metals e.g: Mg_2CO_3.

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

Response: In this section an attempt was done to determine the overall uncertainty and we state that is probably higher than 15%.

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

Response:
The conclusions will be revised.

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