MICROGRAM-LEVEL RADIOCARBON DETERMINATION OF CARBONACEOUS PARTICLES IN FIRN AND ICE SAMPLES: PRETREATMENT AND OC/EC SEPARATION

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ABSTRACT. Carbonaceous particles that comprise organic carbon (OC) and elemental carbon (EC) are of increasing interest in climate research because of their influence on the radiation balance of the Earth. The radiocarbon determination of particulate OC and EC extracted from ice cores provides a powerful tool to reconstruct the long-term natural and anthropogenic emissions of carbonaceous particles. However, this ^{14}C-based source apportionment method has not been applied for the firn section, which is the uppermost part of Alpine glaciers with a typical thickness of up to 50 m. In contrast to glacier ice, firn samples are more easily contaminated through drilling and handling operations. In this study, an alternative decontamination method for firn samples consisting of chiselling off the outer parts instead of rinsing them was developed and verified. The obtained procedural blank of 2.8 ± 0.8 µg C for OC is a factor of 2 higher compared to the rinsing method used for ice, but still relatively low compared to the typical OC concentration in firn samples from Alpine glaciers. The EC blank of 0.3 ± 0.1 µg C is similar for both methods. For separation of OC and EC for subsequent ^{14}C analysis, a thermal-optical method instead of the purely thermal method was applied for the first time to firn and ice samples, resulting in a reduced uncertainty of both the mass and ^{14}C determination. OC and EC concentrations as well as their corresponding fraction of modern for firn and ice samples from Fiescherhorn and Jungfraujoch agree well with published results, validating the new method.

INTRODUCTION

Carbonaceous particles are of increasing interest in climate research because of their influence on the radiation balance of the Earth (IPCC 2007). The total carbon (TC) of carbonaceous particles can operationally be divided into 2 main fractions: weakly refractory organic carbon (OC) consisting of light polycyclic or poly-acidic hydrocarbons; and strongly refractory, highly polymerized, and light-absorbing elemental carbon (EC) or black carbon (BC) (Pöschl 2005). OC is either emitted as primary aerosol particles or is formed from gaseous precursors as secondary organic aerosols from both non-fossil (i.e. biogenic and biomass burning) and fossil sources, while EC derives from incomplete combustion of fossil fuels and biomass (Pöschl 2005). Ambient concentrations of carbonaceous particles have only been determined for the most recent period, whereas little is known about past natural or anthropogenic emissions of OC and EC. For assessing the role of carbonaceous particles in climate change, the inventories of OC and EC emissions, based on wood and fossil-fuel consumption data, are mostly used. However, these inventories are difficult to obtain, especially in the past, and can vary greatly through time and with location, leading to a large uncertainty. Thus, long-term historical records of concentrations of carbonaceous particles and their sources are in high demand.

^{14}C analysis of OC and EC offers a unique and powerful tool for unambiguous distinction between contemporary and fossil sources of carbonaceous particles since the non-fossil carbon contains ^{14}C at a contemporary and known concentration whereas fossil carbon is extinct in ^{14}C due to its half-

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life of 5730 yr (Currie 2000; Szidat et al. 2004a). The ^{14}C-based source apportionment tool has not only been applied for atmospheric aerosols (Szidat et al. 2009, these proceedings; Minguillón et al. 2011) but also for carbonaceous particles in ice cores (Jenk et al. 2006, 2007). The concentrations of OC and EC as well as the corresponding ^{14}C values in ice cores allow a distinction and quantification of natural (biogenic) and anthropogenic (fossil) contributions to carbonaceous particles in the past, which potentially helps to overcome the lack of long-term carbonaceous particle emission data. However, this method has not been applied to the firn part of ice cores, representing the uppermost 10~50 m with lower density and higher porosity. Because of its higher porosity, firn is more prone to contamination during drilling and handling operations than compact ice. Furthermore, the decontamination step used for ice samples, consisting of removing the outer, potentially contaminated layer by rinsing with ultrapure water, cannot be applied to firn. As a consequence, application of the ^{14}C method has been limited to ice samples and has not covered the most recent period overlapping with direct atmospheric data yet.

Separation of OC and EC for subsequent ^{14}C analysis is usually achieved by a 2-step heating process based on different thermal and chemical properties of OC and EC (Szidat et al. 2004b; Zhang et al. 2010). However, with this method both positive (OC charring) and negative artifacts (premature EC removal) have been observed, potentially leading to significant biases in determination of OC and EC mass and their ^{14}C content. This was recently improved by a thermal-optical method (Zhang et al. 2012) utilizing both the special thermal and optical properties of OC and EC, thereby optimizing both the quantification and isolation of OC and EC.

In this work, we contribute to the aim of establishing long-term historical records of concentrations of carbonaceous particles and their sources with 2 method developments: 1) We introduced an alternative decontamination procedure for application on firn samples consisting of chiselling off the outer parts of the firn instead of rinsing as used for ice samples; 2) We applied the thermal-optical separation of particulate OC and EC recently developed for aerosol samples (Zhang et al., these proceedings) to firn and ice samples for ^{14}C determination, in contrast to the purely thermal separation that has been used so far.

EXPERIMENTAL

Sample Preparation

The method for separating the organic (OC) and elemental carbon (EC) fraction of carbonaceous particles for subsequent ^{14}C analysis was initially developed for ambient aerosol samples (Szidat et al. 2004a,b, 2006, 2009), and has been adapted to ice samples (Jenk et al. 2006, 2007). The original method was modified slightly for the adaptation to firn samples. The overall procedure is illustrated in Figure 1 and described in the following: (a) The firn core sections (about 60–70 cm) are cut into pieces in a cold room (–20 °C) and decontaminated by removal of possibly contaminated outer layers (~0.5 cm of the surface) using a stainless steel band saw precleaned with acetone and ultrapure water. (b) The derived samples (150–350 g) are then chiselled with a precleaned stainless steel scalpel to remove possible contamination from the previous step (i.e. dust and/or clothing fibers). Around 10–20% mass of firn sample is lost during the cutting and decontamination steps. As mentioned above, in the previous method (Jenk et al. 2007) the ice samples were additionally rinsed with ultrapure water to remove potential surface contaminations from sample preparation. However, due to its higher porosity this decontamination step is not applicable for firn, since the water would penetrate into the porous firn, transferring the contamination into the inner part of the samples. This step was therefore omitted. (c) The decontaminated samples are then transferred and stored frozen in prewashed containers (Semadeni, PETG) at –20 °C and melted directly before filtration. (d) The partic-

ulate OC and EC in the firn samples are collected on quartz fiber filter (Pallflex Tissuquartz, 2500QAO-UP, ~11 mm diameter) by filtration. Prior to use, containers and the filtration funnel were rinsed 3 times with ~25 mL ultrapure water with low TOC impurity in order to reduce the blank. (e) To remove carbonates, the filter is acidified 3 times with ~50 μL of 0.2M HCl and placed for ~2 to 3 hr in a laminar flow-box to complete dryness. (f) OC and EC is combusted and separated by a commercial thermal-optical OC/EC analyzer (Model4L, Sunset Laboratory Inc, USA) with a recently developed method (Zhang et al. 2012), which is described in detail in the following section. (g) Finally, the resulting CO_2 from the OC/EC analyzer is trapped cryogenically and sealed in glass ampoules for ^{14}C analysis. All materials used in the above steps are almost exclusively made of quartz, glass, stainless steel, and Teflon®. All the glass and quartz materials are freshly prebaked for 4 hr at 450 °C and 850 °C prior to use, respectively. Other materials (i.e. containers) are cleaned by rinsing several times with ultrapure water. A comparison of the methods applied in this study and previously (Jenk et al. 2006) is summarized in Table 1.

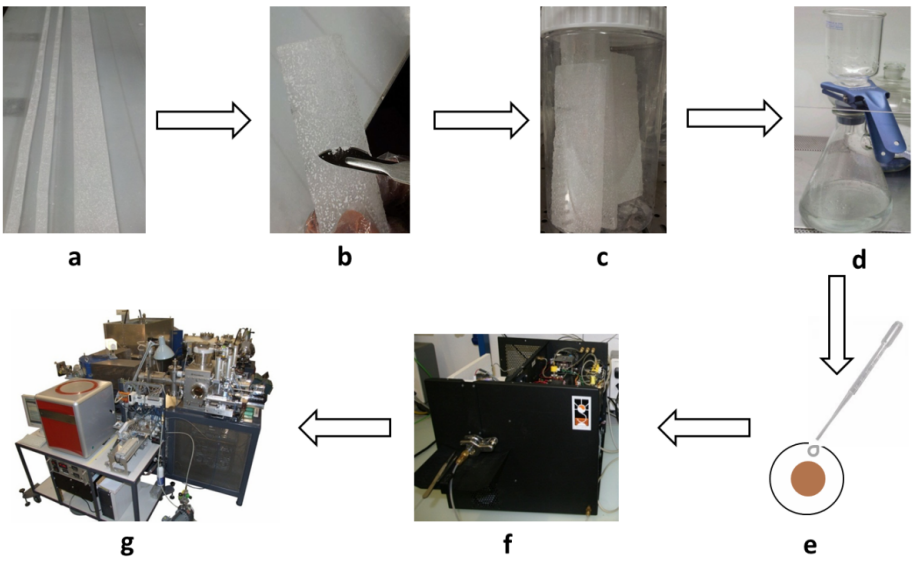

Figure 1 Schematic of sample preparation: a) cutting of inner sticks from a firn core; b) chiseling off outer layers; c) melting in precleaned containers; d) filtering through quartz fiber filter; e) acidification of the filter; f) combustion of OC and EC with the Sunset instrument; g) analysis of ^{14}C with the MICADAS AMS.

Table 1 Comparison of methods applied in this study and previously (Jenk et al. 2006).

Steps	This study	Jenk et al. 2006
Decontamination	Chiseling	Chiseling and water rinsing
Acid treatment	3 × 50 μL 0.2M HCl on the filter/ ~20 mL 1M HCl in the melted water[a]	3 × 50 μL 0.2M HCl on the filter
OC/EC separation and qualification	Thermal-optical analysis	Thermal alone analysis
Graphitization	No	Yes
AMS measurement	MICADAS: 250kV AMS	TANDY: 500kV AMS

[a]A different acid treatment was applied to the 2 ice-core samples from Fiescherhorn glacier (1773–1722 and 1721–1692; see Table 3), which were apparently influenced by a dust event.

OC and EC Separation and Quantification

The methodological details of isolation OC and EC with the thermal-optical method (the Swiss_4S protocol) for ^{14}C-based source apportionment of ambient aerosol samples was previously described by Zhang et al. (2012). In brief, OC is combusted in pure oxygen at 375 °C for ~180 s and subsequently EC is combusted in pure oxygen at 760 °C for ~120 s after complete OC combustion and/or evaporation in pure oxygen at 475 °C for 120 s and in helium at 650 °C for 180 s. In contrast to the previously used purely thermal method (Szidat et al. 2004b), on-line monitoring of the optical transmittance of the filters during the thermal treatment in the commercial OC/EC analyzer is applied to evaluate losses or artificial formation of EC during combustion. The CO_2 resulting from the different steps is quantified by a non-dispersive infrared (NDIR) detector and then trapped cryogenically.

^{14}C Analysis

In the present study, accelerator mass spectrometry (AMS) measurements are carried out with the Mini Carbon Dating System (MICADAS) (Synal et al. 2007) at the Laboratory of Ion Beam Physics of ETH Zurich using a gas ion source (Ruff et al. 2007; Fahrni et al. 2013). This inlet system allows direct injection of the CO_2 gas into the AMS, making ^{14}C measurements of carbon masses as low as 3 µg C faster and more reliable (Ruff et al. 2010; Wacker et al. 2013). All ^{14}C results are expressed as fraction of modern (Fm) defined by the fraction of the measured $^{14}C/^{12}C$ ratio related to the $^{14}C/^{12}C$ ratio of the reference year 1950 (Stuiver and Polach 1977). All reported results are corrected for ^{13}C fractionation and for ^{14}C decay for the time period between 1950 and the year of measurement. Fm values of samples are reported after correction ($Fm_{corrected}$) for the procedural blank if not stated otherwise, applying the equation below (Sigl et al. 2009):

$$Fm_{corrected} = \frac{m_{meas} \cdot Fm_{meas} - m_{PB} \cdot Fm_{PB}}{m_{meas} - m_{PB}}$$

where m_{meas} and Fm_{meas} denote the measured carbon mass and Fm of the sample (i.e. OC and EC), respectively. m_{PB} and Fm_{PB} denote the average carbon mass and Fm of procedural blanks, respectively.

RESULTS AND DISCUSSION

Procedural Blank

For blank assessment and verification of the new firn decontamination method, we attempted producing artificial firn from ice grains formed by freezing droplets, but the contamination resulting from this procedure was too high. Instead, as the best approximation, we used about 300 to 900 g of artificial ice obtained by freezing of ultrapure water that was treated the same way as described in the experimental sections. The resulting carbon mass (µg C) and the fraction of modern carbon (Fm) of procedural blanks are presented as mean values with a 1 standard deviation in Table 2. Carbon masses of the procedure blank for both OC and EC are independent of the masses of the artificial ice, indicating that the contamination did not originate from artificial ice blanks themselves but mainly from the sample preparation steps. The procedural blank for EC is consistent with the previously reported value of 0.3 ± 0.1 µg (Jenk et al. 2007; Sigl et al. 2009), whereas the procedural OC blank is about 2 times higher than the OC blank (1.3 ± 0.6 µg) reported by Jenk et al. (2007), but is still in the same order of magnitude. The higher OC blank indicates that rinsing is more efficient for decontamination than chiseling. To obtain sufficient carbon for ^{14}C determination, CO_2 is trapped continuously from 2 subsequent blanks treated with the OC/EC analyzer. Still, Fm could not be measured

for EC because the carbon mass of the EC blank (0.32 ± 0.14 μg) is by a factor of 10 lower than the limit of detection (~3–5 μg) of the AMS measurement. The Fm of the OC procedural blank (0.81 ± 0.13) in this study is substantially higher than the Fm values (0.60 ± 0.10) published by Jenk et al. (2007), indicating additional contamination from modern sources. Nevertheless, the blanks obtained in this study are relatively low compared to the typical amounts of about 50 μg/L OC and 15 μg/L EC found in firn samples from Alpine glaciers (Legrand et al. 2007). For EC, the estimated Fm_{PB} from Jenk et al. (2007) is used, i.e. 0.30 ± 0.30. The relative contribution of the blank correction to the final uncertainty of Fm ranged from 5% to 8% for firn samples from Jungfraujoch.

Table 2 Mass concentrations (μg) and fraction of modern (Fm) of particulate OC and EC of the procedural blanks obtained in this study.

Sample label	Mass (g)	Nr of filters	OC/filter (μg)	EC/filter (μg)	Fm (OC)
BK1	845	3	1.78 ± 0.11	0.20 ± 0.05	
BK2	340	1	1.27 ± 0.15	0.42 ± 0.08	
BK3	402	1	2.53 ± 0.17	0.47 ± 0.07	
BK4	304	1	3.42 ± 0.15	0.41 ± 0.04	
BK5	578	2	2.81 ± 0.10	0.29 ± 0.05	
BK6	928	4	3.95 ± 0.09	0.13 ± 0.04	0.83 ± 0.01
BK7	290	1	2.74 ± 0.16	0.41 ± 0.05	
BK8	897	3	2.40 ± 0.10	0.57 ± 0.04	0.67 ± 0.03
BK9	790	3	3.44 ± 0.10	0.21 ± 0.05	0.97 ± 0.01
BK10	720	2	3.23 ± 0.12	0.13 ± 0.04	0.78 ± 0.02
BK11	489	2	2.65 ± 0.25	0.29 ± 0.04	
Mean			2.75 ± 0.77	0.32 ± 0.14	0.81 ± 0.13

Validation of the New OC and EC Thermal-Optical Separation

In order to validate the new decontamination method and the thermal-optical method (the Swiss_4S protocol) for particulate OC and EC separation, we re-analyzed several ice-core samples from Fiescherhorn glacier (FH), which were previously measured with the thermal method by Jenk et al. (2007) (Table 3). The OC mass obtained with the thermal-optical method is higher than with the purely thermal method, whereas the EC mass shows the opposite trend. These new results are considered more reliable compared to the previous method, since the continuous monitoring of transmittance of the filter during analysis with the thermo-optical analyzer prevents biases in OC and EC separation. Nevertheless, there is no significant difference of the corresponding Fm for both OC and EC fractions except for 2 samples from the pre-industrial period. Concerning EC, it should be noted that the EC values reported by Jenk et al. (2007) were simply multiplied by a factor of 2.0 ± 0.3 to account for a 50 ± 8% loss of EC during the thermal treatment in a muffle furnace for elimination of OC. This resulted in considerably higher uncertainty of the EC mass. In the present study, evolving CO_2 is determined continuously together with on-line monitoring of the laser transmittance of the filter, which is used to quantify the EC yield. This resulted in a more accurate determination of EC. The anthropogenic contribution from fossil fuels during the period before 1800 was already significant with about 10% and 50% to OC and EC emissions, respectively, according to Jenk et al. (2006). The authors argued that the unexpected Fm of EC was at least partly biased by old (^{14}C-depleted) carbonate from Saharan dust events. Another hypothesis was that gases released from the Saharan dust minerals during combustion interfered during the graphitization step. Here, to fully exclude artifacts from carbonates, the 2 samples from before 1800 were treated differently. In short, after complete melting of the ice samples, the container was rinsed 3 times with ~ 20 mL 1M HCl

instead of 25 mL ultrapure water, which was then transferred for filtration. As discussed above, graphitization was no longer needed because the gas ion source was used. Since we do not observe a significant anthropogenic contribution for both OC and EC fractions in the pre-industrial samples, we assume that the finding from the earlier work was rather a methodical problem. Therefore, this modified acidification method is highly recommended to be applied for both firn and ice samples to eliminate all the carbonate carbon.

Table 3 Concentrations and fraction of modern (Fm) of particulate OC and EC of ice core samples from Fiescherhorn glacier analyzed by the new method in this study compared to previous results by Jenk et al. (2006).

	This study					Jenk et al. 2006				
Sample year	Mass (g)	OC (μg/kg)	EC (μg /kg)	Fm (OC)	Fm (EC)	Mass (g)	OC (μg/kg)	EC (μg/kg)	Fm (OC)	Fm (EC)
1928–1933	685	49.5±2.8	23.0±1.4	0.78±0.01	0.31±0.02	957	40.5±0.8	25.1±0.1	0.77±0.02	0.31±0.03
1925–1927	432	42.2±2.7	22.4±1.5	—	0.33±0.02	650	30.2±0.8	22.2±0.1	—	0.39±0.08
1915–1917	279	28.9±0.8	16.2±0.5	0.83±0.01	0.33±0.03	405	19.3±1.5	51.8±0.5	0.82±0.07	0.29±0.02
1912–1914	301	29.4±0.8	12.6±0.3	0.83±0.01	0.30±0.03	495	29.1±1.3	38.9±0.4	0.82±0.04	0.31±0.02
1773–1722	495	46.3±2.3	8.3±0.3	1.01±0.01	0.97±0.04	841	29.2±0.7	12.0±0.2	—	0.42±0.10
1721–1692	690	64.1±1.8	12.3±0.3	1.04±0.02	0.94±0.02	803	44.9±0.9	13.2±0.2	0.94±0.02	—

Validation of the New Firn Decontamination Method with Samples from Jungfraujoch

Two firn samples collected on 23 April 2010 at the high-alpine site of Jungfraujoch (JFJ), Switzerland, were used to perform a preliminary test of the new method. These samples were collected from the previous winter snow layer after removing the topmost 10 cm of snow that contained ash particles from the eruption of the Eyjafjallajökull Volcano in Iceland (Bukowiecki et al. 2011). The snow was sampled in a plastic tube, lined with a polyethylene bag, and compacted with a pusher to mimic a firn core. Average particulate OC and EC concentrations are 32.6 ± 0.3 and 5.6 ± 0.2 μg/kg (Table 4), respectively, which is in the same range as values from Fiescherhorn and Colle Gnifetti glacier (Jenk et al. 2006; Sigl et al. 2009). The Fm values of the corresponding carbon fractions show a fossil contribution of 29 ± 1%, 40 ± 2%, and 28 ± 2% to the OC, EC, and TC, respectively. The Fm of TC is in good agreement with values derived from ambient aerosol samples at European background sites (May et al. 2009) and particles extracted from ice samples from Grenzgletscher (Steier et al. 2006).

Table 4 The concentrations and fraction of modern (Fm) of particulate OC and EC of 2 firn samples from Jungfraujoch (JFJ) collected in 2010.

Sample name	Mass (g)	OC (μg/kg)	EC (μg/kg)	Fm (OC)	Fm (EC)	Fm (TC)
JFJ-01	241	32.9 ± 3.0	5.4 ± 0.8	0.80 ± 0.03	0.68 ± 0.02	0.78 ± 0.04
JFJ-02	323	32.3 ± 3.6	5.8 ± 0.7	0.77 ± 0.02	0.66 ± 0.03	0.75 ± 0.04

CONCLUSION

A new decontamination method consisting of chiseling instead of rinsing was developed for determining the concentrations and ^{14}C content (fraction of modern) of extracted particulate OC and EC fractions of carbonaceous particles in firn samples in order to account for the higher porosity of firn compared to ice. The procedural OC blank is a factor of 2 higher compared to the rinsing method. Nevertheless, the OC blank is sufficiently low for analyzing ^{14}C in samples from mid- and low-latitude glaciers with relatively high concentrations of carbonaceous particles. By using a new thermal-

optical separation of OC and EC instead of the previously used purely thermal method for subsequent ^{14}C analysis, possible biases for mass and ^{14}C determination of OC and EC from losses or artificial formation of EC during analysis were potentially reduced. The results on firn samples from the Jungfraujoch site suggest contemporary sources (biomass burning and/or biogenic) contribute higher than fossil sources to both OC and EC fractions.

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