

**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

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On the quantification of atmospheric carbonate carbon by thermal/optical analysis protocols

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Carbonaceous species, usually classified into two categories, organic carbon (OC) and elemental carbon (EC), constitute an important component of the atmospheric aerosol. Carbonate carbon (CC), or inorganic carbon, another constituent of carbonaceous material, is often not considered in many atmospheric chemistry studies. The reason for this may be its low contribution to fine particle mass in most areas studied, along with the difficulties in its analytical determination in atmospheric aerosols. The objective of this study was the quantification of atmospheric carbonate concentrations using the thermal optical transmittance method (Sunset Laboratory, Inc.). Three different temperature protocols (two modified NIOSH protocols and the EUSAAR-2 protocol) were tested on filter samples containing known amounts of CC. Moreover, the performance of the two most widely used protocols across European countries (NIOSH and EUSAAR-2) was also checked on two different instruments namely the semi-continuous OCEC analyzer and the laboratory OCEC analyzer. NIOSH-840 thermal protocol (NIOSH protocol with a maximum temperature of 840 °C in the He-mode) can be used for the detection and quantification of atmospheric carbonate concentrations. CC was determined in ambient PM₁₀ and PM_{2.5} samples From Athens and Barcelona by using the NIOSH-840 thermal protocol. The results confirm that in South European countries CC may constitute a significant fraction of carbonaceous aerosols (~15%), thus it should not be neglected. However, the NIOSH-840 protocol seems to overestimate the OC concentrations when compared to the EUSAAR-2 protocol. The results suggest that during dust episodes, common for the Southern Europe, the analytical laboratories could use the NIOSH-840 protocol as a suitable method for the carbonate determination and manually integrate the sharp peak that appears in the maximum temperature step in the inert mode. Afterwards, carbonate should be evaporated by a fumigation method and one could then apply the EUSAAR-2 protocol for the precise determination of OC and EC fractions.

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

Carbonaceous species, usually classified into two categories, organic carbon (OC) and elemental carbon (EC), constitute an important component of the atmospheric aerosol (Pio et al., 2001). They form typically 10 to 50% of the total PM₁₀ mass (Jimenez et al., 2009; Seinfeld and Pandis, 1998). OC can be of both primary and secondary origin, associated to particulate organic compounds emitted directly into the atmosphere or formed by the condensation of compounds produced by the atmospheric photo-oxidation of volatile organic species (Fuzzi et al., 2006). In contrast, EC is exclusively of primary origin.

Thermal-optical analysis has been widely used for the determination of EC and OC (Phuah et al., 2009). According to this method, the carbonaceous material of aerosol particles is thermally desorbed first in an inert atmosphere (He) and then in an oxidizing atmosphere (He/O₂). OC desorbs in the pure He atmosphere while EC combusts in the oxidizing atmosphere at high temperature. Some OC is pyrolytically converted to EC (char) when heated in inert atmosphere, and darkens the filter. For charring correction, the transmittance (or reflectance) of the filter is continuously monitored (Bae et al., 2004; Birch and Cary, 1996). The most commonly employed methods for the analysis of EC and OC are the IMPROVE and the NIOSH 5040 protocols (Park et al., 2006; Bae et al., 2004; Currie et al., 2002; Birch and Cary, 1996; Eller and Cassinelli, 1996; Chow et al., 1993). Although these two protocols show good agreement for total carbon (TC) they yield different split points between OC and EC (Chow et al., 2001; Schmid et al., 2001). Recently, Cavalli et al. (2010) identified and minimised the major positive and negative artifacts of EC and OC determination and developed a new protocol, EUSAAR-2 optimised for analysing carbonaceous aerosols at European regional background sites.

Carbonate carbon (CC), or inorganic carbon, another constituent of carbonaceous material, is often not considered in many atmospheric chemistry studies. The reason for this may be its low contribution to fine particle mass in most areas studied (Sillanpää

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



et al., 2005), along with the difficulties in its analytical determination in atmospheric aerosols (Jankowski et al., 2008). Nevertheless, CC can affect atmospheric chemical processes and aerosol characteristics given that the acid neutralizing capacity of these species facilitates the heterogeneous conversion of sulfur and nitrogen oxides to particulate sulfate and nitrate (Dentener et al., 1996).

Depending on the area of study or the meteorological conditions (e.g. type of soil, African dust events) CC concentrations may be significant. Recently, Querol et al. (2009) reported that across the Mediterranean basin and during the intrusion of air masses from North Africa, carbonates may form up to 40% of the PM₁₀ particle mass. Sillanpää et al. (2005), measured carbonaceous aerosol in six European cities (Duisburg, Prague, Amsterdam, Helsinki, Barcelona and Athens), and detected CC in the coarse particles of Athens and Barcelona but not elsewhere. In that study CC was mainly present as CaCO₃ and accounted for 55% and 11% of the PM_{2.5-10} in Athens and Barcelona, respectively.

Moreover, the interference of CC with the signal of EC or OC may lead to overestimations of either of these two carbon fractions during thermal-optical analysis (Sillanpää et al., 2005; Schmid et al., 2001). Carbonate decomposes at a relatively high temperature of about 800 °C, so its occurrence in particulate samples would lead to an overestimation of the OC or EC concentrations depending on the thermal protocol used. Koulouri et al. (2008) found that during thermal-optical analysis 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. Other studies reporting weak Saharan dust intrusion in the Mediterranean marine environment (Eleftheriadis et al., 2006) did not report on this effect although the comparison of BC data from filter based techniques and EC from EC/OC thermo-optical analysis revealed deviation due to light absorption from desert dust (hematite).

The objective of this study was the detection and quantification of atmospheric carbonate concentrations using the thermal optical transmittance method (Sunset Laboratory, Inc.). Three different temperature protocols (two modified NIOSH protocols and

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the EUSAAR-2 protocol) were tested on filter samples containing known amounts of CC. The method that yielded the best results was applied on ambient samples from areas with frequent African dust intrusions like Athens (Greece) and Barcelona, (Spain). Moreover, the performance of the two most widely used protocols across European countries (NIOSH and EUSAAR-2) was also checked on two different instruments namely, the semi-continuous OCEC analyzer and the laboratory OCEC analyzer both provided by Sunset Laboratory Inc.

2 Methodology

2.1 Instrumentation

In this study two OCEC Sunset analyzers were used, the semi-continuous OCEC field instrument installed at the N.C.S.R. “Demokritos” Athens urban background site (GAW-DEM, <http://gaw.empa.ch/gawsis/reports.asp?StationID=2076202728>) and the laboratory OCEC analyzer installed at Barcelona (IDAEA, <http://www.idaea.csic.es/>). The latter is primarily used for analysis of samples previously collected at a Barcelona urban site, belonging to the local air quality monitoring network and samples collected at the EUSAAR regional background site, Montseny (MSY, <http://www.eusaar.net/files/overview/infrastructures-descript.cfm>). For the determination of OC and EC on a routine basis the EUSAAR-2 thermal protocol is used.

The semi-continuous instrument is equipped with an inline parallel carbon denuder, so that the sample is denuded of volatile gases during sampling. Aerosol particles are collected at a sampling flow rate of 8 L/min in two round 16-mm quartz filters, which are mounted inside the instrument. After collection, the oven of the instrument is purged with helium and the temperature is increased in multiple programmed steps based on the selected thermal protocol. The evolved organic carbon flows through a manganese dioxide (MnO₂) oxidizing oven and all carbon is transformed into carbon dioxide (CO₂). The CO₂ is then quantified by a non-dispersive infrared (NDIR) detector. The oven is

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



cooled prior to the second part of the analysis, where the oven is purged with a mixture of 2% oxygen in helium and the sample is again heated in steps. During this stage, all remaining carbon on the filter, including elemental carbon, is oxidized, the oxidation products are carried through the MnO₂ oven, and carbon is detected by the NDIR detector as CO₂. For charring correction a He-Ne laser beam monitors the sample transmittance throughout the heating process. The time when the laser signal returns to its initial value (before heating) is called the split point of OC and EC, and char is considered to split from native EC in the sample at this critical point (Birch and Cary, 1996).

The laboratory OCEC analyzer is designed to analyse quartz filters samples previously collected in the field. The principle of its operation is similar to the semi-continuous analyzer with the difference that during the detection of carbon the produced CO₂ is previously converted to methane CH₄ and a Flame Ionization Detector (FID) is used for the quantification of CH₄.

2.2 Standard samples and thermal protocols

A number of 32 standard samples containing CC were prepared in the laboratory by depositing known amounts of powdered calcium carbonate (Merck, CaCO₃) on pre-weighted filter punches (PALLFLEX, Tissuquartz). Although powdered calcium carbonate may be differing by its form in atmospheric particles this technique was found to be simple and efficient to quantify CaCO₃. Previously, Jankowski et al. (2008) used powdered calcium carbonate as a standard for carbonate carbon. The concentrations of CaCO₃ were selected to be in the range of the average atmospheric CaCO₃ concentrations. As reported in Sillanpää et al. (2005) in the areas of Athens and Barcelona, CaCO₃ determined in PM_{2.5-10} ranged from 0.3 to 29 µg m⁻³. Converting this concentration into mass (for a 24h sampling with a flow rate of 16.7 l min⁻¹), approximately 0.007–0.7 mg of CaCO₃ were collected on the filter (Ø4 cm). For this reason the concentration of CC in the prepared filter punches (Ø1.5 cm) was in the range of 0.03–0.25 mg. All weighing was conducted with a Sartorius microbalance after 48 h of

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



equilibration in a room maintained at 20 ± 1 °C and $50 \pm 5\%$ RH (according to EN12341, 1998). After CaCO_3 was deposited on the filter punch, a second blank filter punch was placed above it to avoid any losses of the powder (in the semi-continuous instrument two filter punches are used during the analysis). The samples were subsequently analyzed using the semi-continuous OCEC field instrument (Sunset Laboratory Inc.). It should be noted that CC is not automatically determined by either of the OCEC analyzers but during the processing, the analyst may calculate carbonate (if evolved as a single peak) by using the manual integration feature available in the calculation program. The fact that this calculation is manual and analyst-dependent includes an uncertainty in the quantification of CC, which is difficult to estimate.

In the framework of thermal/optical analysis, three different thermal protocols were examined: (1) NIOSH-840, a NIOSH protocol with a maximum temperature of 840 °C in the He-mode, (2) NIOSH-700, a modified NIOSH protocol with a maximum temperature of 700 °C in the He-mode and (3) EUSAAR-2 protocol with a maximum temperature of 650 °C in the He-mode. A detailed description of each protocol is given in Table 1.

NIOSH protocol (NIOSH, 1999), with a maximum temperature in the He-mode around 840 °C, has been extensively used for urban aerosol samples. When applying this protocol, Subramanian et al. (2006) have observed loss of light-absorbing carbon in the He-mode. They suggested keeping the temperature at 700 °C, in order to avoid premature evolution of EC. Chow et al. (2001) also support that the fraction of carbon evolving at around 850 °C in inert-mode may be elemental carbon, which is oxidized by oxygen supplied by mineral oxides in the particle mixture on the filter. Nevertheless, the observed increase in light transmittance and reflectance at 850 °C in the He stage may be also attributed to the evolution of the light-absorbing intermediate OC products instead of the oxidation of EC (Yu et al., 2002). In these NIOSH protocols (NIOSH-840, NIOSH-700) the temperature steps during the first phase of the analysis allow inorganic carbonate to appear as a unique peak in the analysis. In the present work, both proposed maximum temperatures were examined, since CC was expected to volatilize at the maximum temperature step of the He-mode.

Regarding EUSAAR-2, it has been recently developed for regional background sites in order to improve the accuracy of the discrimination between OC and EC. The use of longer residence times at each temperature step aims at the reduction of pyrolysis and incomplete evolution of OC (by favouring its volatilization), while early evolution of light absorbing carbon species is prevented due to the lower temperatures in the He-mode (Cavalli et al., 2010).

2.3 Fumigation with HCl

In order to further examine the effectiveness of the NIOSH protocol in the quantification of carbonate carbon, two high-loaded urban aerosol samples from Barcelona, as well as a standard carbonate sample, were fumigated with HCl prior to thermal-optical analysis, for the removal of their CC content (Cachier et al., 1989). During fumigation procedure, the filter punches were placed on a perforated tray and set above a glass beaker containing concentrated hydrochloric acid (Merck, 37%). They were exposed to the acid vapors for about one hour and then were placed in a clean hood for one hour again, in order to allow the residual acid to volatilize. It must be noted however that this procedure has been known to cause damage in the combustion oven of the OCEC analyzer due to the possible incomplete volatilization of the residual acid (JRC Report, 2009).

3 Results

3.1 Quantification of carbonate

Standard samples of known CC-content were analyzed by the use of the three thermal protocols. According to the analysis results, the NIOSH-840 thermal protocol provided an accurate estimate of the CC content. The regression line between the measured CC and the CC quantities initially added on the filter blanks presented an R^2 value

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



close to and a negligible intercept (Fig. 1). The slope of the regression was 0.90, revealing an underestimation of CC concentrations of 10%. However, as mentioned before the calculation of CC is manual and analyst-dependent, so the uncertainty in its determination could not be easily calculated.

5 The two other thermal protocols underestimated the CC content significantly. The respective regression analysis results are presented in Figs. 2 and 3. Both protocols yielded low intercept values but the corresponding slope values were much lower than 1.00, (0.43 and 0.25 for NIOSH-700 and EUSAAR-2 protocol respectively), resulting in a significant underestimation of CC content, especially in the case of high loadings (above 0.10 mg). However, both these methods were relatively precise given that high R^2 values were obtained, 0.93 and 0.88 for NIOSH-700 and EUSAAR-2 protocol, respectively.

In order to better understand the influence of each temperature protocol on the measured CC content, the generated thermograms were studied. The thermograms of two standard CC samples, analyzed by NIOSH-840 protocol, are depicted in Fig. 4. The thermogram obtained by the analysis of a blank filter is also included for comparison. Similar thermograms were produced for all ambient samples analyzed with NIOSH-840. The CC peak was always very sharp and clear and corresponded to the maximum temperature step of the He-mode (at 155–160 s).

20 The NIOSH-700 thermograms presented a quite different pattern (Fig. 5). Again there was a clear peak corresponding to the CC content at the maximum temperature step of the He-mode (at 150–195 s). Nevertheless, the peak was not as sharp as in the case of the NIOSH-840 protocol. 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/O₂-mode, quantified as EC. The same pattern was observed when the EUSAAR-2 protocol was applied, even for low-loading filters (Fig. 6). It should be noted that the EUSAAR-2 protocol is not designed to quantify carbonate carbon concentrations neither for urban sites (Cavalli et al., 2010).

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The results validate once again that the NIOSH-840 protocol with a maximum temperature of 840 °C in the He-mode is suitable for the CC determination, as carbonate decomposes at a relatively high temperature of about 800 °C. Thus, CC can be reliably quantified from the thermal optical analysis thermograms and subtracted from the OC fraction with the help of the manual integration. Conversely, the thermograms produced by using NIOSH-700 and EUSAAR-2 are not sufficiently clear with regards to the CC peaks. Thus, they result in too high uncertainties for CC determination. In an analysis of a real ambient sample containing OC and EC it would be unclear using NIOSH-700 or EUSAAR-2 protocol, to determine which peak to subtract from OC or EC to interpret as CC.

3.2 Fumigation with HCl

The quantification of CC by the NIOSH-840 protocol was further tested through the use of the HCl fumigation procedure for the removal of CC (NIOSH, 1999). This procedure was not tested with NIOSH-700 and EUSAAR-2 protocols due to the negative results described in the previous sections. One standard CC filter sample, as well as punches from two urban aerosol filters collected in Barcelona site (with high CC content), were fumigated with HCl, prior to being analyzed by the NIOSH-840 protocol. The results show that fumigation led to a large decrease of the CC content (by approximately 86%, in both of the ambient filter samples). It is also interesting to note that the peak absent after fumigation corresponded indeed to the one quantified as carbonate carbon. However, the small wide peak (about 14% of the CC peak area) that remains after the treatment with HCl indicates the presence of other compounds quantified as CC. The thermograms obtained from one of the urban aerosol samples, with and without HCl fumigation, are presented in Fig. 7.

However, the fumigation procedure did not affect only CC but the other two carbonaceous constituents as well, by decreasing the OC and increasing the EC content. The examination of the thermograms revealed that, in reality, the fumigated samples presented both EC and OC peaks with larger areas in relation to the untreated samples.

In addition, fumigation shifted the split point towards earlier steps in the He/O₂-mode, thus attributing to EC part of the peaks corresponding to OC in the untreated samples.

Regarding the standard CC sample, fumigation treatment clearly removed CC (by approximately 99% according to the initial quantity added). The results of this short experiment confirm the observations of previous research works: Acid fumigation procedure seems effective in relation to CC removal but may lead to a significant over-estimation of EC and under- or over-estimation of OC (Jankowski et al., 2008; Chow et al., 1993). Furthermore, it might cause damage to the combustion oven of the OCEC analyzer (JRC Report, 2009).

3.3 Comparison of the two protocols: NIOSH-840 and EUSAAR-2

The NIOSH-840 protocol that yielded the best results concerning the CC determination and the EUSAAR-2 protocol recently developed for the European regional background sites, were used to analyse 25 ambient PM high volume samples (with a sampling duration of 24 h) collected in the Barcelona urban site. The purpose of this comparison was to quantify the differences between these two protocols with regards to the EC and OC content, when they are implemented on the same instrument and with the possible occurrence of CC.

The comparison between EC and OC determined by the NIOSH-840 and EUSAAR-2 thermal protocols using the laboratory Sunset analyzer is shown in Fig. 8. It should be noted that for the NIOSH-840 protocol the CC concentration (if CC appeared as a single peak) was calculated and consequently subtracted from the OC content. The CC peak was always very sharp and clear and corresponded to the maximum temperature step of the He-mode. CC was detected in 19 samples in a total of 25. A rather good correlation with R^2 of 0.81 was obtained for OC determined by the two protocols, Fig. 8a. However, NIOSH-840 protocol overestimated (average of 25%) OC concentrations with respect to EUSAAR-2 in 10 aerosol samples. With reference to EC concentrations calculated by the EUSAAR-2 protocol they were consistently higher (average of 11%) in all samples compared to the NIOSH-840 protocol. Similar trends

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



were observed when the semi-continuous Sunset analyzer was used, (Fig. 9), with an average OC overestimation of 13% by NIOSH-840 and an average EC overestimation of 18% by EUSAAR-2.

These differences concerning the EC concentrations could be explained by the fact that when using EUSAAR-2 protocol the CC content cannot be detected. As it was shown in Fig. 6 when CaCO_3 was present in the filter the thermogram of EUSAAR-2 protocol presented a very wide peak in the He mode, and also a sharper one in the He/ O_2 -mode, quantified as EC.

An explanation about the higher values of OC calculated by the NIOSH-840 protocol could be found in the observation that the split point between OCEC depends strongly upon the temperature program used, especially during the He mode. It has been reported that the chemical nature of carbon evolving in the He mode at temperature around 850°C is actually EC. Chow et al. (2001) suggested that EC is partly oxidised from the oxygen provided by the mineral oxides present in the sample. Their supporting evidence is that during this temperature step in the He mode the reflectance/transmittance increases. Cavalli et al. (2010) also report that using high temperatures during the He mode ($>750^\circ\text{C}$) might lead to a premature evolution of light absorbing carbon (LAC) possibly containing EC. In that study, more than 20% of LAC prematurely evolved when the maximum He-mode temperature is 850°C as in a NIOSH-type protocol. For these reasons in the EUSAAR-2 protocol the maximum temperature in the He mode is set at 650°C , to prevent LAC pre-combustion and to accurately determine carbon sub-fractions.

3.4 Comparison of the two OCEC analyzers

As mentioned before 25 ambient PM high volume samples collected in the Barcelona urban site were analysed using the two protocols, NIOSH-840 and EUSAAR-2 by means of the laboratory and the semi-continuous OCEC analyzers. Consequently, the next step of this study was to compare the two OCEC analyzers: the semi-continuous analyzer and the laboratory instrument. Concerning the EC content calculated by the

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**A. Karanasiou et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

EUSAAR-2 protocol employed in the two different instruments a very good agreement was achieved. Although the regression line between the EC measured by the semi-continuous and laboratory analyzer deviated from unity (1.1), the correlation coefficient was high $R^2 = 0.94$ and a low intercept was calculated (Fig. 10a). Given that, for the EUSAAR-2 protocol the calculated uncertainty in EC determination is in the range 2–7% (Cavalli et al., 2010) and the results obtained by the two instruments varied on average by less than 15%, the two analyzers appear to be quite comparable. Similar results were obtained also when the NIOSH-840 was employed in the two analysers (Fig. 10b) and the EC concentration was compared.

However, the OC determined by the semi-continuous Sunset analyzer was higher compared to that obtained by the laboratory analyzer. In particular, when NIOSH-840 thermal protocol was used the difference was about 30%, (Fig. 11a and b). Furthermore, a poor correlation was calculated ($R^2 = 0.66$, and $R^2 = 0.63$).

The reason for this discrepancy could be the different technical characteristics of the two analyzers. In Sunset analyzers, the relationship between the filter temperature and the oven temperature measured by the oven temperature sensor varies between different instruments (Phuah et al., 2009). Furthermore, Bauer et al. (2009) report that excessive noise from the nondispersive infrared (NDIR) laser in the semi-continuous Sunset OCEC analyzer could result in a worsened determination of OC and EC.

3.5 Urban aerosol measurements

Finally, CC was determined in two sets of ambient samples representative of Mediterranean urban aerosols, collected in Barcelona and Athens during different periods. Carbonate was determined in PM_{10} , $PM_{2.5}$ and PM_1 24 h samples collected using MCV high volume samplers, at the urban monitoring site in Barcelona (IDAEA-CSIC) during February–August 2008. CC was also determined during field measurements, by the semi-continuous Sunset instrument, in Athens urban background site (GAW-DEM, 2007). Sampling was conducted on a 3-h basis, during

November 2009–February 2010. A $PM_{2.5}$ cut-off cyclone impactor was employed along with the semi-continuous OCEC analyzer.

OC, EC and CC concentrations recorded during the semi-continuous $PM_{2.5}$ measurements at Athens and 24 h PM_{10} , $PM_{2.5}$ and PM_1 at Barcelona site are presented in Table 2. Carbonate could be quantified accurately at both sites by the manual integration using the NIOSH-840 protocol, in the 24 h PM_{10} and $PM_{2.5}$ samples and also during the semi-continuous $PM_{2.5}$ measurements. However, CC could not be accurately determined in the finest PM_1 fraction due to the very low concentrations detected. As it was expected, CC in PM_{10} and $PM_{2.5}$ was generally low in relation to OC, but the range of its maximum values reached half of the EC ambient concentration values. For instance in PM_{10} fraction at Barcelona site the mean concentration of CC was $0.59 \mu\text{g m}^{-3}$ about 10% of the average concentration of carbonaceous aerosol, while the maximum concentration measured $1.3 \mu\text{g m}^{-3}$ was almost half of the maximum EC content. This result evidences that in South European countries CC may constitute a significant fraction of carbonaceous aerosols (~15%), thus it should not be neglected.

For the 24 h samples collected at the Barcelona urban site a complete chemical characterisation was available. Subsequently, when the CO_3^{2-} content (calculated by the CC concentrations determined with NIOSH-840 protocol) was plotted against the Ca^{2+} equivalent concentrations (calculated by calcium concentrations determined by Inductively coupled plasma atomic emission spectroscopy, ICP-AES) a high correlation was established $R^2 = 0.93$ and $R^2 = 0.97$ for PM_{10} and $PM_{2.5}$ fraction, respectively (Fig. 12). The average ratio of $\text{Ca}^{2+}/\text{CO}_3^{2-}$ is equal to 0.90 revealing that most of the calcium determined in PM_{10} fraction is being present as CaCO_3 . Calcium carbonate probably represents the main form of CC in aerosol particles. For the maximum measured values of CC both at Athens and Barcelona sites back-trajectories analysis (Draxler and Rolph, 2010) revealed African dust intrusions. For Athens site these events were detected at 18–19 November 2009 and 18–20 February 2010 while for Barcelona during 25–26 August 2008, Fig. 13.

**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The results of these measurements have demonstrated that CC concentration may be significant, and comparable to EC levels, especially under certain meteorological conditions. In these cases, it is essential that CC is quantified along with the other carbonaceous constituents since, if not considered, it may interfere with the EC or OC signal, leading to positive artefacts in their estimation.

3.6 Estimation of carbonate carbon uncertainty

As it has been previously reported in the literature 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). Huebert et al. (2004) estimated combined uncertainty (due to flow rates, sample handling, analyzer) at 26%. For the semi-continuous Sunset analyzer Bauer et al. (2009) have calculated a relative standard deviation of 5% and 24% for thermal OC and EC, respectively. The high relative standard deviation of thermal EC was attributed to its low values at the sampling site. Peltier et al. (2007) estimated the overall uncertainty in the semi-continuous Sunset analyzer at $\pm 20\%$.

In the case of CC the main sources of uncertainty are the analyst (as the integration of the CC peak is done manually), the sampling uncertainty (flow rate, filter handling), the repeatability and the reproducibility of the measurement and the recovery of the CC present on the filter. Then the combined uncertainty can be calculated by the quadratic sum of the different uncertainty components. However, some of these uncertainties cannot be easily quantify. In this work we estimated the standard uncertainty of CC based on replicate measurements of the real ambient samples. This was in the range of 5–15% with the higher uncertainty at lower concentrations. The recovery of the CaCO_3 added on filter blanks was about 90% (Fig. 1). However, the fumigation with HCl of real atmospheric samples has shown that probably a small percentage of the peak area identified as CC might include other organic compounds. As a result an estimation of the CC uncertainty would be $\sim 15\%$ or even higher.

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Conclusions

The objective of this study was the identification and quantification of atmospheric carbonate concentrations using the thermal optical transmittance method (Sunset Laboratory, Inc.). Three different temperature protocols, two modified NIOSH protocols and the EUSAAR-2 protocol were tested on filter samples containing known amounts of CC. NIOSH-840 thermal protocol was proved to accurately quantify atmospheric carbonate concentrations while the other two thermal protocols (NIOSH-700 and EUSAAR-2) underestimated the CC content significantly. The NIOSH-840 and the EUSAAR-2 protocols were tested in two Sunset OCEC analyzers, the semi-continuous and the laboratory analyzer. The NIOSH-840 protocol seems to substantially overestimate the organic carbon concentrations when compared to the EUSAAR-2 protocol, while a rather good agreement was established for the elemental carbon content. The two analyzers agreed well in the determination of the EC content but the estimation of OC was higher with the semi-continuous analyzer.

CC was determined in ambient PM₁₀ and PM_{2.5} samples from Athens and Barcelona by using the NIOSH-840 thermal protocol. Its concentrations were in the range of 0.07–1.3 µg m⁻³ while the maximum values observed reached half of the maximum EC levels. These results confirm that in South European countries CC may constitute a significant fraction of carbonaceous aerosols (~15%), thus it should not be neglected.

However, the fumigation with HCl of real atmospheric samples has shown that probably a small percentage of the peak area identified as CC might also include other organic compounds. This fact increases the uncertainty involved in the CC determination.

This study provides useful insight into the performance of the most widely used thermal protocols concerning the carbonate determination. The results suggest that during dust episodes, common for the Southern Europe, the analytical laboratories could use the NIOSH-840 protocol as a suitable method for the carbonate determination and manually integrate the sharp peak that appears in the maximum temperature step in

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



the inert mode. Afterwards, carbonate should be evaporated by a fumigation method in order to eliminate any interference and one could then apply the EUSAAR-2 protocol for the precise determination of OC and EC fractions.

Acknowledgements. This work was partly carried out in the framework of the EUSAAR project, www.eusaar.net. The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (<http://www.arl.noaa.gov/ready.php>) used in this publication. The authors also thank the Spanish Ministry of Science and Innovation (Ramón y Cajal Programme).

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On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

Table 1. Thermal protocols used: Temperature (°C), Duration (s).

	NIOSH-840	NIOSH-700	EUSAAR-2
Step	Temperature, Duration	Temperature, Duration	Temperature, Duration
He 1	600, 95	600, 95	200, 120
He 2	840, 90	700, 90	300, 150
He 3	0, 33	0, 33	450, 180
He 4	550, 2	550, 2	650, 180
He 5			0, 33
He/O ₂ 1	550, 30	550, 30	500, 120
He/O ₂ 2	550, 25	550, 25	550, 120
He/O ₂ 3	650, 45	650, 45	700, 70
He/O ₂ 4	870, 80	870, 80	850, 80

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



AMTD

3, 5375–5409, 2010

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

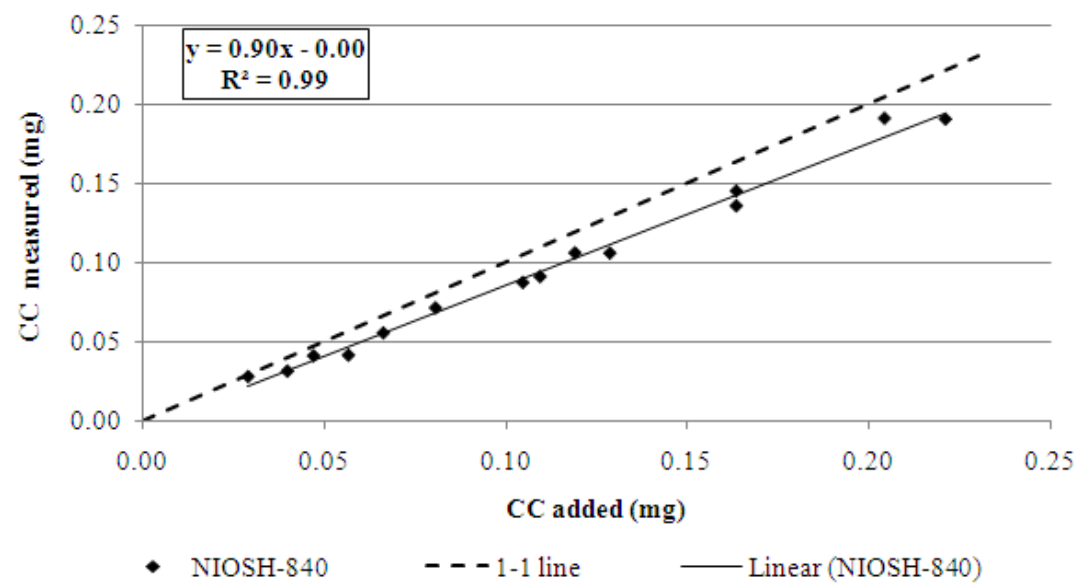


Fig. 1. Regression between CC quantities measured by the use of the NIOSH-840 thermal protocol and CC quantities initially added on filter blanks.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



AMTD

3, 5375–5409, 2010

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

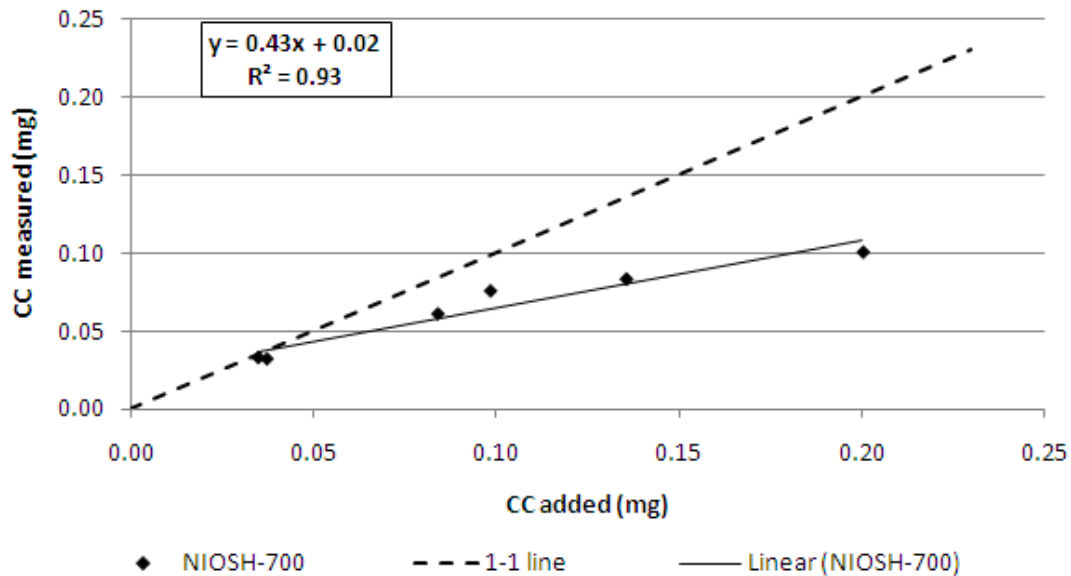


Fig. 2. Regression between CC quantities measured by the use of the NIOSH-700 thermal protocol and CC quantities initially added on filter blanks.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

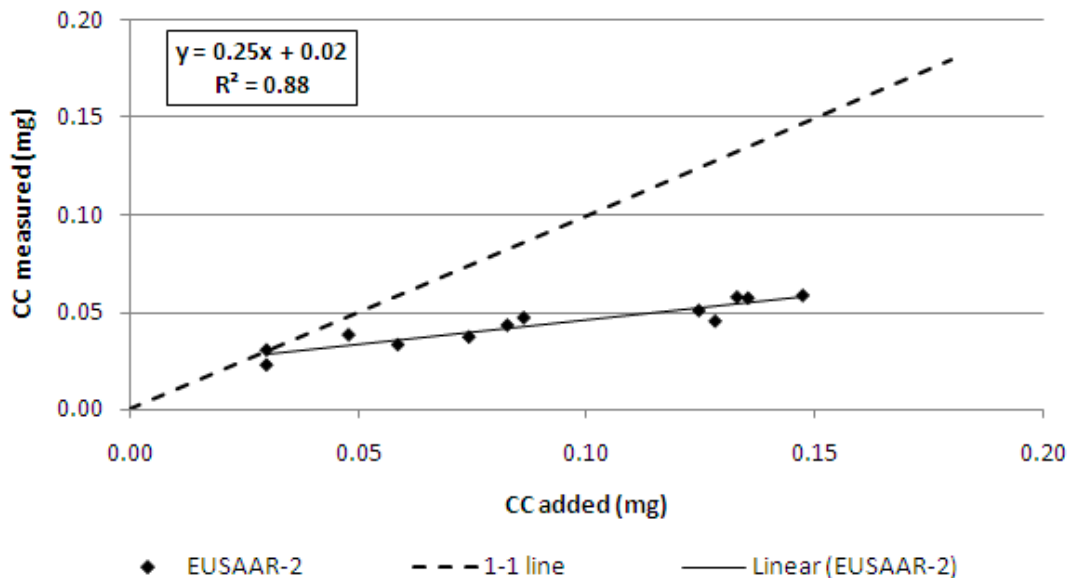


Fig. 3. Regression between CC quantities measured by the use of the EUSAAR-2 thermal protocol and CC quantities initially added on filter blanks.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

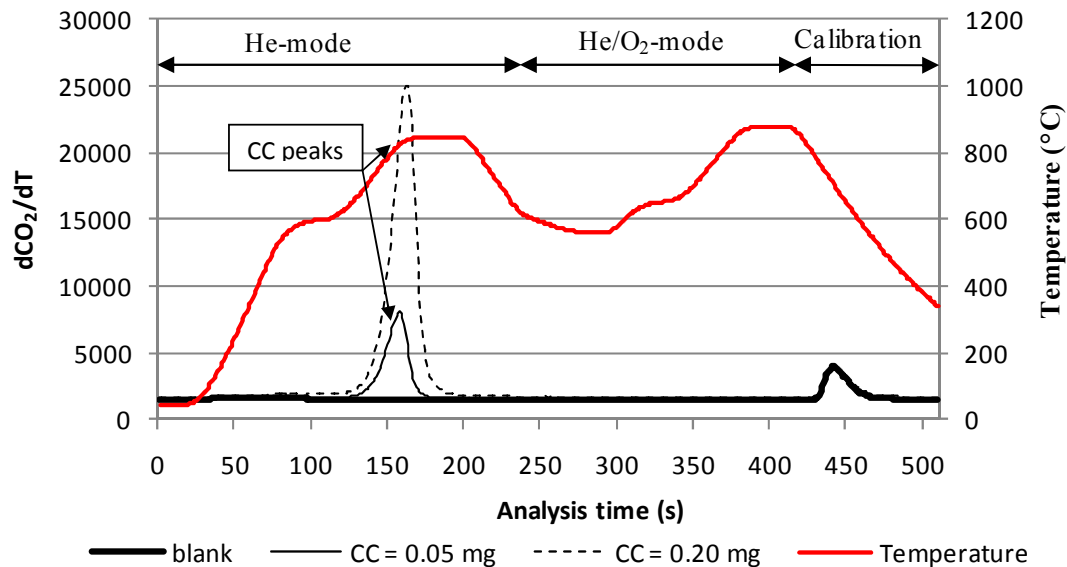


Fig. 4. NIOSH-840 thermogram for a blank and two CC-loaded filters (He-mode: 1–230 s, He/O₂-mode: 231–410 s and Calibration-mode: 410–510 s).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

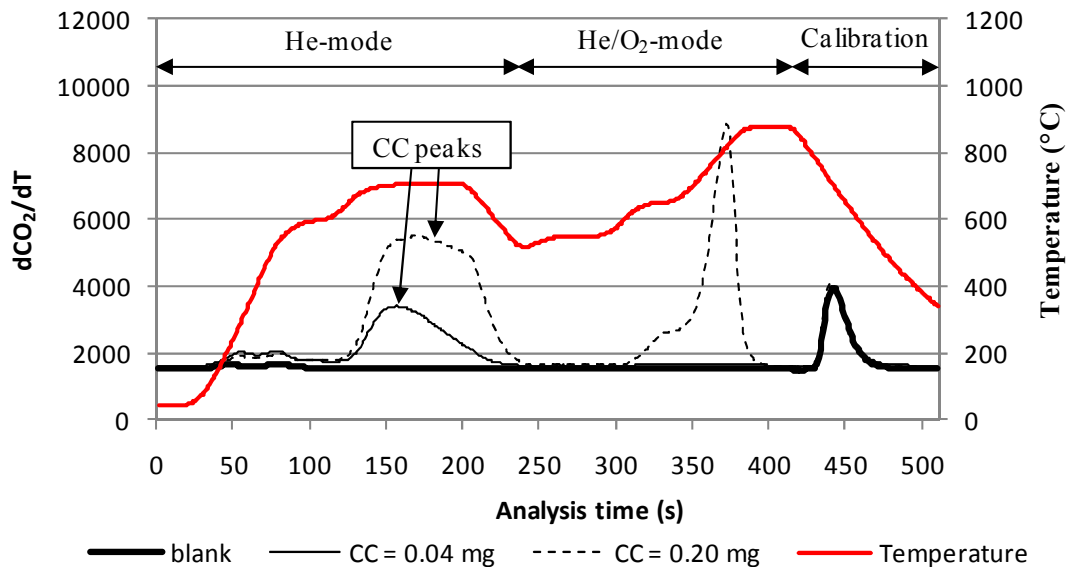


Fig. 5. NIOSH-700 thermogram for a blank and two CC-loaded filters (He-mode: 1–230 s, He/O₂-mode: 231–410 s and Calibration-mode: 410–510 s).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

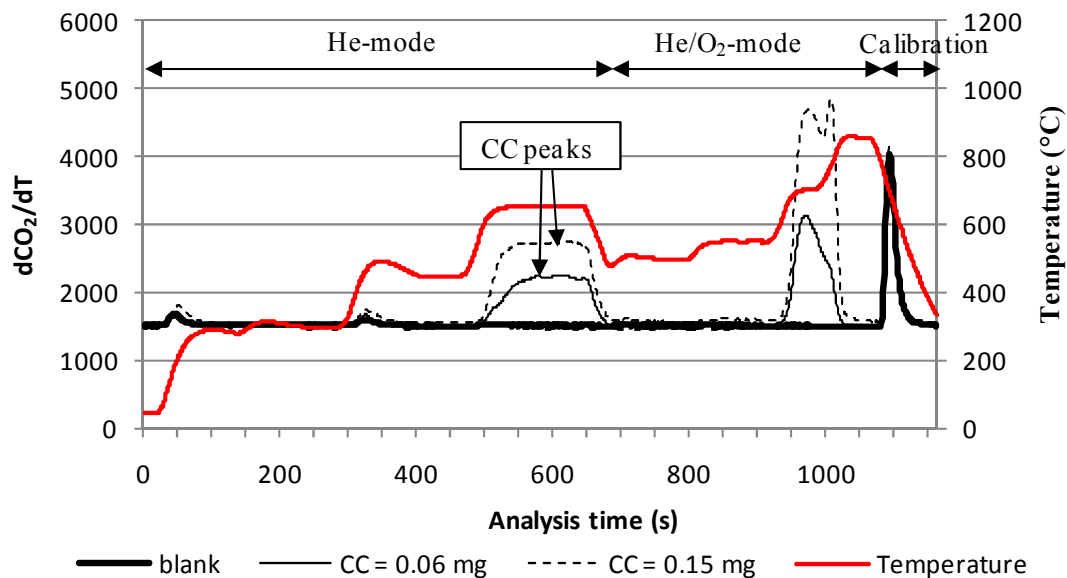


Fig. 6. EUSAAR-2 thermogram for a blank and two CC-loaded filters (He-mode: 1–673 s, He/O₂-mode: 674–1063 s and Calibration-mode: 1064–1163 s). The vertical lines represent the splint point between OC and EC.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

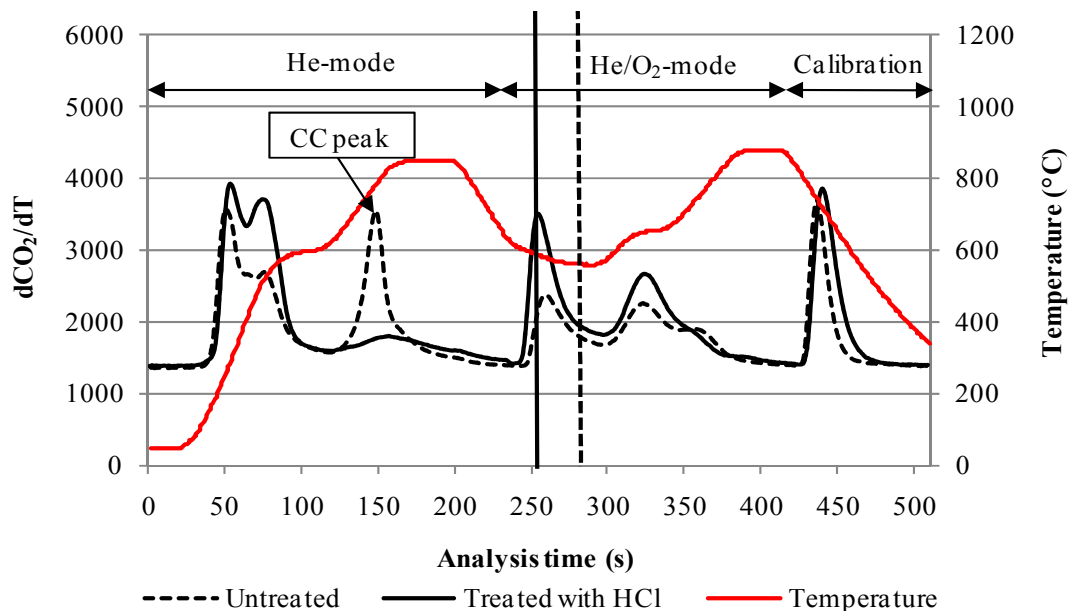


Fig. 7. NIOSH-840 thermogram for a sample filter treated with HCl and untreated (He-mode: 1–230 s, He/O₂-mode: 231–410 s and Calibration-mode: 410–510 s).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

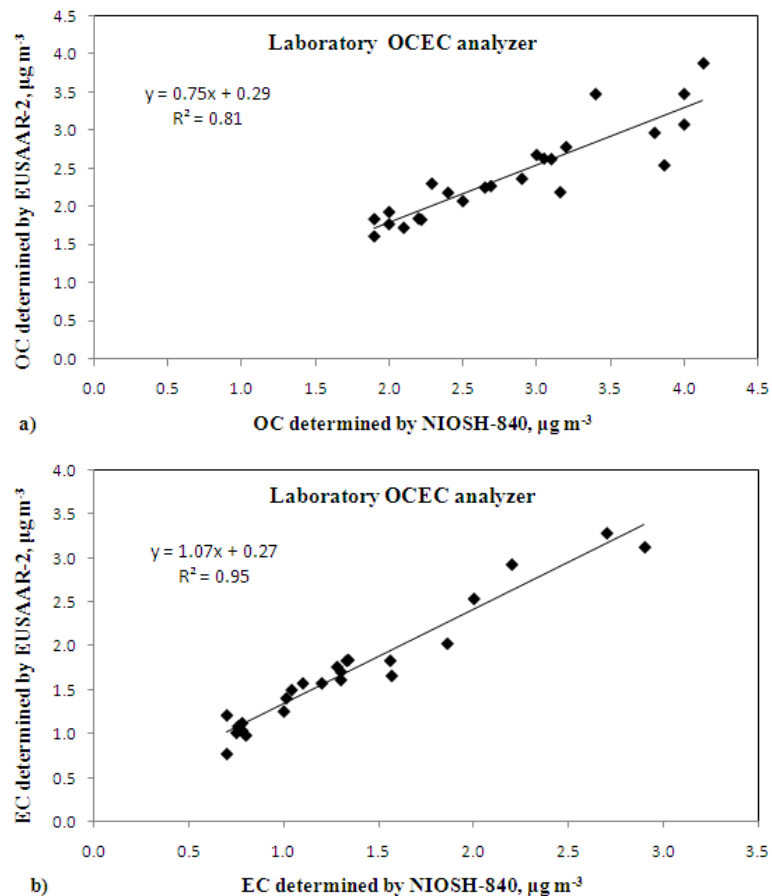


Fig. 8. Regression between (a) OC and (b) EC concentrations determined by the NIOSH-840 and the EUSAAR-2 thermal protocols using the Laboratory OCEC analyzer.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

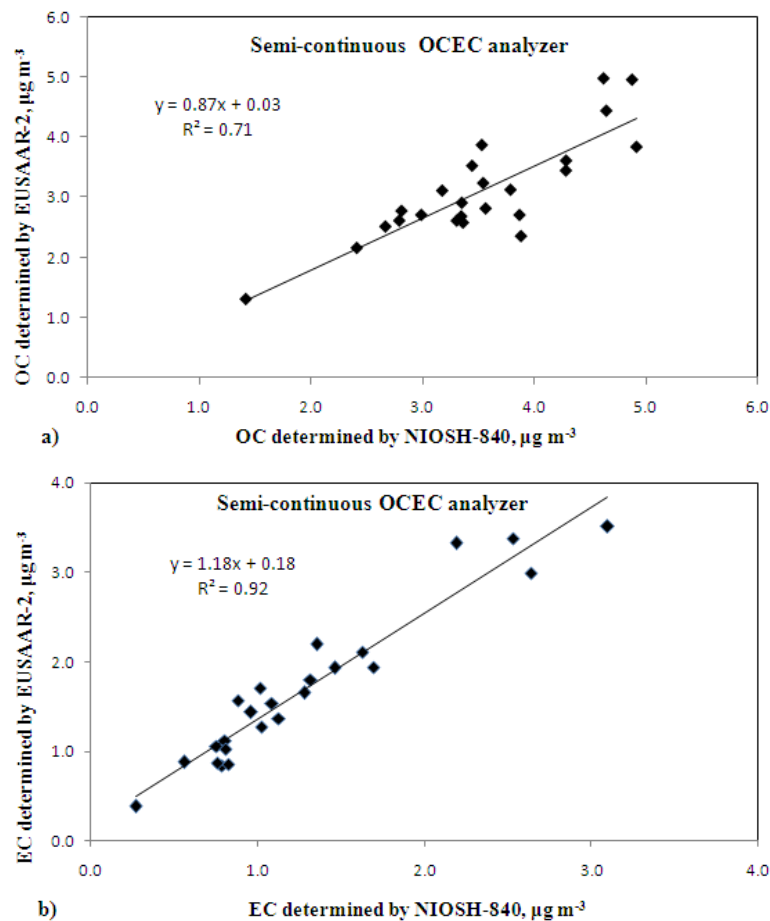
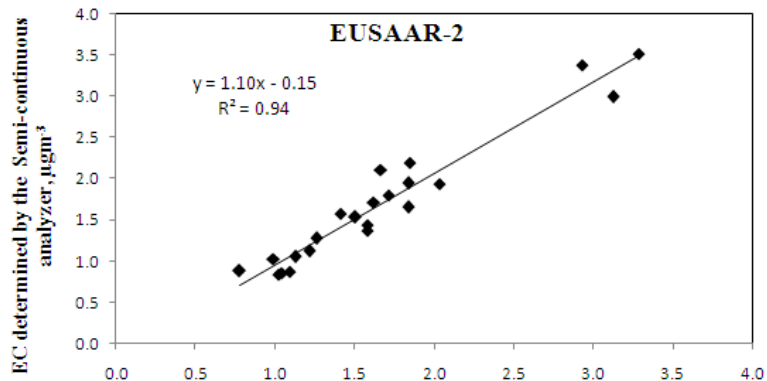
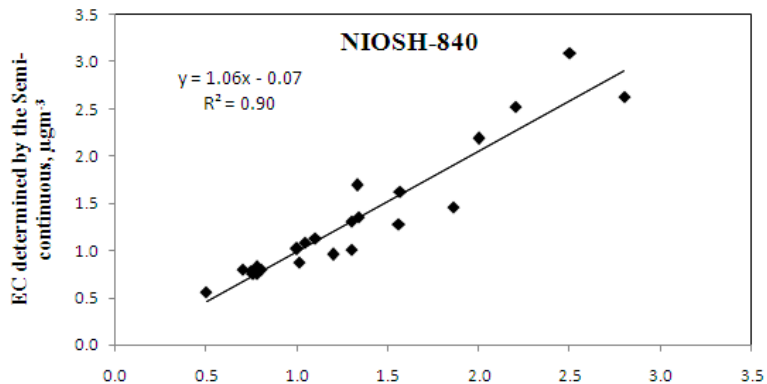


Fig. 9. Regression between **(a)** OC and **(b)** EC concentrations determined by the NIOSH-840 and the EUSAAR-2 thermal protocols using the Semi-continuous OCEC analyzer.



a) EC determined by the Laboratory analyzer, μgm^{-3}



b) EC determined by the Laboratory analyzer, μgm^{-3}

Fig. 10. Regression between the EC concentrations determined by the semi-continuous analyzer and the Laboratory analyzer using (a) EUSAAR-2 protocol and (b) NIOSH-840 protocol.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



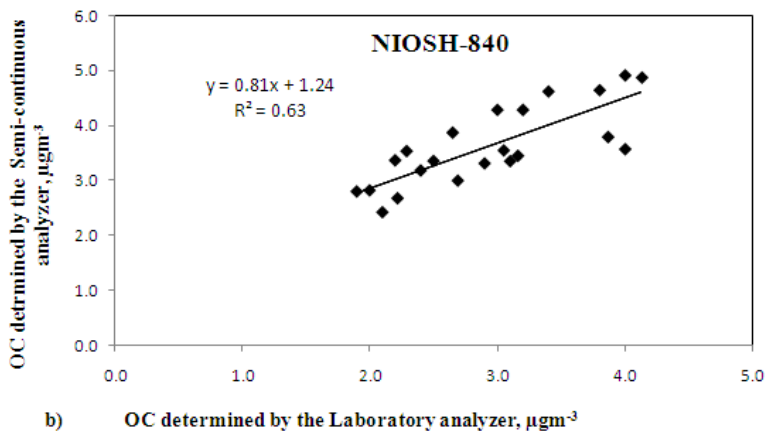
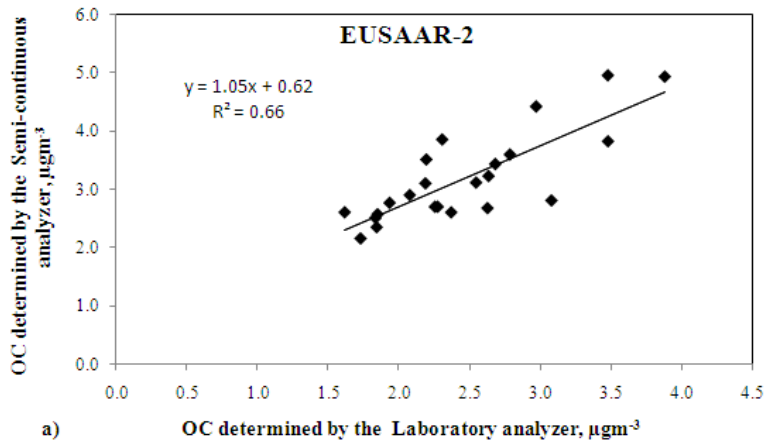


Fig. 11. Regression between the OC concentrations determined by the semi-continuous analyzer and the laboratory analyzer using (a) EUSAAR-2 protocol and (b) NIOSH-840 protocol.

**On the quantification
of atmospheric
carbonate carbon**

A. Karanasiou et al.

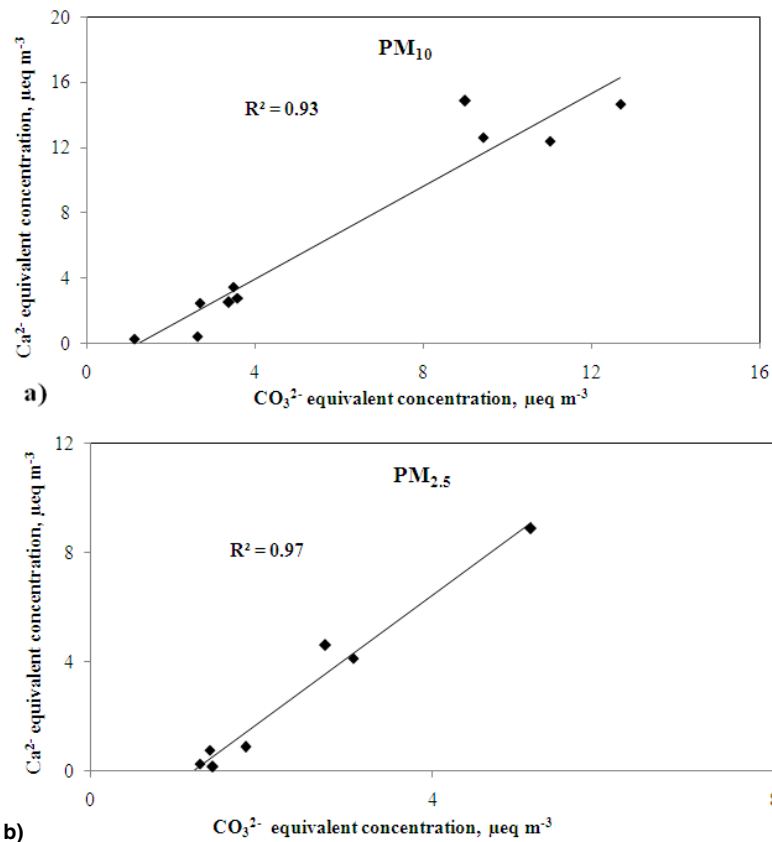


Fig. 12. Ca²⁺ plotted against CO₃²⁻ (calculated by the CC content) equivalent concentrations for **(a)** PM₁₀ and **(b)** PM_{2.5} size fraction in Barcelona site.

On the quantification of atmospheric carbonate carbon

A. Karanasiou et al.

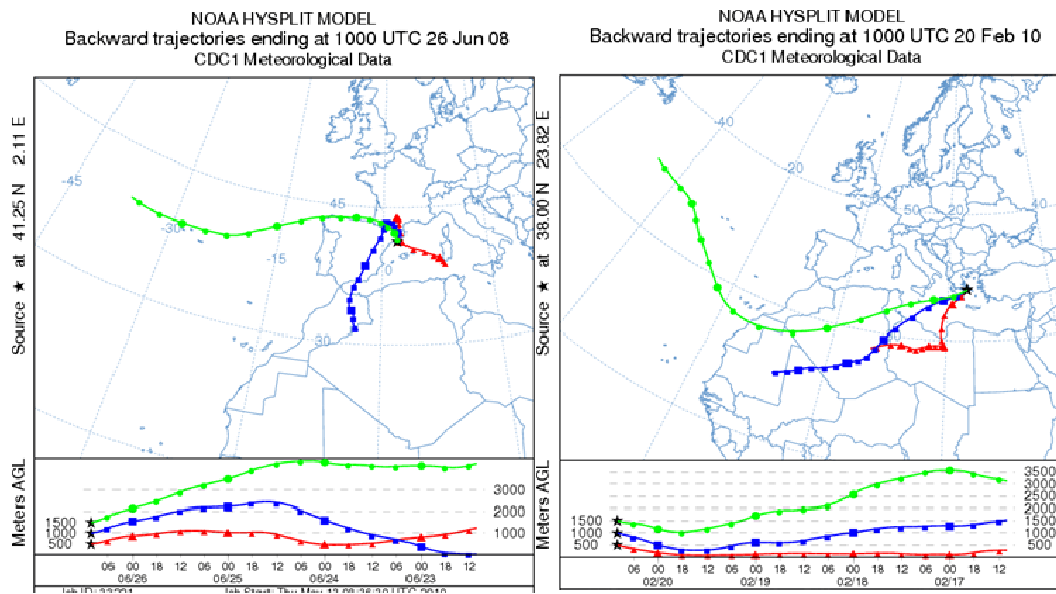


Fig. 13. HYSPLIT back-trajectory analysis at different vertical levels (red: 500 m, blue: 1000 m, green: 1500 m) ending over Barcelona (26 June 2008) and Athens (20 February 2010) showing dust episodes.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

