**Atmospheric
Chemistry
and Physics**

Quantification of the carbonaceous matter origin in submicron marine aerosol by ^{13}C and ^{14}C isotope analysis

D. Ceburnis[1], A. Garbaras[2], S. Szidat[3], M. Rinaldi[4], S. Fahrni[3], N. Perron[5,*], L. Wacker[6], S. Leinert[7], V. Remeikis[2], M. C. Facchini[4], A. S. H. Prevot[5], S. G.Jennings[1], M. Ramonet[8], and C. D. O'Dowd[1]

[1]School of Physics and Centre for Climate & Air Pollution Studies, Ryan Institute, National University of Ireland, Galway, University Road, Galway, Ireland
[2]Center for Physical Sciences and Technology, Institute of Physics, Vilnius, Lithuania
[3]Department of Chemistry and Biochemistry & Oeschger Centre for Climate Change Research, University of Berne, Switzerland
[4]Institute of Atmospheric Sciences and Climate, National Research Council, Bologna, Italy
[5]Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen, Switzerland
[6]Laboratory of Ion Beam Physics, Swiss Federal Institute of Technology – ETH, Zurich, Switzerland
[7]Environmental Protection Agency of Ireland, Dublin, Ireland
[8]Laboratoire des Sciences du Climat et de l'Environment (LSCE), Gif sur Yvette, France
[*]now at: Department of Nuclear Physics, University of Lund, Sweden

Abstract. Dual carbon isotope analysis of marine aerosol samples 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 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 terrestrial origin. By contrast, for polluted air advected 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 (Fors, 2010 #177) (Shaw, 1983; Charlson et al., 1987). 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 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 (Blanchard, 1964; Hoffman and Duce, 1977; Middlebrook 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 (MSA) and plankton exudates (lipopolysaccharides) (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., 2008a; 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. Marine atmosphere can also be significantly perturbed by terrestrial anthropogenic pollution via long-range transport making Northern Hemisphere more polluted than the Southern due to larger land masses. Chesselet et al. (1981) concluded that more than 80 % of atmospheric particulate organic carbon was of continental origin over remote marine areas in late 1970s.

The first long-term assessment of carbonaceous particulate matter sources on a regional scale has been presented by Gelencser et al. (2007). Using radiocarbon, thermal optical, organic tracer analysis and statistical techniques authors were able to apportion carbonaceous particulate matter between fossil fuel, biomass burning carbon, biological particles and secondary organic aerosol. The approach was further developed in a study of Gilardoni et al. (2011) where more organic tracer species and Quasi-Monte Carlo statistical method were used to apportion between eight sources, and which included seasonal analyses.

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). A number of studies have even attempted compound specific stable carbon analysis: Turekian et al. (2003) were able to derive isotope ratio of oxalate attributing it to mostly marine precursors; Li et al. (2010) developed a method for isoprene biomarkers; Fisseha et al. (2006) and Wang and Kawamura (2006) were able to perform stable carbon analysis of organic acids; Kim et al. (2005) and Zhang et al. (2009) developed an isotope analysis of polycyclic aromatic hydrocarbons. However, stable carbon isotope analysis is somewhat inconclusive due to inability to separate continental non-fossil and fossil fuel sources which can only be reliably done by radiocarbon analysis (Szidat et al., 2009). Furthermore, without application of strict sampling criteria to separate clean marine and anthropogenicaly perturbed continental air masses, stable carbon apportionment method has relatively large uncertainty.

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 (Currie, 2004; Szidat et al., 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. Gustafsson et al. (2009) conclusively determined relative contribution of fossil fuel versus biomass burning in brown clouds over South Asia. 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. Such an approach was used by Raymond (2005) and Avery et al. (2006) in an attempt to apportion carbonaceous material in rainwater, but has not been attempted in aerosol phase.

In this study, dual carbon isotope analysis of fine aerosol particles in marine atmosphere has been conducted for the first time demonstrating its potential in source apportionment between three principal sources: marine, terrestrial (nonfossil) and fossil fuel.

2 Experimental methods

Marine aerosol samples were collected over the N.E. Atlantic at *Mace Head* (Jennings et al., 2003; O'Connor et al., 2008) from January to November 2006 and on the R/V *Celtic Explorer* during June–July 2006 (MAP project). Fine particulate matter samples ($D_{50} < 1.5 \, \mu m$) 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.

An 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 an Aaethalometer (AE-16, Magee Scientific, single wavelength at 880 nm) 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 presented in Fig. 1 for selected samples discussed in Figs. 4 and 5 using the HYSPLIT model (Draxler and Hess, 1997). Taking into account the above sampling conditions clean marine samples were among the cleanest possible to obtain in the anthropogenicaly perturbed Northern Hemisphere. Despite the number of more remote regions like Greenland or Northern Canada, the west coast of Ireland can be as clean as the most remote locations in the Northern Hemisphere when exposed to the established oceanic air masses.

Polluted air masses were sampled during all other conditions but clean and thus represented varying degree of pollution from the European continent. Clearly, "clean marine" and "polluted" definitions are somewhat ambiguous, because clean marine samples can be slightly anthropogenicaly perturbed while polluted samples may contain significant amount of biogenic matter. However, that was exactly
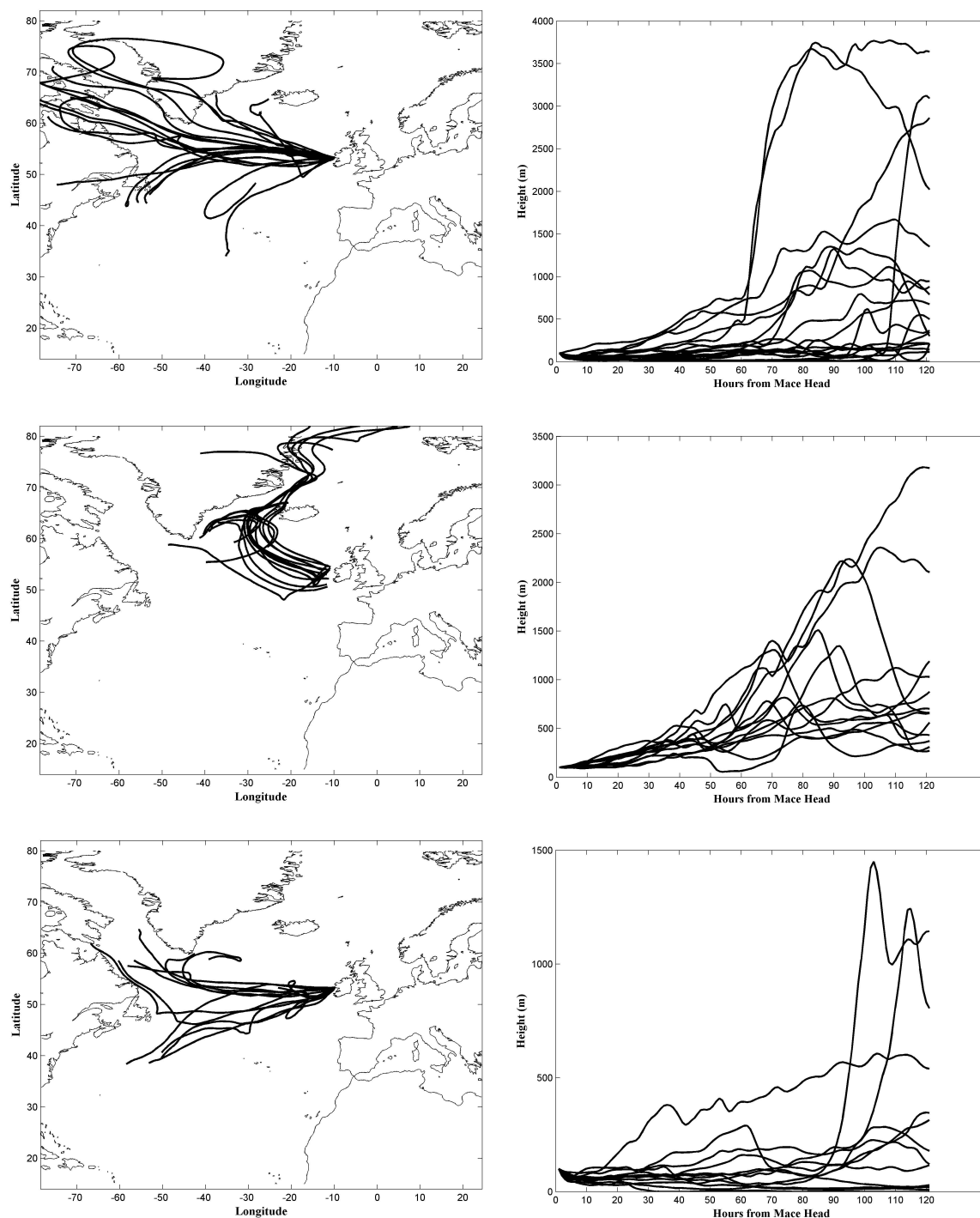
Fig. 1. HYSPLIT 120 h air mass back trajectory plots (every 12 h) ending at 100 m height along with trajectory height along the trajectory during three marine samples presented in Fig. 5 of the paper: 12–26/04/06 (top), 12–15/06/06 (middle), 05–12/07/06 (bottom).

the scope of the study trying to quantify those contributions. In total 915 sampling hours of clean marine air and 811 sampling hours of polluted air were sampled during the entire year. Samples were collected on quartz filters (SKC Inc.)

pre-fired at 900 °C before sampling using a HiVol Sierra Andersen sampler at 1 m³ min⁻¹ flow rate, equipped with a cascade impactor unit capable of separating particles at 1.5 µm. Samples were frozen at −20 °C until analysis.

Twelve clean marine samples were collected throughout different seasons with a typical sample spanning approximately 1 calendar week (but for 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 the R/V *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 the R/V *Celtic Explorer* have 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.

Carbon-13 and carbon-14 isotope analyses were performed to quantify the biogenic marine carbon (i.e. carbon derived from marine plants), continental non-fossil 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 by Usdowski and Hoefs (1988) which would compromise the above assumption. The study of Wang and Kawamura (2006) suggested isotopic fractionation based on different isotopic ratios of di-carboxylic acids (DCAs). However, one could obtain different delta ^{13}C ratios of different DCAs if precursors of various DCAs have different sources, e.g. some produced by secondary processes, some by heterogeneous ageing of primary material.

Physicochemical properties of isotopes arise from quantum mechanical effects with lighter isotopes possessing higher vibration energy levels and, therefore, weaker intermolecular bonds (Hoefs, 2009). Also lighter isotope species have lower vapour pressures facilitating faster phase transitions. Consequently, secondary aerosol formation processes can induce isotopic fractionation due to condensation favouring the lighter isotope although for the large organic molecules the effect would likely be small. However, most of the marine organic aerosol is primary in origin according to the latest research (O'Dowd et al., 2004; Sciare et al., 2009; Rinaldi et al., 2010; Russell et al., 2010). If primary organic matter is preserved and only gaining mass through oxidation (addition of oxygen) then the carbon isotope ratio should remain unchanged. Condensation of lighter organic species would drive isotope ratio to more negative values while evaporation – to more positive. Rinaldi et al. (2010) suggested that there is likely a limited amount of truly secondary organic carbon in marine aerosol with the majority being either primary or processed primary material, hence, little organic mass contributed via condensation processes. Fractionation during evaporation in marine aerosol would only be

possible if primary sea spray organics would be losing mass during oxidation processes producing small volatile organic molecules when, for example, breaking unsaturated double bonds. Evaporation of entirely primary organic compounds will not change the isotope ratio and is probably hardly possible due to chemical species present (long chain hydrocarbons, typical of phospholipids (Facchini et al., 2008b)). In summary, current knowledge about the origin and nature of marine organic aerosol matter suggests that isotopic fractionation is expected to be small and within analytical uncertainty of ~0.2‰ in marine organic aerosol. It should be acknowledged that there is a lack of specific targeted studies at isotopic fractionation in the aerosol phase. Last but not least is the absence of an isotopic fractionation signature in polluted air masses (practically stable isotope ratio throughout the year) where secondary processes, condensation and evaporation are established phenomena (refer to discussion of Fig. 4). Overall, while acknowledging the issue of isotopic fractionation it is not clear of how to estimate it quantitatively.

Total carbon (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 °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 (semi-continuous OC/EC field analyzer RT 3042, Sunset Laboratory Inc Hillsborough, NC, USA) using the EUSAAR-2 protocol (Cavalli et al., 2010).

2.1 ^{13}C analyses

^{13}C isotope analysis was performed using a stable Isotope Ratio Mass Spectrometer (IRMS) calibrated by the primary Pee Dee Belemnite (PDB) standard (Garbaras et al., 2008; Garbaras et al., 2009). The filters were analysed with the elemental analyzer FlashEA 1112 connected to the stable isotope ratio mass spectrometer Thermo Finnigan Delta Plus Advantage. An 1/8th part of a filter was placed into the tin capsule and combusted in the oxidation furnace at the temperature of 1020C in excess of oxygen. Later this gas was transferred into the reduction furnace (650C). The water from the sample in the helium flow was removed by the magnesium perchlorate trap. Then the gas mixture was separated in the column PoraPlot Q (50C). Separated gas was delivered to the mass spectrometer ionization cell through the gas distribution device ConFlow III. Before the analysis of a series of samples the calibration CO_2 gas was delivered to the mass spectrometer until the isotopic ratio uncertainty was better than 0.15 %.

The analysis comprised evaluation of the ^{13}C to ^{12}C isotope ratio (R), expressed as δ (delta) values and defined as the

Table 1. Carbon 13 analyses results.

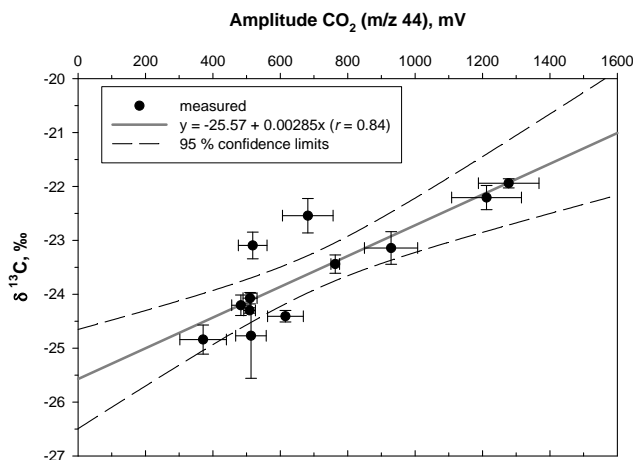| Sample	TC, $\mu g/m^3$	$\delta^{13}C$, ‰	$\delta^{13}C^*_{marine}$, ‰
Clean marine			
11–18/01/2006	0.14±0.02	−24.38±0.79	−23.51±0.48
29/03–05/04/2006	0.14±0.02	−24.23±0.27	−22.83±0.74
12–26/04/2006	0.17±0.02	−21.61±0.22	−21.04±0.18
12–19/06/2006	0.26±0.03	−21.44±0.32	−20.31±0.34
19–28/06/2006	0.18±0.02	−21.76±0.25	−20.27±0.48
12–15/06/2006	0.35±0.04	−22.56±0.30	−21.90±0.24
16–20/06/2006	0.26±0.03	−23.42±0.19	−22.22±0.52
05–12/07/2006	0.35±0.04	−21.34±0.09	−20.77±0.17
16–23/08/2006	0.19±0.02	−22.54±0.17	−21.46±0.39
03–08/09/2006	0.075±0.01	−23.63±0.05	−22.56±0.49
05–11/10/2006	0.071±0.01	−23.28±0.11	−22.12±0.49
15–22/11/2006	0.070±0.01	−23.96±0.11	−23.17±0.39
Polluted			
25–30/01/2006	0.41±0.04	−26.32±0.05	
05–12/04/2006	0.11±0.01	−25.95±0.32	
03–10/05/2006	0.6±0.06	−24.70±0.07	
15–21/07/2006	1.40±0.07	−25.71±0.04	
24–30/08/2006	0.33±0.03	−25.69±0.12	
21–28/09/2006	0.42±0.04	−25.66±0.73	
11–18/10/2006	1.57±0.07	−25.48±0.18	
08–15/11/2006	0.36±0.04	−25.03±0.05	

* $\delta^{13}C_{marine}$ was calculated without fossil and continental non-fossil fuel contribution and the uncertainty range is corresponding to the uncertainty of non-marine $\delta^{13}C$ value (−28±2 ‰).

Fig. 2. $\delta^{13}C$ filter blank estimation by regression analysis.

standard-normalised difference from the reference standard, and expressed as $\delta^{13}C$ in parts per mill (‰):

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

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

Filter blanks were measured and were also estimated from regression analysis. Filter blanks for the measurements were obtained by carrying pre-fired filter to the station and loading it into the sampler, but not exposing it for the duration of the sample. 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±0.9 ‰ (average value of three blanks). 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. 2, which yielded −25.6 ‰ filter blank value with a regression correlation coefficient $r = 0.84$ ($P \ll 0.01$). The uncertainty range of the intercept was also clearly outside the range of clean marine samples. Therefore, overall, the 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 the same result with a blank value of −25.8±0.4 ‰. It should be noted, that the width of the 95 % confidence limit is also dependent on the absence of very low values (IRMS detection limit is around 200 mV in amplitude of m/z 44) and very high values (TC concentration in the clean sector is generally low). As the blank CO_2 value was very low (about 180 mV) we give preference to the regressed value, but they both were very similar. The field $\delta^{13}C$ samples were corrected for blank contribution using isotope mixing equation and CO_2 signal in millivolts (mV) assuming a constant contribution from filter field blank:

$$\delta^{13}TC_{sample} \times CO_{2(sample)} = \delta^{13}TC_{blank} \times CO_{2(blank)} \qquad (2)$$
$$+ \delta^{13}TC_{aerosol} \times (CO_{2(sample)} - CO_{2(blank)})$$

where $CO_{2(blank)}$ and $CO_{2(sample)}$ are corresponding raw signals in mV of the measured blank (−25.4 ‰) and the sample obtained by IRMS.

Similarly, $\delta^{13}C_{marine}$ was calculated to exclude fossil and continental non-fossil contribution using Eq. (3) and presented in Table 1 and Fig. 4:

$$\delta^{13}TC_{sample} \times CO_{2(sample)} = \delta^{13}TC_{marine} \qquad (3)$$
$$\times (CO_{2(sample)} - CO_{2(anthr)}) + \delta^{13}TC_{anthr} \times CO_{2(anthr)}$$

where CO_2 (non-marine) was calculated from Fig. 2 regression equation taking 50 ng m^{-3} concentration as explained below.

BC measurements (by aethalometer AE16 and multi-angle absorption photometer MAAP) are routinely performed at the Mace Head station and show low but discernable BC levels even in clean air masses. $\Delta^{14}C$ analysis is suggesting the same based on corresponding ratios. We attempted

Table 2. Carbon 14 analyses results.

Date	Episode	OC/TC	Δ^{14}C(TC) [‰]	TC_{nf} [%]	Δ^{14}C(OC) [‰]	OC_{nf} [%]
12–26/04/2006	Clean	0.88±0.03	−176±19	78±2	−89±19*	84
12–15/06/2006	Clean	0.94±0.03	−222±21	73±2	−182±21*	76
05–12/07/2006	Clean	n.d.	−111±22	84±3	−63±22*	87
15–22/11/2006	Clean	0.99±0.11	n.d.	n.d.	n.d.	n.d.
03–10/05/2006	Polluted	n.d.	−366±15	58±3	−281±17	67±2
21–28/09/2006	Polluted	0.85±0.02	−344±14	60±3	−260±14	69±2
11–18/10/2006	Polluted	0.86±0.05	−342±12	60±3	−154±17	78±3

nf is non-fossil

n.d. is not determined/measurement not performed

* Δ^{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.

to calculate marine δ^{13}C ratio assuming a certain amount of carbon being non-marine. The concentration of BC in clean marine air masses is always below 50 ng m^{-3} (in selectively sampled clean marine air masses as outlined in the Methods section), but some of this carbon must be organic carbon (absorption measurements cannot distinguish between black carbon and other absorbing OC species as found by Kanaya et al. (2008) and Lack et al. (2008)). This calculation was based on the assumption that all black carbon was from non-marine sources and had a δ^{13}C ratio of −28±2 ‰ which is independent from the value of −29 ‰ (fossil fuel) and −26 ‰ (continental non-fossil) obtained by error minimisation approach in chapter 2.3. The range of the reference anthropogenic δ^{13}C literature values is rather broad: −29.2 ‰ for black carbon (Rumpel et al., 2006); wildfire origin δ^{13}C value of −30.9 ‰ (Ulevicius et al., 2010); −27.3 ‰ (Huang et al., 2006), −25.6 ‰ (Ho et al., 2006), −26 ‰ (Widory et al., 2004), −27 ‰ (Currie, 2000). However, Bakwin et al. (1998) presented a range of fossil fuel carbon δ^{13}C values from a global network of sites with an average value of −28.3±2.4 ‰ which encompasses all of the above values including the ones of this study (the above value of −28 ‰ and the value of −29 ‰ from Sect. 2.3.). It should be noted that none of the ^{13}C techniques can separate fossil and continental non-fossil sources, therefore, there is an inherent ambiguity about fossil versus continental non-fossil carbon in ^{13}C analysis. Accounting for the variability of δ^{13}C fossil fuel values as −28±2 ‰ a corresponding range of corrected marine δ^{13}C values is presented in Table 1. Some of the corrected marine δ^{13}C values are more negative than the reference value of −20 ‰ derived from dual carbon isotope source apportionment which highlights the aforementioned ambiguity and uncertainty in non-marine carbon concentration of 50 ng m^{-3}.

Stable Isotope Ratio Mass Spectrometer (IRMS) raw CO_2 signal in millivolts (mV) was compared against independent total carbon (TC) analysis (above Sect. 2). A good agreement between TC and CO_2 signal amplitude (m/z 44 signal in mV) presented in Fig. 3 ($r = 0.98$, $P \ll 0.01$) showed that
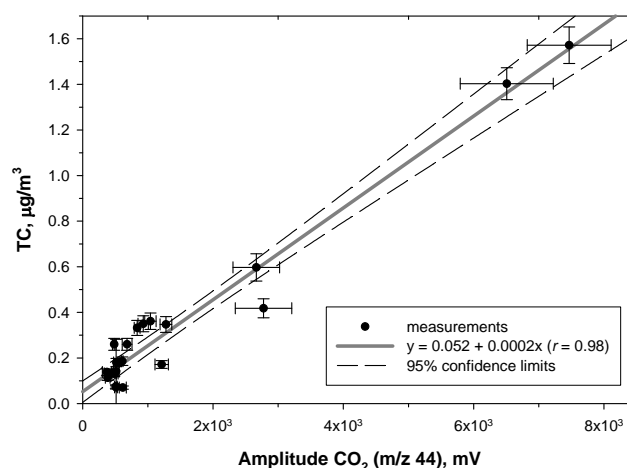

Fig. 3. TC concentration versus IRMS CO_2 (m/z 44) signal amplitude (mV).

IRMS system was well tuned to provide consistent results, even though the IRMS is not designed to provide a quantitative TC concentration.

2.2 ^{14}C analyses

In a similar manner to ^{13}C, Δ^{14}C is calculated from radiocarbon analysis to determine the separation of fossil carbon from non-fossil carbon, which was performed by accelerated mass spectrometry (AMS) (Szidat et al., 2006; Szidat et al., 2009). Three cases each of clean marine and polluted sample sub-sets had sufficient total-carbon loadings to be analysed for Δ^{14}C due to analytical constraints. In addition, Δ^{14}C analysis in polluted samples was also conducted for OC. For clean marine samples, Δ^{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 combusted for ^{14}C analysis from the filters in pure oxygen at 340 °C and 650 °C, respectively

(Szidat et al., 2004; Szidat et al., 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 transferring the mixture it into a cesium sputter gas ion source – constructed for 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 using Eq. (4). Individual sample measurements are summarised in Table 2. The ^{14}C results in Table 2 are accompanied by total uncertainties (around 3–5 %) including contributions from the ^{14}C measurements (mainly from counting statistics) and the correction of the field blank.

$$\Delta^{14}C = \left[\frac{R_{\text{sample(norm)}}}{R_{\text{standard(corr)}}} - 1 \right] \times 1000 \qquad (4)$$

where the ^{13}C isotopic fractionation in the sample, irrespective of environment, is taken into account by normalizing to $\delta^{13}C = -25\,‰$ and the standard is corrected for its decay since the reference year 1950.

The filter blank for ^{14}C analysis was $0.19\,\mu g\,cm^{-2}$ obtained by analyzing $35\,cm^2$ of filter material (mixture of blank 1 and blank 2 filters) gaining approximately $6\,\mu g$ of carbon, with which we successfully performed the ^{14}C analysis. Both values (the amount in $\mu g\,cm^{-2}$ and the ^{14}C result) were attributed with conservatively high uncertainties of 30 % (1 sigma) in order to account for additional blank variability which was not covered by the blank filters.

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:

$$\delta^{13}TC = \delta^{13}TC_{\text{marine}} \times k_1 \qquad (5)$$
$$+ \delta^{13}TC_{\text{cont}} \times k_2 + \delta^{13}TC_{\text{fossil}} \times (1 - k_1 - k_2)$$

$$\Delta^{14}TC = \Delta^{14}TC_{\text{marine}} \times k_1 \qquad (6)$$
$$+ \Delta^{14}TC_{\text{cont}} \times k_2 + \Delta^{14}TC_{\text{fossil}} \times (1 - k_1 - k_2)$$

where k_1, k_2, k_3 are contributions of marine, continental (all non-fossil sources, whether natural or man-made) and fossil fuel sources

The above equations are solved when the calculated isotopic ratios converge to the measured ratios fixing reference source ratios in all sample solutions, but allowing k coefficients to vary for each sample. The above two equations contain two unknowns for each sample and can be explicitly solved. It should be stressed that Eqs. (5) and (6) 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. (5) clearly separates the marine source and Eq. (6) clearly separates the fossil fuel source due to distinctly different source ratios. One can start with any conceivable set of reference source ratios and then fine tune them by error minimisation approach. For marine, continental and fossil sources, the respective $\delta^{13}C$ ratios of $-20\,‰$, $-26\,‰$, $-29\,‰$, and $\Delta^{14}C$ ratios of $-50\,‰$, $100\,‰$, $-1000\,‰$ were obtained. These ratios were obtained using the error minimisation approach according to Eq. (6) until the error was minimised to match the individual analytical error:

$$S_{\text{min}} = \qquad (7)$$
$$\sqrt{\left(\frac{\delta^{13}TC_{\text{calc}} - \delta^{13}TC_{\text{meas}}}{\delta^{13}TC_{\text{meas}}} \right)^2 + \left(\frac{\Delta^{14}TC_{\text{calc}} - \Delta^{14}TC_{\text{meas}}}{\Delta^{14}TC_{\text{meas}}} \right)^2} \times 100$$

where $\delta^{13}TC_{\text{calc}}$ and $\Delta^{14}TC_{\text{calc}}$ are the values obtained by Eqs. (5) and (6) and $\delta^{13}TC_{\text{meas}}$ and $\Delta^{14}TC_{\text{meas}}$ are corresponding measured values.

In the end there was only one unique set of $\delta^{13}C$ and $\Delta^{14}C$ values and corresponding k coefficients to match calculated and measured ratios with the 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 $\delta^{13}C$ values are consistent with literature values of $\delta^{13}C$ and $\Delta^{14}C$ values for marine, continental and fossil fuel sources (Raymond, 2005). The uncertainty of the k coefficients was, indeed, somewhat dependent on the reference source ratio values. By varying reference $\delta^{13}C$ ratios within $\pm 1\,‰$ and $\Delta^{14}C$ ratios within $\pm 50\,‰$, the uncertainty of the k coefficients was typically within 5 %. More of the uncertainty and sensitivity analysis will be discussed later.

3 Results and discussion

The results of the ^{13}C isotope analysis are shown in Fig. 4. The clean marine aerosol samples revealed distinctly different $\delta^{13}C$ isotopic ratios when compared to polluted samples. Marine $\delta^{13}C$ 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 absence of significant seasonal signal, especially when compared winter and summer values, suggests that isotopic fractionation was of limited importance overall as in polluted air masses secondary particle formation processes, condensation and evaporation (all of which should facilitate isotopic fractionation) are established phenomena (Jimenez et al., 2009). The less-negative values of $\delta^{13}C$, corresponding to a higher concentrations of ^{13}C, occur during the period
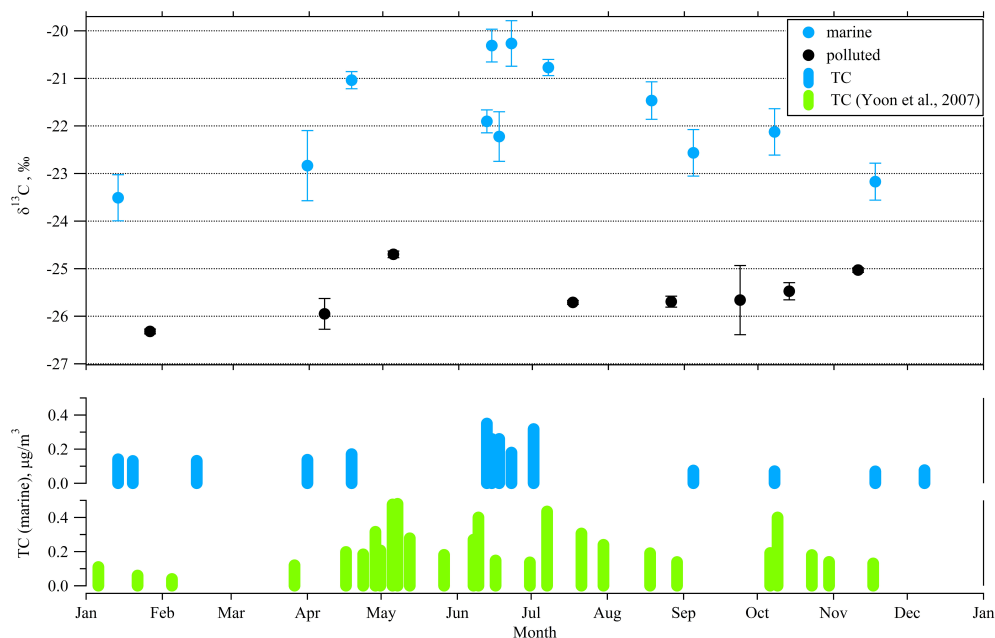
Fig. 4. Seasonal pattern of δ^{13}C in clean marine and polluted samples during 2006 at Mace Head (top). Also shown is the clean marine total carbon concentration (TC) for the 2006 data (middle) and for 2002–2005 (Yoon et al., 2007) (bottom).

of peak organic aerosol enrichment associated with peak bi-
ological activity as has been detailed by Yoon et al. (2007)
whose data are presented for the purpose of consistency. This
enrichment results from carbon isotopic fractionation occur-
ring 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
δ^{13}C to less-negative values during summer results from ac-
celerated plankton carbon fixation during bloom conditions
(Deuser, 1970). Indeed, many of the more recent studies re-
ported less negative δ^{13}C ratios of particulate organic car-
bon (-26.5 to -20.2 ‰) (Bentaleb et al., 1996; Bauer et
al., 2002), 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 are
at their 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 the R/V *Celtic Explorer*
which most likely resulted from mixing of organic material
from greater depths where the competition for inorganic car-
bon is lower. Distribution of δ^{13}C values suggested a lower
estimate of a marine sector δ^{13}C value which should be at
least -20 ‰ or less negative to accommodate any contribu-
tion of terrestrial sources (Table 1). This lower estimate has
a 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 so-
lution of isotope mixing equations also required the marine
δ^{13}C value of -20 ‰, demonstrating consistency between
^{13}C and ^{14}C measurements.

Using Eq. (5) it is possible to separate the marine source
contribution to total organic carbon using only δ^{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 a significant over-
lap of δ^{13}C values of continental non-fossil and fossil fuel
sources and no constrain on δ^{13}C values of either marine or
continental (non-fossil + fossil) sources (Eq. 2). Following
the above considerations and unconstrained δ^{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 δ^{13}C values we obtain a large
uncertainty in marine source contribution. Therefore, with-
out Δ^{14}C it is impossible to separate the contribution of fossil
fuel sources and thereby continental non-fossil sources. In a
similar way it is not possible to separate the marine sources
using Δ^{14}C data alone. Combining both isotopes allows for
a separation of all three sources in a tightly constrained man-
ner. Using Eqs. (5) and (6) and a subset of six samples
where both isotope ratios were measured, the contribution
of the three principal sources was estimated and presented
in Fig. 5a. For three of the marine samples, between 70 %
and 84 % is marine organic, the remainder being fossil fuel
carbon (8–20 %) and continental non-fossil carbon (4–10 %).
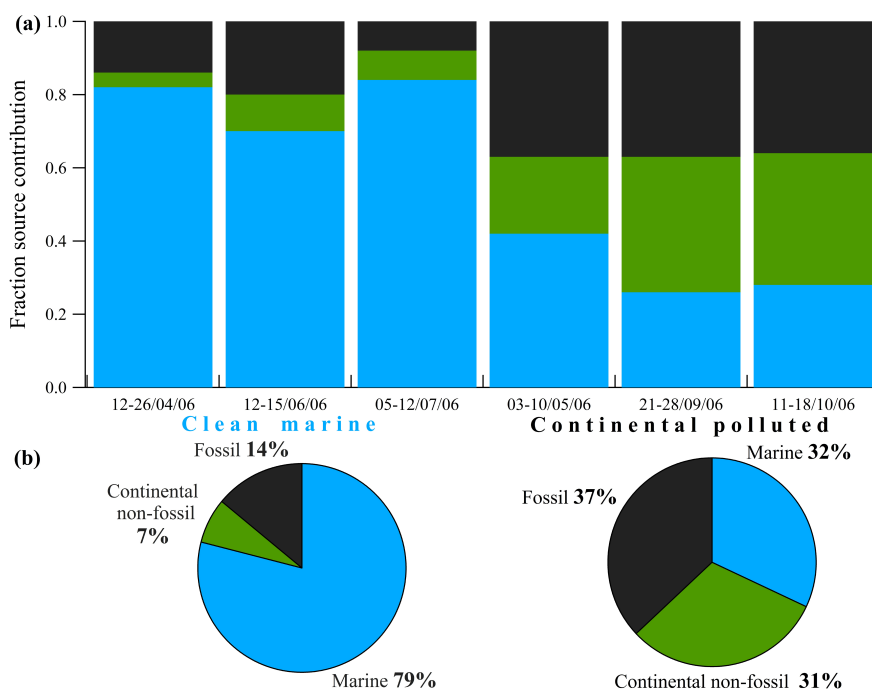Table 2 exhibits similar results based on Δ^{14}C data (within

Fig. 5. (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 for average source contributions over all samples for marine and continental air masses.

the uncertainty range) given the absence of continental non-fossil source. This marine contribution even makes up to 76–87 % if considering only the OC fraction (Table 2). A small fraction of continental non-fossil source is likely a remainder of North American emissions, while additional fossil fuel source present in clean marine samples (since it is larger than continental non-fossil source) could be from shipping fossil fuel combustion.

By contrast, non-marine (polluted to a different degree) samples comprised between 21 % and 37 % of continental non-fossil carbon and about 37 % fossil fuel carbon with the remainder being attributed to marine carbon (26 to 42 %). There was a certain degree of variability from sample to sample in both clean marine and polluted sample subsets; however, within the subsets samples were similar to each other. On average, as shown in Fig. 5b, carbon in marine samples comprised 79 % marine biogenic carbon, 14 % fossil fuel carbon and 7 % continental non-fossil carbon while in non-marine air masses 37 % are attributed to fossil fuel, 31 % continental (non-fossil carbon) and 32 % marine biogenic carbon. The presence of a 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 (continental non-fossil and fossil fuel) sources.

Regarding the contribution of non-fossil sources in polluted air masses we observe about 60 % of non-fossil carbon which is in agreement with the study of Hodzic et al. (2010). However, that same 60 % is split between marine and continental non-fossil sources, reducing the contribution of the latter. Indeed, in many continental locations, marine source contribution would be negligible, but that is not the case in Ireland which is an island surrounded by biologically active waters in the North Sea, the English Channel and the Irish Sea.

We can hypothesize several reasons for the relatively large contribution of fossil sources in continental air masses (especially during the warm season). Firstly, the United Kingdom (UK) and Ireland have very little forested areas (under 10 % in Ireland and just over 10 % in the United Kingdom compared to an average of 46 % in continental Europe) with even lower percentage of true forest ecosystems. It is well established that forests contribute significantly to SOA formation (Carslaw et al., 2010). Secondly, intensive shipping in the English Channel and the Irish Sea can contribute additional fossil carbon to that originating from traffic. The latter can be supported by the fact that in the same air masses passing over the sea we observe significant contribution of marine sources, presumably from English Channel and the Irish Sea. Continental air masses passing over relatively bare land (mainly grasslands) and intensive shipping areas, can possibly explain the observed pattern. It is worth noting, however, that Heal et al. (2011) also observed large percentage of

fossil fuel source over the British Midlands up to and above of 50 %.

The other reason for a relatively large contribution of a fossil fuel source in polluted air masses can be the low solubility of particles containing larger percentage of fossil fuel carbon (assuming larger contribution of elemental carbon and significant degree of external mixture). The particles containing continental non-fossil carbon would be more soluble and conceivably derived from secondary processes, facilitating a more efficient washout from the boundary layer.

This study is a continuation of experimental work on sources and chemical composition of marine aerosols being performed at Mace Head over the last decade or more, but this time using a combination of dual carbon isotope analysis. The concept of clean marine air masses being sampled at Mace Head has been discussed in several papers (Cavalli et al., 2004; Yoon et al., 2007; Rinaldi et al., 2010) showing typical air mass back-trajectories and discussing various elemental tracers. This time in addition to back-trajectories (Fig. 1), demonstrating that clean marine air masses (sampled in this study) had no contact with land for at least 5 days before advecting at Mace Head and spent the last three-to-four days in the boundary layer, we show that our classified marine aerosol also exhibited extremely low radon concentrations (^{222}Rn $\sim$100–200 mBq m^{-3} and ^{220}Rn $\sim$1–2 mBq m^{-3}) (Table 3). The latter fact is a quantitative proof of truly marine air masses with no contact with land for about a week (e.g. Biraud et al., 2000). Considering ^{222}Rn concentration in polluted (continental) air masses of the order of several thousands of mBq m^{-3}, values presented for marine samples are generally less then 10 % of the continental ones. Allocating some of the ^{222}Rn measured in marine air masses to continental shelf emissions (upwind of Mace Head) leaves room for extremely low contribution of North American continental aerosol in clean marine air masses sampled at Mace Head. Our results suggest that the North Atlantic marine boundary layer can be exceptionally clean and largely devoid of anthropogenic material even in the generally polluted Northern Hemisphere most likely due to both dry and wet deposition during long-range transport across the North Atlantic Ocean. Indeed, the situation can be different above the boundary layer where the absence of vigorous mixing and often clouds can preserve significant amounts of the terrestrial carbon.

Previous studies of marine aerosol δ^{13}C ratios have indicated marine sources significantly contributing to submicron carbonaceous aerosol: 20 % in the submicron mode and 80 % in the supermicron (Chesselet et al., 1981); 38 % in both the sub- and super-micron modes (Turekian et al., 2003); 45 % in the sub-micron mode (Narukawa et al., 2008); 46–72 % in the sub-micron mode (Miyazaki et al., 2010). All those studies only used δ^{13}C ratios and were conducted under conditions of varying degrees 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

Table 3. Radon concentration (mBq m^{-3}) during clean marine sampling periods presented in Fig. 4 of the paper.

Sample period	^{222}Rn	^{220}Rn
11–18/01/2006	191	0.1
29/03–05/04/2006	n.d.	n.d.
12–26/04/2006	n.d.	n.d.
12–19/06/2006	n.d.	n.d.
19–28/06/2006	145	2.53
12–15/06/2006	n.d.	n.d.
16–20/06/2006	136	0.88
05–12/07/2006	223	1.23
16–23/08/2006	166	2.36
03–08/09/2006	123	0.68
05–11/10/2006	167	0.44
15–22/11/2006	60	0.1

n.d. no data

studies but, our results for clean marine air (up to 84 % of carbon was deemed to be marine in origin) are in contrast to these studies as a result of the unique combinations of both δ^{13}C and Δ^{14}C ratios and strict classification of clean marine air masses.

These results are the first quantitative estimates of the magnitude of marine versus anthropogenic source in marine aerosol and they are very well in line with other measurements performed at the site (Cavalli et al., 2004; O'Dowd et al., 2004; Yoon et al., 2007; Dall'Osto et al., 2010) where a dominant contribution of biogenic organic matter to marine aerosol during periods of high biological activity in oceanic surface waters has been demonstrated. The latest study presented by Ovadnevaite et al. (2011) has revealed an even higher contribution of primary biogenic organic matter to marine aerosol (2–3 µg m^{-3}). This contribution is far greater than previously determined by off-line measurement techniques and can even exceed typical terrestrial concentrations (1–3 µg m^{-3}) (Dall'Osto et al., 2010). More specifically, an almost negligible contribution of aromatic compounds in clean marine air masses (Cavalli et al., 2004) compares well with a small percentage of fossil fuel source quantified in this study. Also, significant contribution of MSA in regionally polluted air masses (Dall'Osto et al., 2010) supports a significant contribution of marine source in polluted air masses.

3.1 Sensitivity and uncertainty analysis

It was mentioned above that the uncertainty of source specific contributions was, indeed, somewhat dependent on the selected reference source values. However, by varying reference δ^{13}C ratios within ±1 ‰ and the Δ^{14}C ratio within ±50 ‰, the uncertainty of source specific contributions was typically within 5 %, suggesting that the dual isotope method was rather insensitive to the reference delta values of both isotopes.

The range of marine δ^{13}C values found in the literature is from $-18‰$ to $-23‰$ (Williams and Gordon, 1970; Bauer et al., 2002). Quite clearly, a reference marine source δ^{13}C value of $-23‰$ can not apply as clean marine samples collected during summer had heavier isotope values without even correcting for anthropogenic influence. Polluted samples could utilise isotope value of $-23‰$, however, we strongly believe that same reference marine source δ^{13}C value should apply for all clean and polluted samples. If we used $-23‰$ δ^{13}C value in marine samples, we would obtain a discrepancy between measurements and calculations in excess of 1‰, which is beyond any conceivable analytical error. It is possible to accommodate a marine source δ^{13}C value of $-18‰$, but in this case continental non-fossil and fossil fuel source values would have to be even more negative than the ones used in this study in order to bring closure to the equations. However, a fossil fuel source value of $-29‰$ is already at the lower negative end of literature values as discussed above. The source apportionment was, however, quite insensitive to a small variation of either continental non-fossil or fossil fuel source values, as by definition the ^{13}C method cannot reliably distinguish between continental non-fossil and fossil fuel sources. After all, Bakwin et al. (1998) presented a range of fossil fuel carbon δ^{13}C values from a global network of sites with an average value of $-28.3\pm2.4‰$, which encompasses both of our values, $-26‰$ and $-29‰$.

A non-modern ^{14}C value of the reference marine source ($-50‰$) may seem unexpected, but we believe it can be justified. Beaupre and Druffel (2009) indicated for the Pacific Ocean near California that Δ^{14}C values for surface ocean waters were stable from 1991–2004. Assuming that this is valid for the Atlantic Ocean, we can take the values from Bauer et al. (2002) without correction so that Δ^{14}C for Mace Head should be considered as -170 (±80)‰. However, these are the values not from the open ocean but from coastal (shallow) waters and from the slope ($\sim$100km from the coast). Taking only the slope values, which are closer to the open ocean conditions, we calculate a value -210 (±60)‰. This shows that open ocean might even be lower. Δ^{14}C (POC) and Δ^{14}C (DIC) were 30‰ and 60‰ respectively for the slope and thus also slightly lower than the biogenic value of the atmosphere, which was 120‰ in 1994. In conclusion, we should assume for our campaign $-210‰$ for DOC (slope waters from Bauer et al. (2002) without any correction for the time between 1994 and 2006), $+30‰$ for DIC (value from Beaupre and Druffel (2009) for 2004 – differences between Pacific and Atlantic Ocean should be negligible for DIC) and 0‰ for POC (if DIC decreases by 30‰ within the 10 years, we can justify the same for POC). A reference selected value of $-50‰$ would lead to a POC vs. DOC ratio of $\sim$3:1 following a dominant contribution, in sea spray samples, of water insoluble organic carbon attributed to POC (Facchini et al., 2008b).

4   Conclusions

Dual carbon isotope analysis method was applied to a subset of six clean marine and polluted aerosol 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 fine carbonaceous particles in clean marine air over the N.E. Atlantic albeit based on a limited number of samples. 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. Marine sources can contribute around 30% to the amount of total carbon in polluted air masses sampled at Mace Head which has not been quantified so far. The presence of marine source in polluted air masses should not be neglected even though its absolute magnitude may be relatively low.

References

Avery, G. B., Willey, J. D., and Kieber, R. J.: Carbon isotopic characterization of dissolved organic carbon in rainwater: Terrestrial and marine influences, Atmos. Environ., 40, 7539–7545, doi:10.1016/j.atmosenv.2006.07.014, 2006.

Bakwin, P. S., Tans, P. P., White, J. W. C., and Andres, R. J.: Determination of the isotopic (C-13/C-12) discrimination by terrestrial biology from a global network of observations, Global Biogeochem. Cy., 12, 555–562, 1998.

Bauer, J. E., Druffel, E. R. M., Wolgast, D. M., and Griffin, S.: Temporal and regional variability in sources and cycling of DOC and POC in the northwest Atlantic continental shelf and slope, Deep-Sea Res. Part II-Top. Stud. Oceanogr., 49, 4387–4419, 2002.

Beaupre, S. R. and Druffel, E. R. M.: Constraining the propagation of bomb-radiocarbon through the dissolved organic carbon (DOC) pool in the northeast Pacific Ocean, Deep-Sea Res., 56, 1717–1726, doi:10.1016/j.dsr.2009.05.008, 2009.

Bentaleb, I., Fontugne, M., Descolas Gros, C., Girardin, C., Mariotti, A., Pierre, C., Brunet, C., and Poisson, A.: Organic carbon isotopic composition of phytoplankton and sea-surface pCO$_{(2)}$ reconstructions in the Southern Indian Ocean during the last 50,000 yr, Org. Geochem., 24, 399–410, 1996.

Benthien, A., Zondervan, I., Engel, A., Hefter, J., Terbruggen, A., and Riebesell, U.: Carbon isotopic fractionation during a mesocosm bloom experiment dominated by Emiliania huxleyi: Effects of CO2 concentration and primary production, Geochim. Cosmochim. Ac., 71, 1528–1541, doi:10.1016/j.gca.2006.12.015, 2007.

Biraud, S., Ciais, P., Ramonet, M., Simmonds, P., Kazan, V., Monfray, P., O'Doherty, S., Spain, T. G., and Jennings, S. G.: European greenhouse gas emissions estimated from continuous atmospheric measurements and radon 222 at Mace Head, Ireland, J. Geophys. Res.-Atmos., 105, 1351–1366, 2000.

Blanchard, D. C.: Sea-to-air transport of surface active material, Science, 146, 396–397, 1964.

Cachier, H.: Isotopic characterization of carbonaceous aerosols, Aerosol Sci. Tech., 10, 379–385, 1989.

Carslaw, K. S., Boucher, O., Spracklen, D. V., Mann, G. W., Rae, J. G. L., Woodward, S., and Kulmala, M.: A review of natural aerosol interactions and feedbacks within the Earth system, Atmos. Chem. Phys., 10, 1701–1737, doi:10.5194/acp-10-1701-2010, 2010.

Cavalli, F., Facchini, M. C., Decesari, S., Mircea, M., Emblico, L., Fuzzi, S., Ceburnis, D., Yoon, Y. J., O'Dowd, C. D., Putaud, J. P., and Dell'Acqua, A.: Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, J. Geophys. Res.-Atmos., 109, D24215, doi:10.1029/2004jd005137, 2004.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J. P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, Atmos. Meas. Tech., 3, 79–89, doi:10.5194/amt-3-79-2010, 2010.

Charlson, R. J., Lovelock, J. E., Andreae, M. O., and Warren, S. G.: Oceanic phytoplankton, atmospheric sulfur, cloud albedo and climate, Nature, 326, 655–661, 1987.

Chesselet, R., Fontugne, M., Buatmenard, P., Ezat, U., and Lambert, C. E.: The origin of particulate organic carbon in the marine atmosphere as indicated by its stable carbon isotopic composition, Geophys. Res. Lett., 8, 345–348, 1981.

Currie, L. A.: Evolution and multidisciplinary frontiers of C-14 aerosol science, Radiocarbon, 42, 115–126, 2000.

Currie, L. A.: The remarkable metrological history of radiocarbon dating II, J. Res. Natl. Inst. Stand. Technol., 109, 185–217, 2004.

Dall'Osto, M., Ceburnis, D., Martucci, G., Bialek, J., Dupuy, R., Jennings, S. G., Berresheim, H., Wenger, J., Healy, R., Facchini, M. C., Rinaldi, M., Giulianelli, L., Finessi, E., Worsnop, D., Ehn, M., Mikkila, J., Kulmala, M., and O'Dowd, C. D.: Aerosol properties associated with air masses arriving into the North East Atlantic during the 2008 Mace Head EUCAARI intensive observing period: an overview, Atmos. Chem. Phys., 10, 8413–8435, doi:10.5194/acp-10-8413-2010, 2010.

Degens, E. T., Guillard, R. R., Sackett, W. M., and Hellebus, J. A.: Metabolic fractionation of carbon isotopes in marine plankton I. Temperature and respiration experiments, Deep-Sea Res., 15, 1–9, 1968.

Deuser, W. G.: Isotopic evidence for diminishing supply of available carbon during diatom bloom in Black-Sea, Nature, 225, 1069–1071, 1970.

Draxler, R. R. and Hess, G. D.: Description of the Hysplit_4 modeling system, NOAA Tech. Memo, ERL ARL-224, 24 pp., 1997.

Facchini, M. C., Decesari, S., Rinaldi, M., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Moretti, F., Tagliavini, E., Ceburnis, D., and O'Dowd, C. D.: Important Source of Marine Secondary Organic Aerosol from Biogenic Amines, Environ. Sci. Technol., 42, 9116–9121, doi:10.1021/Es8018385, 2008a.

Facchini, M. C., Rinaldi, M., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Flanagan, R., Nilsson, E. D., de Leeuw, G., Martino, M., Woeltjen, J., and O'Dowd, C. D.: Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, Geophys. Res. Lett., 35, L17814, doi:10.1029/2008gl034210, 2008b.

Fisseha, R., Saurer, M., Jaggi, M., Szidat, S., Siegwolf, R. T. W., and Baltensperger, U.: Determination of stable carbon isotopes of organic acids and carbonaceous aerosols in the atmosphere, Rapid Commun. Mass Spectrom., 20, 2343–2347, doi:10.1002/rcm.2586, 2006.

Garbaras, A., Andriejauskien, J., Bariseviciute, R., and Remeikis, V.: Tracing of atmospheric aerosol sources using stable carbon isotopes, Lith. J. Phys., 48, 259–264, doi:10.3952/lithjphys.48309, 2008.

Garbaras, A., Rimselyte, I., Kvietkus, K., and Remeikis, V.: Delta C-13 values in size-segregated atmospheric carbonaceous aerosols at a rural site in Lithuania, Lith. J. Phys., 49, 229–236, doi:10.3952/lithjphys.49202, 2009.

Gelencser, A., May, B., Simpson, D., Sanchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., and Legrand, M.: Source apportionment of PM2.5 organic aerosol over Europe: Primary/secondary, natural/anthropogenic, and fossil/biogenic origin, J. Geophys. Res.-Atmos., 112, D23S04, doi:10.1029/2006jd008094, 2007.

Gilardoni, S., Vignati, E., Cavalli, F., Putaud, J. P., Larsen, B. R., Karl, M., Stenstrm, K., Genberg, J., Henne, S., and Dentener, F.: Better constraints on sources of carbonaceous aerosols using a combined ^{14}C-macro tracer analysis in a European rural background site, Atmos. Chem. Phys., 11, 5685–5700, doi:10.5194/acp-11-5685-2011, 2011.

Gustafsson, O., Krusa, M., Zencak, Z., Sheesley, R. J., Granat, L., Engstrom, E., Praveen, P. S., Rao, P. S. P., Leck, C., and Rodhe, H.: Brown Clouds over South Asia: Biomass or Fossil Fuel Combustion?, Science, 323, 495–498, doi:10.1126/science.1164857, 2009.

Heal, M. R., Naysmith, P., Cook, G. T., Xu, S., Duran, T. R., and Harrison, R. M.: Application of C^{-14} analyses to source apportionment of carbonaceous $PM_{2.5}$ in the UK, Atmos. Environ., 45, 2341–2348, doi:10.1016/j.atmosenv.2011.02.029, 2011.

Ho, K. F., Lee, S. C., Cao, J. J., Li, Y. S., Chow, J. C., Watson, J. G., and Fung, K.: Variability of organic and elemental carbon, water soluble organic carbon, and isotopes in Hong Kong, Atmos. Chem. Phys., 6, 4569–4576, doi:10.5194/acp-6-4569-2006, 2006.

Hodzic, A., Jimenez, J. L., Prevot, A. S. H., Szidat, S., Fast, J. D., and Madronich, S.: Can 3-D models explain the observed fractions of fossil and non-fossil carbon in and near Mexico City?, Atmos. Chem. Phys., 10, 10997–11016, doi:10.5194/acp-10-10997-2010, 2010.

Hoefs, J.: Stable Isotope Geochemistry, Springer-Verlag, Berlin Heidelberg, 285 pp., 2009.

Hoffman, E. J. and Duce, R. A.: Organic-carbon in marine atmospheric particulate matter – concentration and particle-size dis-

tribution, Geophys. Res. Lett., 4, 449–452, 1977.

Huang, L., Brook, J. R., Zhang, W., Li, S. M., Graham, L., Ernst, D., Chivulescu, A., and Lu, G.: Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment, Atmos. Environ., 40, 2690–2705, doi:10.1016/j.atmosenv.2005.11.062, 2006.

Jennings, S. G., Kleefeld, C., O'Dowd, C. D., Junker, C., Spain, T. G., O'Brien, P., Roddy, A. F., and O'Connor, T. C.: Mace head atmospheric research station characterization of aerosol radiative parameters, Boreal Environ. Res., 8, 303–314, 2003.

Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., Dunlea, E. J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.

Kanaya, Y., Komazaki, Y., Pochanart, P., Liu, Y., Akimoto, H., Gao, J., Wang, T., and Wang, Z.: Mass concentrations of black carbon measured by four instruments in the middle of Central East China in June 2006, Atmos. Chem. Phys., 8, 7637–7649, doi:10.5194/acp-8-7637-2008, 2008.

Kawamura, K. and Sakaguchi, F.: Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics, J. Geophys. Res.-Atmos., 104, 3501–3509, 1999.

Kim, M. K., Kennicutt, M. C., and Qian, Y. R.: Polycyclic aromatic hydrocarbon purification procedures for compound specific isotope analysis, Environ. Sci. Technol., 39, 6770–6776, doi:10.1021/es050577m, 2005.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R., and Ravishankara, A. R.: Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, Aerosol Sci. Tech., 42, 1033–1041, doi:10.1080/02786820802389277, 2008.

Li, Q. A., Wang, W., Zhang, H. W., Wang, Y. J., Wang, B., Li, L., Li, H. J., Wang, B. J., Zhan, J., Wu, M., and Bi, X. H.: Development of a Compound-Specific Carbon Isotope Analysis Method for 2-Methyltetrols, Biomarkers for Secondary Organic Aerosols from Atmospheric Isoprene, Anal. Chem., 82, 6764–6769, doi:10.1021/ac100214p, 2010.

Loh, A. N., Bauer, J. E., and Druffel, E. R. M.: Variable ageing and storage of dissolved organic components in the open ocean, Nature, 430, 877–881, doi:10.1038/nature02780, 2004.

Maberly, S. C., Raven, J. A., and Johnston, A. M.: Discrimination between C-12 and C-13 by marine plants, Oecologia, 91, 481–492, 1992.

McArdle, B. H.: The structural relationship – regression in biology,

Can. J. Zool.-Rev. Can. Zool., 66, 2329–2339, 1988.

Middlebrook, A. M., Murphy, D. M., and Thomson, D. S.: Observations of organic material in individual marine particles at Cape Grim during the First Aerosol Characterization Experiment (ACE 1), J. Geophys. Res.-Atmos., 103, 16475–16483, 1998.

Miyazaki, Y., Kawamura, K., and Sawano, M.: Size distributions of organic nitrogen and carbon in remote marine aerosols: Evidence of marine biological origin based on their isotopic ratios, Geophys. Res. Lett., 37, L06803, doi:10.1029/2010gl042483, 2010.

Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., and Suzuki, K.: Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea-salt particles, J. Geophys. Res.-Atmos., 107, 4325, doi:10.1029/2001jd001278, 2002.

Narukawa, M., Kawamura, K., Li, S. M., and Bottenheim, J. W.: Stable carbon isotopic ratios and ionic composition of the high-Arctic aerosols: An increase in delta C-13 values from winter to spring, J. Geophys. Res.-Atmos., 113, D02312, doi:10.1029/2007jd008755, 2008.

O'Connor, T. C., Jennings, S. G., and O'Dowd, C. D.: Highlights of fifty years of atmospheric aerosol research at Mace Head, Atmos. Res., 90, 338–355, doi:10.1016/j.atmosres.2008.08.014, 2008.

O'Dowd, C. D., Facchini, M. C., Cavalli, F., Ceburnis, D., Mircea, M., Decesari, S., Fuzzi, S., Yoon, Y. J., and Putaud, J. P.: Biogenically driven organic contribution to marine aerosol, Nature, 431, 676–680, doi:10.1038/Nature02959, 2004.

Oppo, C., Bellandi, S., Innocenti, N. D., Stortini, A. M., Loglio, G., Schiavuta, E., and Cini, R.: Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols, Mar. Chem., 63, 235–253, 1999.

Ovadnevaite, J., O'Dowd, C., Dall'Osto, M., Ceburnis, D., Worsnop, D. R., and Berresheim, H.: Detecting high contributions of primary organic matter to marine aerosol: A case study, Geophys. Res. Lett., 38, L02807, doi:10.1029/2010gl046083, 2011.

Raymond, P. A.: The composition and transport of organic carbon in rainfall: Insights from the natural (C^{-13} and C^{-14}) isotopes of carbon, Geophys. Res. Lett., 32, L14402, doi:10.1029/2005gl022879, 2005.

Rinaldi, M., Facchini, M. C., Decesari, S., Carbone, C., Finessi, E., Mircea, M., Fuzzi, S., Ceburnis, D., Ehn, M., Kulmala, M., de Leeuw, G., and O'Dowd, C. D.: On the representativeness of coastal aerosol studies to open ocean studies: Mace Head – a case study, Atmos. Chem. Phys., 9, 9635–9646, doi:10.5194/acp-9-9635-2009, 2009.

Rinaldi, M., Decesari, S., Finessi, E., Giulianelli, L., Carbone, C., Fuzzi, S., O'Dowd, C. D., Ceburnis, D., and Facchini, M. C.: Primary and secondary organic marine aerosol and oceanic biological activity: recent results and new perspectives for future studies, Adv. Meteorol., 310682, doi:10.1155/2010/310682, 2010.

Ruff, M., Wacker, L., Gaggeler, H. W., Suter, M., Synal, H. A., and Szidat, S.: A gas ion source for radiocarbon measurements at 200 kV, Radiocarbon, 49, 307–314, 2007.

Rumpel, C., Alexis, M., Chabbi, A., Chaplot, V., Rasse, D. P., Valentin, C., and Mariotti, A.: Black carbon contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture, Geoderma, 130, 35–46, doi:10.1016/j.geoderma.2005.01.007, 2006.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates, T. S.: Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, P. Natl. Acad. Sci. USA, 107, 6652–6657, doi:10.1073/pnas.0908905107, 2010.

Sciare, J., Favez, O., Sarda-Esteve, R., Oikonomou, K., Cachier, H., and Kazan, V.: Long-term observations of carbonaceous aerosols in the Austral Ocean atmosphere: Evidence of a biogenic marine organic source, J. Geophys. Res.-Atmos., 114, D15302, doi:10.1029/2009jd011998, 2009.

Shaw, G. E.: Bio-controlled thermostasis involving the sulfur cycle, Clim. Change, 5, 297–303, 1983.

Smith, B. N. and Epstein, S.: 2 categories of C-13/C-12 ratios for higher plants, Plant Physiol., 47, 380–384, 1971.

Stuiver, M. and Polach, H. A.: Reporting of C^{-14} data – Discussion, Radiocarbon, 19, 355–363, 1977.

Szidat, S., Jenk, T. M., Gaggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., Kalberer, M., Samburova, V., Wacker, L., Saurer, M., Schwikowski, M., and Hajdas, I.: Source apportionment of aerosols by C^{-14} measurements in different carbonaceous particle fractions, Radiocarbon, 46, 475–484, 2004.

Szidat, S., Jenk, T. M., Synal, H. A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by C^{-14} , J. Geophys. Res.-Atmos., 111, D07206, doi:10.1029/2005jd006590, 2006.

Szidat, S., Ruff, M., Perron, N., Wacker, L., Synal, H. A., Hallquist, M., Shannigrahi, A. S., Yttri, K. E., Dye, C., and Simpson, D.: Fossil and non-fossil sources of organic carbon (OC) and elemental carbon (EC) in Goteborg, Sweden, Atmos. Chem. Phys., 9, 1521–1535, doi:10.5194/acp-9-1521-2009, 2009.

Turekian, V. C., Macko, S. A., and Keene, W. C.: Concentrations, isotopic compositions, and sources of size-resolved, particulate organic carbon and oxalate in near-surface marine air at Bermuda during spring, J. Geophys. Res.-Atmos., 108, 4157, doi:10.1029/2002jd002053, 2003.

Ulevicius, V., Bycenkiene, S., Remeikis, V., Garbaras, A., Kecorius, S., Andriejauskiene, J., Jasineviciene, D., and Mocnik, G.: Characterization of pollution events in the East Baltic region affected by regional biomass fire emissions, Atmos. Res., 98, 190–200, doi:10.1016/j.atmosres.2010.03.021, 2010.

Usdowski, E. and Hoefs, J.: C^{-13}/C^{-12} fractionation during the chemical absorption of CO2 gas by the NH3-NH4CL buffer, Chem. Geol., 73, 79–85, 1988.

Wang, H. B. and Kawamura, K.: Stable carbon isotopic composition of low-molecular-weight dicarboxylic acids and ketoacids in remote marine aerosols, J. Geophys. Res.-Atmos., 111, D07304, doi:10.1029/2005jd006466, 2006.

Widory, D., Roy, S., Le Moullec, Y., Goupil, G., Cocherie, A., and Guerrot, C.: The origin of atmospheric particles in Paris: a view through carbon and lead isotopes, Atmos. Environ., 38, 953–961, doi:10.1016/j.atmosenv.2003.11.001, 2004.

Williams, P. M. and Gordon, L. I.: C-13-C-12 ratios in dissolved and particulate organic matter in sea, Deep-Sea Res., 17, 19–27, 1970.

Yoon, Y. J., Ceburnis, D., Cavalli, F., Jourdan, O., Putaud, J. P., Facchini, M. C., Decesari, S., Fuzzi, S., Sellegri, K., Jennings, S. G., and O'Dowd, C. D.: Seasonal characteristics of the physicochemical properties of North Atlantic marine atmospheric aerosols, J. Geophys. Res.-Atmos., 112, D04206, doi:10.1029/2005jd007044, 2007.

Zhang, L. W., Bai, Z. P., You, Y., Wu, J. H., Feng, Y. C., and Zhu, T.: Chemical and stable carbon isotopic characterization for PAHs in aerosol emitted from two indoor sources, Chemosphere, 75, 453–461, doi:10.1016/j.chemosphere.2008.12.063, 2009.