Quantification of the carbonaceous matter origin in submicron marine aerosol particles by dual carbon isotope analysis

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Abstract

Dual carbon isotope analysis has been performed for the first time demonstrating a potential in organic matter apportionment between three principal sources: marine, terrestrial (non-fossil) and fossil fuel due to unique isotopic signatures. The results presented here, utilising combinations of dual carbon isotope analysis, provides a conclusive evidence of a dominant biogenic organic fraction to organic aerosol over biologically active oceans. In particular, the NE Atlantic, which is also subjected to notable anthropogenic influences via pollution transport processes, was found to contain 80% organic aerosol matter of biogenic origin directly linked to plankton emissions. The remaining carbonaceous aerosol was of fossil-fuel origin. By contrast, for polluted air advecting out from Europe into the NE Atlantic, the source apportionment is 30% marine biogenic, 40% fossil fuel, and 30% continental non-fossil fuel. The dominant marine organic aerosol source in the atmosphere has significant implications for climate change feedback processes.

1 Introduction

Aerosol particles in marine air can affect climate by acting as nuclei for cloud condensation (Charlson et al., 1987; Shaw, 1983). It has been long postulated that submicron sizes, where cloud nuclei number concentration is important, predominantly comprises sulphate mass; however, recent studies (O’Dowd et al., 2004) revealed significant enrichments of carbonaceous aerosol during periods of high plankton activity, suggesting a biogenic source from both organically-enriched sea-spray and condensable ocean-derived organic vapours. Organic matter has been observed, to different degrees, in marine aerosol particles for many decades and has been linked to enrichment of sea-spray by biogenic matter transferred from the sea-surface into the tropospheric boundary layer through bubble-mediated production processes (Blandchard, 1964; Middlebrooke et al., 1998; Oppo et al., 1999; Russell et al., 2010). The enrichment of organic...
matter in sea-spray has important implications for marine aerosol haze and cloud layers, ultimately contributing to current and future climate change. Apart from identification of methane-sulphonic acid and plankton exudates (lipopolisaccarides) (Facchini et al., 2008a), other postulated biogenic organic species (e.g. specific carboxylic acids, amines and carbohydrates) (Kawamura and Sakaguchi, 1999; Mochida et al., 2002; Cavalli et al., 2004; Facchini et al., 2008; Russell et al., 2010) are not necessarily exclusive to marine sources. Indeed, all aforementioned compounds, except MSA and plankton exudates, can be of terrestrial origin as well, either natural, anthropogenic or biomass burning.

Stable carbon isotope analysis has been attempted to apportion marine aerosol organic matter on several occasions (Chesselet et al., 1981; Cachier, 1989; Turekian et al., 2003; Narukawa et al., 2008; Miyazaki et al., 2010). Turekian et al. (2003) were able to even derive compound specific isotope ratio of oxalate attributing it to mostly marine precursors. However, stable carbon isotope analysis is somewhat inconclusive due to varying pollution degree and to not being able to apportion contribution of fossil fuel which can only be reliably done by radiocarbon analysis (Szidat, 2009). Furthermore, Gustafsson et al. (2009) conclusively determined relative contribution of fossil fuel versus biomass burning in brown clouds over South Asia.

In this study dual carbon isotope analysis has been attempted demonstrating its potential in source apportionment between three principal sources: marine, terrestrial (non-fossil) and fossil fuel.

2 Experimental methods

Submicron \( (D_p < 1.5 \mu m) \) marine aerosol samples were collected over the NE Atlantic at Mace Head (O’Connor et al., 2008; Jennings et al., 2003) from January to November 2006 and on the RV Celtic Explorer during June–July 2006 (MAP project). Samples were collected on a weekly basis (aiming at two samples per month) using automated sector control system to separate clean marine and polluted air masses. Automated
control system separated clean marine air masses by sampling air within 190–300 deg sector at Mace Head (representing North Atlantic Ocean) when condensation nucleus counts (CN) did not exceed 700 particles/cm$^3$ (measured by TSI 3010 particle counter). Active control of the sampling conditions excluded sampling during occasional short-term spikes of CN either due to coastal nucleation events or occasional local ship traffic. Post-sampling analysis revealed that such air masses did not have contact with land for 4–5 days (as confirmed by air mass back-trajectories) and BC concentration measured by aethalometer (AE-16) did not exceed 50 ng/m$^3$. Such air masses have been spending the last 48 h (at least) in the marine boundary layer as demonstrated by Cavalli et al. (2004). Taking into account the above sampling conditions clean marine samples were likely the cleanest possible to obtain in anthropogenically perturbed Northern Hemisphere. Polluted air masses were sampled during all other conditions but clean and thus represented varying degree of pollution from European continent. Clearly, “clean marine” and “polluted” definitions are somewhat ambiguous, because clean marine samples can be slightly anthropogenically perturbed while polluted samples may contain significant amount of biogenic matter. However, that was exactly the scope of the study trying to quantify those contributions. In total 915 h of clean marine air and 811 h of polluted air were sampled during the entire year. Samples were collected on quartz filters (SKC Inc.) pre-fired at 900$^\circ$C before sampling using HiVol Sierra Andersen sampler at 1 m$^3$/min flow rate, equipped with cascade impactor unit capable of separating particles at 1.5 µm.

Twelve clean marine samples were collected throughout different seasons with a typical sample spanning approximately 1 calendar week (but different number of hours depending on clean sector conditions) to accumulate sufficient mass for analysis. In addition, eight polluted samples were collected during all other non-clean-sector marine conditions. Three of the clean sector samples among those twelve were collected onboard RV Celtic Explorer cruising outside continental shelf area off the west coast of Ireland during June–July 2006. Chemical and physical similarities between the samples collected at Mace Head and RV Celtic Explorer has been discussed in detail by
Rinaldi et al. (2009) concluding that clean marine samples collected at the coastal site (under the strict sampling conditions) were representative of the open ocean environment.

The samples were treated to carbon isotope analysis to quantify the biogenic marine carbon (i.e. carbon derived from marine plants), continental non-fossil fuel carbon (i.e. carbon derived from terrestrial plant emissions and/or biomass burning emissions), and fossil fuel carbon emissions. The carbon isotopic composition of the carbonaceous aerosol is assumed to be practically stable during transport from source-to-receptor sites, even if they undergo chemical transformations. Isotopic fractionation has, indeed, been demonstrated (e.g., Usdowski and Hoefs, 1988) which would compromise the above assumption, however, the suggested effect would mainly manifest itself via secondary aerosol formation due to preferential condensation of compounds depleted in heavy isotope. Most of the studies, however, conducted to elucidate marine organic aerosol origin (O’Dowd et al., 2004; Sciare et al., 2009; Russell et al., 2010) pointed to the dominant primary source of marine organic aerosol which should not be affected by isotopic fractionation and, therefore, isotopic fractionation is probably of limited importance to source attribution. The carbon isotope $^{14}C$ is produced in the upper atmosphere and enters the biological carbon cycle with the relatively constant initial ratio to $^{12}C$ (Szidat, 2009). On the other hand, $^{14}C$ is completely depleted in fossil fuels due to radioactive decay. The $^{14}C/^{12}C$ ratio therefore elucidates the contributions of contemporary carbon biomass emissions and fossil fuel emissions. Further, the ratio of $^{13}C/^{12}C$ elucidates carbon emissions associated with different plants, both terrestrial and oceanic, due to preferential photosynthesis uptake routes of heavier or lighter inorganic carbon isotopes (Smith and Epstein, 1971; Maberly et al., 1992). Thus, the combination of ratios of $^{12}C$, $^{13}C$, and $^{14}C$ enables the quantification of different carbon source contributions to carbonaceous samples as demonstrated below.

TC concentrations of all samples were performed by an Analytik Jena Multi N/C2100 elemental analyzer equipped with a solid furnace module. Inside the instrument furnace, the sample was exposed to a constant temperature of 950 $^\circ$C in 100% O$_2$ and
the TC was determined as the total evolved CO$_2$ by a non-dispersive infrared (NDIR) detector.

OC/TC ratios of selected samples for $^{14}$C analysis were determined with a commercial thermo-optical transmission instrument (Sunset Laboratory, Tigard, OR, USA).

2.1 $^{13}$C analyses

$^{13}$C isotope analysis was performed using a stable Isotope Ratio Mass Spectrometer (IRMS, Thermo Finnigan Delta Plus Advantage) calibrated by the primary Pee Dee Belemnite (PDB) standard (Garbaras et al., 2009). The analysis comprised evaluation of the $^{13}$C to $^{12}$C isotope ratio ($R$), expressed as $\delta$ (delta) values and defined as the standard-normalised difference from the reference standard, and expressed as $\delta^{13}$C in parts per mill (‰):

$$\delta^{13}C = \left[ \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] \times 1000$$ (1)

Three replicates of each sample were analysed. $^{13}$C analytical error ($\pm 1\sigma$) was mostly within 1% (0.5–3.0%) of the value which is listed in Table 1.

Three filter blanks were analysed directly and estimated from regression analysis. Direct analysis of the filter blank was quite uncertain due to very low total carbon blank of the pre-fired quartz filters. The measured $\delta^{13}$C value of the filter blank was $-25.4\pm0.9‰$. An independent method was used to estimate the filter blank from the regression analysis since the blank $\delta^{13}$C value was significantly different from the $\delta^{13}$C values of clean marine samples and the filter blank impact would be minimal at high carbon loading. The regression analysis of $\delta^{13}$C versus total carbon mass is presented in Fig. 1, which yielded $-25.6‰$ filter blank value with a regression correlation coefficient $r=0.84 (P<0.01)$. The uncertainty range of the intercept was also clearly outside the range of clean marine samples. Therefore, overall, two approaches agreed very well. Standard least squares regression analysis is considered of limited reliability when two variables are of very different magnitude. McArdle (1988) suggested that reduced major axis (RMA) regression should be used when the error rate in $x$ exceeds one-third
of the error rate in $y$ as it is in our case. However, RMA produced same result with a blank value of $-25.8\pm0.4\%$. It should be noted, that the width of 95% confidence limit is also dependent on the absence of very low values (IRM detection limit is around 200 mV in amplitude of $m/z$ 44) and very high values (TC concentration in clean sector is generally low). The field $\delta^{13}C$ samples were corrected for blank contribution using isotope mixing equation:

$$\delta^{13}{\text{TC}}_{\text{sample}} \times C_{\text{sample}} = \delta^{13}{\text{TC}}_{\text{blank}} \times C_{\text{blank}} + \delta^{13}{\text{TC}}_{\text{aerosol}} \times (C_{\text{sample}} - C_{\text{blank}})$$  \hspace{1cm} (2)

where $C_{\text{blank}}$ and $C_{\text{sample}}$ are corresponding raw signals of the measured blank ($-25.4\%$) and the sample obtained by IRMS.

Similarly, $\delta^{13}C_{\text{marine}}$ was calculated to exclude fossil and continental non-fossil contribution using Eq. (2) and presented in Table 1 and Fig. 1. This calculation was based on the assumption that all black carbon (set at 40 ng/m$^3$ which is consistent with $<50$ ng/m$^3$ limit value in clean marine sector) was from non-marine sources and had $\delta^{13}C$ ratio of $-29\%$ which is consistent with the literature value of $-29.2\%$ for black carbon (Rumpel et al., 2006) or wildfire origin $\delta^{13}C$ value of $-30.9\%$ (Ulevicius et al., 2010).

Stable Isotope Ratio Mass Spectrometer raw signal was compared against independent total carbon analysis, though IRMS is not designed to give a quantitative result. Nevertheless, a good agreement between TC and CO$_2$ ($m/z$ 44) signal amplitude presented in Fig. 2 ($r=0.98$, $P \ll 0.01$) showed that IRMS system was well tuned to provide consistent results.

### 2.2 $^{14}C$ analyses

In a similar manner to $^{13}C$, $\Delta^{14}C$ is calculated from radiocarbon analysis to determine the separation from fossil fuel carbon and non-fossil fuel carbon, which was performed by accelerated mass spectrometry (AMS) (Szidat, 2009; Szidat et al., 2006). Three cases each of clean marine and polluted sample sub-sets had sufficient total-carbon loadings to be analysed for $\Delta^{14}C$ due to analytical constraints. In addition, $\Delta^{14}C$ analysis in polluted samples was also conducted for OC. For clean marine samples, $\Delta^{14}C$ of
OC was estimated from the $^{14}$C measurements of TC by subtraction of the EC component (typically <10% of TC) under the assumption of a non-fossil contribution of 20% to EC.

OC and TC were isolated for $^{14}$C analysis by oxidation from the filters in pure oxygen at 340°C and 650°C, respectively (Szidat et al., 2004; Szidat, 2009). Evolving CO$_2$ was cryo-trapped and then sealed in glass ampoules. $^{14}$C measurement was performed by mixing the CO$_2$ with He and transfer into a self-constructed cesium sputter gas ion source of the 200 kV mini-radiocarbon dating system MICADAS (Ruff et al., 2007). $\Delta^{14}$C values of the filter samples were calculated according to Stuiver and Polach (1977) and corrected for a filter blank. Individual sample measurements are summarised in Table 2.

### 2.3 Isotope mixing equations and source contribution

The source quantification was performed using isotope mixing equations applied to both $\delta^{13}$C and $\Delta^{14}$C isotope ratios as follows:

\[
\delta^{13}\text{TC} = \delta^{13}\text{TC}_{\text{marine}} \times k_1 + \delta^{13}\text{TC}_{\text{cont}} \times k_2 + \delta^{13}\text{TC}_{\text{fossil}} \times (1 - k_1 - k_2) \tag{3}
\]

\[
\Delta^{14}\text{TC} = \Delta^{14}\text{TC}_{\text{marine}} \times k_1 + \Delta^{14}\text{TC}_{\text{cont}} \times k_2 + \Delta^{14}\text{TC}_{\text{fossil}} \times (1 - k_1 - k_2) \tag{4}
\]

where $k_1, k_2, k_3$ are contributions of marine, continental and fossil fuel sources.

The above equations are solved when the calculated isotopic ratios converge on the measured ratios. It should be stressed that Eqs. (3) and (4) can be solved explicitly only if individual source ratios are fixed (i.e. firmly established). In fact, they are not and that makes the solution slightly uncertain. However, the solution is rather tightly constrained with little degrees of freedom when selecting individual source ratios, primarily because Eq. (3) clearly separates the marine source and Eq. (4) clearly separates the fossil fuel source due to distinctly different source ratios. For marine, continental and fossil sources, the respective $\delta^{13}$C ratios are $-20\%$, $-26\%$, $-29\%$, and $50\%$.
100‰, −1000‰ for \( \Delta^{14} \text{C} \) ratios. These ratios were obtained using the error minimisation approach according to Eq. (5) until the error was minimised to match the individual analytical error:

\[
S_{\text{min}} = \sqrt{\left( \frac{\delta^{13} \text{TC}_{\text{calc}} - \delta^{13} \text{TC}_{\text{meas.}}}{\delta^{13} \text{TC}_{\text{meas.}}} \right)^2 + \left( \frac{\Delta^{14} \text{TC}_{\text{calc}} - \Delta^{14} \text{TC}_{\text{meas.}}}{\Delta^{14} \text{TC}_{\text{meas.}}} \right)^2} \times 100
\]

where \( \delta^{13} \text{TC}_{\text{calc.}} \) and \( \Delta^{14} \text{TC}_{\text{calc.}} \) are the values obtained by Eqs. (3) and (4) and \( \delta^{13} \text{TC}_{\text{meas.}} \) and \( \Delta^{14} \text{TC}_{\text{meas.}} \) are corresponding measured values.

In the end there was only one unique set of \( \delta^{13} \text{C} \) and \( \Delta^{14} \text{C} \) values and corresponding \( k \) coefficients to match calculated and measured ratios with a smallest error (individual as well as the total error \( \sum S \)). Even more so, that obtained typical source ratios (−20‰, −26‰, −29‰, and 50‰, 100‰, −1000‰) must have been the same for all samples while \( k \) coefficients varied between the samples. The above \( \delta^{13} \text{C} \) values are consistent with literature values of \( \delta^{13} \text{C} \) and \( \Delta^{14} \text{C} \) values for marine, continental and fossil fuel sources (Raymond, 2005). The uncertainty of \( k \) coefficients was, indeed, somewhat dependent on the selected source ratio values. By varying individual \( \delta^{13} \text{C} \) ratios within ±1‰ and \( \Delta^{14} \text{C} \) ratio ±50‰, the uncertainty of \( k \) coefficients was typically within 5%.

3 Results and discussions

The results of the \(^{13}\text{C} \) isotope analysis are shown in Fig. 3. The clean marine aerosol samples revealed distinctly different \( \delta^{13} \text{C} \) isotopic ratios when compared to polluted samples. Marine \( \delta^{13} \text{C} \) values were in the range of −20‰ to −23.3‰, with least-negative values occurring during summer months (periods of high biological activity) while polluted sample values exhibited more-negative values over a much smaller range of −24.7‰ to −26.3‰ with little seasonality seen. The less-negative values of \( \delta^{13} \text{C} \), corresponding to the enrichment in \(^{13}\text{C} \), occurs during the period of peak organic aerosol enrichment associated with peak biological activity as has been detailed.
by Yoon et al. (2007) which data are presented for the purpose of consistency. This enrichment results from carbon isotopic fractionation occurring during photosynthetic carbon assimilation (Degens et al., 1968) whereby marine plants get enriched in $^{13}$C relative to terrestrial plants due to limited supply of inorganic carbon in water during peak biological activity. The isotopic shift in $\delta^{13}$C to less-negative values during summer results from plankton accelerated carbon fixation during bloom conditions (Deuser, 1970). This interpretation is supported by the corresponding $\delta^{13}$C ratios of particulate organic carbon ($-26.5$ to $-20.2\%$) (Bentaleb et al., 1996), protein-like fraction, carbohydrates and dissolved organic carbon in ocean water ($-21.5$ to $-20.5\%$) (Loh et al., 2004). In clean marine air, larger negative values during winter are most likely due to higher availability of inorganic carbon when biological activity and water temperature is at its lowest according to mesocosm bloom experiments performed by Benthien et al. (2007). Similarly, the more-negative values during summer were observed in samples during a significant storm onboard RV Celtic Explorer most likely resulted from mixing of organic material from greater depths where the competition for inorganic carbon is lower. Distribution of $\delta^{13}$C values suggested a lower estimate of marine sector $\delta^{13}$C value which should be at least $-20\%$ or less negative to accommodate any contribution of terrestrial sources (Table 1). This lower estimate is significantly less negative value than reported in any other studies (Chesselet et al., 1981; Cachier, 1989; Turekian et al., 2003; Narukawa et al., 2008; Miyazaki et al., 2010). The solution of isotope mixing equations also required the marine $\delta^{13}$C value of $-20\%$, demonstrating consistency between $^{13}$C and $^{14}$C measurements.

Using Eq. (3) it is possible to separate the marine source contribution to total organic carbon using only $\delta^{13}$C data due to distinctly different marine source isotope ratio. It must be noted, however, that such source apportionment would have quite a large error, primarily due to significant overlap of $\delta^{13}$C values of continental non-fossil and fossil fuel sources and no constrain on $\delta^{13}$C values of either marine nor continental (non-fossil+fossil) sources (Eq. 2). Following the above considerations and unconstraint $\delta^{13}$C values for marine ($-19$ to $-21\%$) and continental ($-26$ to $29\%$)
sources, we get marine source contribution for clean marine samples in the range of 55–96%. Consequently, even using rather conservative range of $\delta^{13}C$ values we get a large uncertainty in marine source contribution. Therefore, without $\Delta^{14}C$ it is impossible to separate the contribution of fossil fuel sources and then continental non-fossil sources. In a similar way it is not possible to separate the marine sources using $\Delta^{14}C$ data alone. Combining both isotopes allows for a separation of all three sources in a tightly constrained manner. Using Eqs. (3) and (4) and a subset of six samples where both isotope ratios were measured, the contribution of three principal sources was estimated and presented in Fig. 4a. For three of the marine samples, between 74% and 85% of the total carbon is of marine origin, the remainder being fossil fuel carbon with no continental (non-fossil carbon) component evident. Table 2 exhibits similar result based on $\Delta^{14}C$ data (within the uncertainty range) given the absence of continental non-fossil source. This marine contribution even makes up 76–87% if considering only the OC fraction (Table 2). It should be noted that absence of the continental non-fossil source in clean marine air masses can be due to 5% uncertainty in source contribution or it was absent all together. Error of the isotope mixing equation solution was slightly increasing in every case when 2–3% of continental non-fossil source contribution was added. Therefore, continental non-fossil source contribution must have been limited to maximum 2–3% at best. A small fraction of fossil fuel present in clean marine samples could be from shipping fossil fuel combustion and not from the North American sources, eliminating the presence of continental sources. If fossil fuel source was from the North American sources including Canadian forest fires then the samples must have contained significant continental non-fossil source contribution which is not evident. Our results suggest that the North Atlantic marine boundary layer can be exceptionally clean and largely devoid of anthropogenic material even in generally polluted Northern Hemisphere most likely due to both dry and wet deposition during long-range transport across the Atlantic Ocean. Indeed, situation can be very different above the boundary layer where absence of vigorous mixing and clouds can preserve significant presence of the terrestrial carbon. By contrast, non-marine (polluted to a
different degree) samples comprised between 19% and 36% of continental non-fossil carbon and about 40% fossil fuel carbon with the remainder being attributed to marine carbon (25 to 41%). There was a certain degree of variability from sample to sample in both clean marine and polluted sample sets, however, within the subsets samples were similar to each other. On average, as shown in Fig. 4b, carbon in marine samples comprised 80% marine biogenic carbon and 20% fossil fuel carbon while in non-marine air masses, carbon is attributed to 40% fossil fuel, 30% continental (non-fossil carbon) and 30% marine biogenic carbon. The presence of the marine source in polluted air masses (and of similar magnitude to the continental non-fossil source) has significant implications in interpreting other experimental results where isotope analysis was not performed. Typically, all organic matter in polluted air masses is attributed to terrestrial and/or anthropogenic sources.

Previous studies into marine aerosol $\delta^{13}C$ ratios have indicated marine sources significantly contributing to submicron carbonaceous aerosol: 20% in submicron mode and 80% in supermicron (Chesselet et al., 1981); 38% in both sub- and super-micron modes (Turekian et al., 2003); 45% in sub-micron mode (Narukawa et al., 2008); 46–72% in sub-micron mode (Miyazaki et al., 2010). All those studies only used $\delta^{13}C$ ratios and were conducted under conditions of varying degree of pollution and were not subjected to our strict classification of clean marine air. Our results for polluted marine air are consistent with the aforementioned studies but, our results for clean marine air (74–85% of carbon was marine in origin) are in contrast to these studies as a result of the unique combinations of both $\delta^{13}C$ and $\Delta^{14}C$ ratios and strict classification of clean marine air masses.

4 Conclusions

Dual isotope analysis method was applied to clean marine and polluted samples demonstrating the ability to discern contribution of three principal sources to atmospheric aerosols: marine, continental non-fossil and fossil fuel. We have conclusively
demonstrated a predominant (80%) marine biogenic source for submicron carbonaceous aerosol in clean marine air over the NE Atlantic. This biogenic carbon component resides in particle sizes predominantly contributing to cloud nuclei, pointing to a direct link between plankton and marine cloud-climate interactions. In addition, the anthropogenic contribution to marine organic carbon aerosol is still significant, illustrating the role of hemispheric and long-range transport having notable impacts in nominally pristine marine environments. The presence of marine source in polluted air masses (30%) should not be neglected even though its absolute magnitude may be relatively low.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/2749/2011/acpd-11-2749-2011-supplement.pdf.

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References


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### Table 1. Carbon 13 analyses results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TC, µg/m³</th>
<th>$\delta^{13}C$,‰</th>
<th>$\delta^{13}C_{\text{marine}}$,‰</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Clean marine</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11–18 Jan 2006</td>
<td>0.14±0.02</td>
<td>-24.38±0.79</td>
<td>-23.27±0.79</td>
</tr>
<tr>
<td>29 Mar–5 Apr 2006</td>
<td>0.14±0.02</td>
<td>-24.23±0.27</td>
<td>-22.47±0.27</td>
</tr>
<tr>
<td>12–26 Apr 2006</td>
<td>0.17±0.02</td>
<td>-21.61±0.22</td>
<td>-20.95±0.22</td>
</tr>
<tr>
<td>12–19 Jun 2006</td>
<td>0.26±0.03</td>
<td>-21.44±0.32</td>
<td>-20.14±0.32</td>
</tr>
<tr>
<td>19–28 Jun 2006</td>
<td>0.18±0.02</td>
<td>-21.76±0.25</td>
<td>-20.03±0.25</td>
</tr>
<tr>
<td>12–15 Jun 2006</td>
<td>0.35±0.04</td>
<td>-22.56±0.30</td>
<td>-21.78±0.30</td>
</tr>
<tr>
<td>16–20 Jun 2006</td>
<td>0.26±0.03</td>
<td>-23.42±0.19</td>
<td>-21.96±0.19</td>
</tr>
<tr>
<td>5–12 Jul 2006</td>
<td>0.35±0.04</td>
<td>-21.34±0.09</td>
<td>-20.69±0.09</td>
</tr>
<tr>
<td>16–23 Aug 2006</td>
<td>0.19±0.02</td>
<td>-22.54±0.17</td>
<td>-21.27±0.17</td>
</tr>
<tr>
<td>3–8 Sep 2006</td>
<td>0.075±0.01</td>
<td>-23.63±0.05</td>
<td>-22.32±0.05</td>
</tr>
<tr>
<td>5–11 Oct 2006</td>
<td>0.071±0.01</td>
<td>-23.28±0.11</td>
<td>-21.88±0.11</td>
</tr>
<tr>
<td>15–22 Nov 2006</td>
<td>0.070±0.01</td>
<td>-23.96±0.11</td>
<td>-22.98±0.11</td>
</tr>
<tr>
<td><strong>Polluted</strong></td>
<td></td>
<td></td>
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<tr>
<td>25–30 Jan 2006</td>
<td>0.41±0.04</td>
<td>-26.32±0.05</td>
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</tr>
<tr>
<td>5–12 Apr 2006</td>
<td>0.11±0.01</td>
<td>-25.95±0.32</td>
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</tr>
<tr>
<td>3–10 May 2006</td>
<td>0.6±0.06</td>
<td>-24.70±0.07</td>
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</tr>
<tr>
<td>15–21 Jul 2006</td>
<td>1.40±0.07</td>
<td>-25.71±0.04</td>
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<tr>
<td>24–30 Aug 2006</td>
<td>0.33±0.03</td>
<td>-25.69±0.12</td>
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<tr>
<td>21–28 Sep 2006</td>
<td>0.42±0.04</td>
<td>-25.66±0.73</td>
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<tr>
<td>11–18 Oct 2006</td>
<td>1.57±0.07</td>
<td>-25.48±0.18</td>
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</tr>
<tr>
<td>8–15 Nov 2006</td>
<td>0.36±0.04</td>
<td>-25.03±0.05</td>
<td></td>
</tr>
</tbody>
</table>

$^{a}$ $\delta^{13}C_{\text{marine}}$ was calculated without fossil fuel contribution.
Table 2. Carbon 14 analyses results.

<table>
<thead>
<tr>
<th>Date</th>
<th>Episode</th>
<th>OC/TC</th>
<th>$\Delta^{14}$C (TC) ($%$)</th>
<th>TC$_{nf}$ ($%$)</th>
<th>$\Delta^{14}$C (OC) ($%$)</th>
<th>OC$_{nf}$ ($%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12–26 Apr 2006</td>
<td>Clean</td>
<td>0.88±0.03</td>
<td>−176±19</td>
<td>78±2</td>
<td>−89±19*</td>
<td>84</td>
</tr>
<tr>
<td>12–15 Jun 2006</td>
<td>Clean</td>
<td>0.94±0.03</td>
<td>−222±21</td>
<td>73±2</td>
<td>−182±21*</td>
<td>76</td>
</tr>
<tr>
<td>5–12 Jul 2006</td>
<td>Clean</td>
<td>n.d.</td>
<td>−111±22</td>
<td>84±3</td>
<td>−63±22*</td>
<td>87</td>
</tr>
<tr>
<td>15–22 Nov 2006</td>
<td>Clean</td>
<td>0.99±0.11</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>21–28 Sep 2006</td>
<td>Polluted</td>
<td>0.85±0.02</td>
<td>−344±14</td>
<td>60±3</td>
<td>−260±14</td>
<td>69±2</td>
</tr>
<tr>
<td>11–18 Oct 2006</td>
<td>Polluted</td>
<td>0.86±0.05</td>
<td>−342±12</td>
<td>60±3</td>
<td>−154±17</td>
<td>78±3</td>
</tr>
</tbody>
</table>

nf non-fossil.
n.d. is not determined/measurement not performed.

* $\Delta^{14}$C (OC) was estimated from the $^{14}$C (TC) by subtraction of the EC component under the assumption of a non-fossil contribution of 20% to EC.
Fig. 1. $\delta^{13}C$ filter blank estimation by regression analysis.
Fig. 2. TC concentration versus IRMS CO$_2$ (m/z 44) signal amplitude.
Fig. 3. Seasonal pattern of $\delta^{13}$C in clean marine and polluted samples during 2006 at Mace Head (top panel). Also shown is the clean marine total carbon concentration (TC) for the 2006 data (middle panel) and for 2002–2005 (Yoon et al., 2007) (bottom panel).
Fig. 4. (a) Source contribution to organic matter in marine and polluted air samples in terms of fossil fuel carbon (black), non-fossil fuel continental carbon (dark green), and marine biogenic carbon (blue) sources; (b) same as (a) except average source values over all samples for marine and continental air masses.