INTERCOMPARISON OF ^{14}C ANALYSIS OF CARBONACEOUS AEROSOLS: EXERCISE 2009

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ABSTRACT. Radiocarbon analysis of the carbonaceous aerosol allows an apportionment of fossil and non-fossil sources of airborne particulate matter (PM). A chemical separation of total carbon (TC) into its subfractions organic carbon (OC) and elemental carbon (EC) refines this powerful technique, as OC and EC originate from different sources and undergo different processes in the atmosphere. Although ^{14}C analysis of TC, EC, and OC has recently gained increasing attention, interlaboratory quality assurance measures have largely been missing, especially for the isolation of EC and OC. In this work, we present results from an intercomparison of 9 laboratories for ^{14}C analysis of carbonaceous aerosol samples on quartz fiber filters. Two ambient PM samples and 1 reference material (RM 8785) were provided with representative filter blanks. All laboratories performed ^{14}C determinations of TC and a subset of isolated EC and OC for isotopic measurement. In general, ^{14}C measurements of TC and OC agreed acceptably well between the laboratories, i.e. for TC within 0.015–0.025 $F^{14}C$ for the ambient filters and within 0.041 $F^{14}C$ for RM 8785. Due to inhomogeneous filter loading, RM 8785 demonstrated only limited applicability as a reference material for ^{14}C analysis of carbonaceous aerosols. ^{14}C analysis of EC revealed a large deviation between the laboratories of 28–79% as a consequence of different separation techniques. This result indicates a need for further discussion on optimal methods of EC isolation for ^{14}C analysis and a second stage of this intercomparison.

INTRODUCTION

Atmospheric particulate matter (PM) has a negative impact on the global climate and public health (Pöschl 2005). A major component of PM is carbonaceous aerosol, which is often denoted as total carbon (TC) and subdivided into organic carbon (OC), i.e. colorless and non-recalcitrant organic compounds of low molecular weight, and elemental carbon (EC) or black carbon (BC), i.e. optically absorptive and refractory products of pyrolysis. The distinction of TC into OC and EC is of special importance, as both fractions have different optical, physical, and chemical properties, which determine their significance as air pollutants. Although OC is typically more abundant under ambient conditions, EC requires special attention as it contributes to global warming when absorbing light and may act as a carcinogen (Andreae and Gelencsér 2006). In order to implement sensible measures for TC reduction, a detailed knowledge of sources of OC and EC is required. Existing emission inventories are however poorly constrained due to the large variety of individual emission

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sources and missing knowledge on the processes especially regarding secondary OC (Hallquist et al. 2009; Penner et al. 2010). Source apportionment based on the analysis of chemical or isotopic tracers within the carbonaceous aerosol may provide more reliable information. However, many of the chemical tracers may not be unambiguously assigned to 1 source category or undergo chemical transformation after emission, which lessens the value of these tracers. Radiocarbon analysis of the carbonaceous aerosol constitutes a rare exception of this limitation (Currie 2000), as all fossil emissions are ^{14}C-free in contrast to non-fossil emissions irrespective individual emission conditions or subsequent chemical transformations in the atmosphere, which has resulted in a wide acceptance of ^{14}C-based source apportionment in PM research (Andreae and Gelencsér 2006; Fuzzi et al. 2006). This analysis has mainly been applied to TC up to now (for an overview see Currie 2000; Hodzic et al. 2010). In recent years, individual ^{14}C measurements of OC, EC, and some other subfractions or specific compounds have gathered importance (Szidat et al. 2004; Zencak et al. 2007; Uchida et al. 2010; Zhang et al. 2012; Bernardoni et al. 2013). Separate ^{14}C measurement of OC and EC is advantageous compared to analysis of TC alone, since the different sources of OC and EC result in diverse ^{14}C levels (Szidat 2009). Whereas OC may be emitted by non-combustion processes or formed in the atmosphere from gaseous precursors with a typical dominance of non-fossil sources, EC solely originates from combustion processes of fossil fuels or wood and is therefore frequently dominated by ^{14}C-free material. ^{14}C analysis of individual TC fractions, however, requires the physical or chemical separation of OC from EC.

Many different approaches have been applied to differentiate and quantify OC and EC. Several interlaboratory exercises (Schmid et al. 2001; Currie et al. 2002; Schauer et al. 2003; Hammes et al. 2007) and review articles (Pöschl 2005; Andreae and Gelencsér 2006; Fuzzi et al. 2006) came to the conclusion that the distinction of OC and EC is strongly method-dependent. The applied methods can mainly be classified into optical and thermal techniques referring to the key properties of OC and EC. Purely optical approaches do not enable a chemical separation of both fractions. Therefore, they are inappropriate for ^{14}C analysis. Thermal approaches physically or chemically separate OC in a first step and then determine the remaining EC in a combustion step. The OC removal is either performed by evaporation in helium or by combustion in oxygen. (Wet chemical oxidation or multiple solvent extraction procedures were also applied earlier, but are rarely used now.) Thermal methods using OC evaporation and EC combustion include monitoring the light transmittance of the filter during analysis, so that this principle is characterized as thermo-optical analysis (TOA). The optical monitoring tracks several artifacts concerning EC that arise during the treatment: (1) *in situ* pyrolysis of OC on the filter produces additional (apparent) EC during the OC removal (positive artifact), which increases the concentration in the EC and is denoted as "charring"; (2) premature losses of EC during the OC step lead to reduced recoveries in the EC (negative artifact); and (3) incomplete removal of refractory OC (positive artifact), which cannot be traced by optical monitoring directly, but may be uncovered from TOA analyses of filters using different thermal treatments (Zhang et al. 2012). Consequently, optical monitoring allows a mathematical correction of the positive and negative artifacts without improving the biases of the chemical separation. The OC evaporation methods are therefore not suited for the chemical separation of EC for further ^{14}C measurements. The oxidative removal of OC and subsequent EC conversion is typically performed as a 2-step heating in air or pure oxygen with the first step conducted at 340–375 °C during <1 to 24 hr (Lavanchy et al. 1999; Gustafsson et al. 2001). Charring is reduced for OC removal by oxidation compared to evaporation in an inert gas (Lavanchy et al. 1999). A further reduction of charring is achieved if water-soluble components are removed from the filter by extraction before the thermal treatment (Andreae and Gelencsér 2006; Piazzalunga et al. 2011; Zhang et al. 2012).

Previous laboratory and method intercomparisons only covered certain aspects of ^{14}C analysis of TC, OC, and EC in PM on filters: 1) Several intercomparisons focused only on the quantification of carbonaceous aerosols and their OC and EC fractions (Schmid et al. 2001; Schauer et al. 2003); 2) there is a continuous round-robin effort on ^{14}C measurement in the ^{14}C community (e.g. Scott et al. 2010), which has exclusively considered typical dating materials such as wood, bones, charcoal, or shell; 3) an earlier approach of a trial on ^{14}C analysis of carbonaceous aerosols (Currie et al. 2002) was performed with SRM 1649a ("urban dust") that was provided as sieved (<100 µm) powder, which is not representative for ambient conditions, as those include PM filter sampling of smaller sizes (typically PM10, PM2.5, or PM1 corresponding to PM with an aerodynamic diameter of <10, <2.5, or <1 µm, respectively). Consequently, an overarching laboratory and method intercomparison quantifying both the concentration and ^{14}C content of TC, OC, and EC in PM on filters is still needed. This is especially necessary because separation methods of OC and EC for ^{14}C analysis differ considerably between the laboratories; the influence of this diversity on the ^{14}C results requires investigation. This work describes a first step to close this gap. Nine laboratories participated in an intercomparison of ^{14}C analysis of carbonaceous aerosols. This exercise included 2 ambient PM samples and 1 PM reference material on filter media (RM 8785) together with representative blank filters. The ^{14}C content of TC, EC, and OC was investigated and different separation methods were compared.

METHODS

The following laboratories participated in this intercomparison (here compiled in alphabetical order and anonymized in the following): Bern/PSI/ETH (Szidat 2009); INFN-LABEC (Calzolai et al. 2011); Irvine (Santos et al. 2007); LLNL (Bench et al. 2007); Lund (Genberg et al. 2011); NIES (Uchida et al. 2010); Stockholm (Zencak et al. 2007), Utrecht; and Woods Hole (Reddy et al. 2002). Five filter samples were distributed among the participants: 2 ambient samples; 1 corresponding blank; and 2 reference materials on filter media. The ambient samples were collected using 2 juxtaposed high-volume samplers with PM10 inlets in northern Italy during fall 2008, one at an urban background station in Milan on 16 October 2008 and the other at a rural station at JRC Ispra from 29 September to 1 October 2008. The corresponding blank was exposed on site. Samples were collected on preheated (800 °C overnight) Pallflex® Tissuquartz filters (2500QAT-UP) with a diameter of 150 mm. To prevent discrepancies between the laboratories due to losses of semivolatile compounds during storage, filters were kept in aluminum foil and air-tight plastic bags at room temperature. Fractions of ~26 and ~70 cm^2 of the loaded and blank filters, respectively, were allocated to each participant. The 2 reference materials on filters were RM 8785 ("air particulate matter dispersed on filter media," produced from SRM 1649a using a PM2.5 size cut, 8.55 cm^2 loaded area) and RM 8786 ("filter blank for RM 8785," 10.75 cm^2) (Klouda et al. 2005; NIST 2005a,b). The samples were shipped from the University of Bern to the participants in cooled containers in order to prevent a bias from excess warming during transport.

Most of the analyses were performed in 2009. For ^{14}C(TC) analysis (i.e. measurement of ^{14}C in TC), aliquots of the filters were combusted at high temperature either in closed vessels using copper oxide or oxygen or in flow tubes using oxygen for oxidation. Two laboratories applied fuming with hydrochloric acid before the thermal treatment to remove carbonates. As this additional step did not result in significantly different ^{14}C(TC) values, carbonates were assumed to be negligible, in agreement with studies on comparable PM samples (Chow and Watson 2002). Therefore, ^{14}C(TC) data with and without acid fuming were combined. ^{14}C(OC) determination was performed by 2 laboratories. Filters were combusted in flow-tube systems with pure oxygen at 340 °C for 10 and 15 min, respectively, with a rapid heating at the beginning. Five laboratories reported ^{14}C(EC) data applying various OC removal procedures (Table 1) and different EC recoveries. Laboratory D applied water extraction before the thermal treatment, laboratories C and F used acid fumigation. OC was removed from the pretreated or untreated filters using these heating procedures: 4 hr at 375 °C in air; 18 hr at 375 °C in air; 24 hr at 375 °C in air; 24 hr at 350 °C in air; 2.5 hr at 340 °C in pure oxygen; and 1 min at 400 °C plus 0.5 min at 520 °C in pure oxygen. Laboratories D and F employed 2 thermal procedures on different samples or sample aliquots. Laboratory E applied *in situ* microacidification after the thermal treatment.

Table 1 Methods of OC removal for ^{14}C(EC) analysis.

Lab	Samples	Step 1: Pretreatment	Step 2: Thermal procedure	Step 3: Follow-up treatment
C	All	Acid fumigation	4 hr at 375 °C in air	None
D	Milan/Ispra	Water extraction	4 hr at 375 °C in air	None
D	Milan/Ispra	Water extraction	1 min at 400 °C + 0.5 min at 520 °C in O_2	None
E	RM 8785	None	18 hr at 375 °C in air	*In situ* microacidification
F	RM 8785	None	24 hr at 375 °C in air	None
F	Milan/Ispra	Acid fumigation	24 hr at 350 °C in air	None
G	All	None	2.5 hr at 340 °C in O_2	None

^{14}C measurements were performed by accelerator mass spectrometry (AMS) after graphitization (8 laboratories) or by direct gas inlet (1 laboratory). Masses of samples fed into the ion source of the AMS ranged from 4 to >1000 µg C. Results were reported by the participants in different notations (i.e. Fm/pMC with and without decay correction between 1950 and year of measurement as well as Δ^{14}C), but are shown here consistently after transformation into F^{14}C (Reimer et al. 2004). All uncertainties as well as intra- and interlaboratory deviations represent 1σ. Concentrations of TC, OC, and EC were determined manometrically from the CO_2 formed during sample preparation.

RESULTS AND DISCUSSION

Tables 2a–c show the ^{14}C results of the uncorrected loaded samples RM 8785, Milan, and Ispra, their corresponding filter blanks, and the blank-corrected data of the loaded filters for the individual laboratories. Tables 2a, 2b, and 2c present ^{14}C(TC), ^{14}C(EC), and ^{14}C(OC) measurements, respectively. Values are given with measurement uncertainties as reported by the laboratories and with intralaboratory deviations for repeated analyses, both related to the single determination, thus reflecting typical measurement conditions of unknown samples. Measurements of TC, EC, and OC concentrations on the filters are reported in addition. It should be noted, however, that these estimations were not performed analogously to state-of-the-art OC/EC measurements. Nevertheless, they may reflect similarity and diversity of the sample preparation between the laboratories. Moreover, they indicate recoveries of the carbonaceous particle fractions from the different sample preparation procedures. Especially for EC isolation, gained EC/TC ratios reflect gentle vs. harsh reaction conditions. Table 3 presents the mean results from all laboratories with the average reported measurement uncertainties and interlaboratory deviations. Figure 1 illustrates the ^{14}C(TC) results of the uncorrected and blank-corrected filters of the individual laboratories, and the mean comparing the reported measurement uncertainties, intra- and interlaboratory deviations.

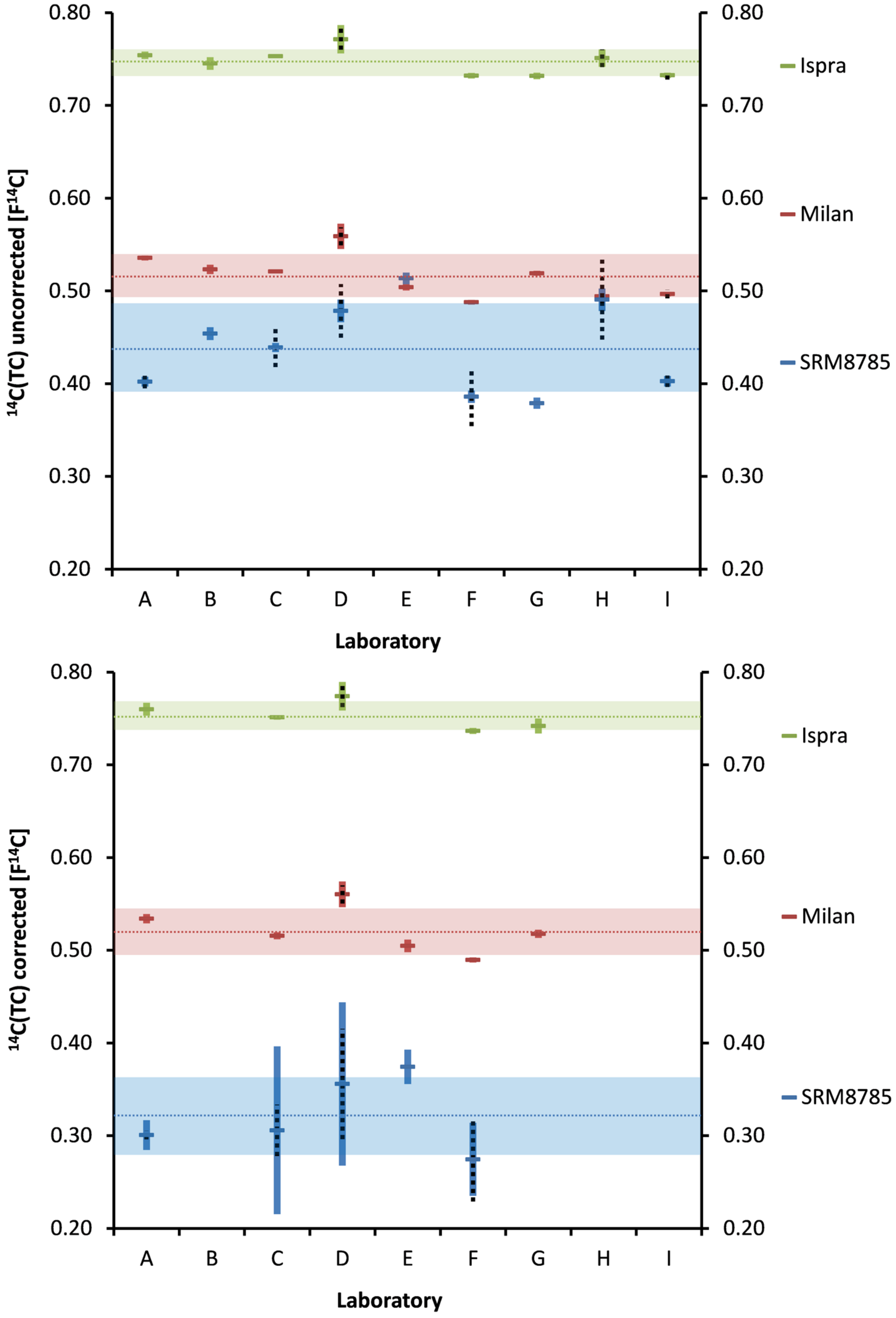

Figure 1 $^{14}C(TC)$ results for samples Ispra, Milan, and RM 8785 uncorrected (top) and corrected for filter blank (bottom). Values of the individual laboratories are presented with reported measurement uncertainties (solid colored bars) and intralaboratory deviations where applicable (dotted black bars) as shown in Table 2a. Vertical dotted lines and shaded areas represent interlaboratory means and deviations, respectively, as summarized in Table 3.

Table 2a ^{14}C(TC) results for samples Milan, Ispra and RM 8785 (all uncorrected and corrected for filter blank) and the corresponding filter blanks (see also Figure 1). Values are given with average measurement uncertainty for single analysis as reported by the laboratories and intralaboratory deviation for single analysis from *n* repeated determinations, estimation of TC concentrations on the filters and TC/PM ratios. n.r. = not reported; n.a. = not applicable.

Sample	Lab	^{14}C(TC) F^{14}C	Uncert. F^{14}C	Intralab deviation F^{14}C	*n*	TC µg/cm^2	TC/PM
Milan (uncorrected)	A	0.536	0.003	n.a.	1	127	n.a.
	B	0.523	0.005	n.a.	1	n.r.	n.a.
	C	0.521	0.001	n.a.	1	126	n.a.
	D	0.559	0.014	0.010	2	118	n.a.
	E	0.504	0.004	n.a.	1	97	n.a.
	F	0.488	0.003	n.a.	1	124	n.a.
	G	0.519	0.003	n.a.	1	139	n.a.
	H	0.494	0.008	0.001	3	n.r.	n.a.
	I	0.497	0.002	0.005	2	114	n.a.
Ispra (uncorrected)	A	0.754	0.004	n.a.	1	130	n.a.
	B	0.745	0.007	n.a.	1	n.r.	n.a.
	C	0.753	0.001	n.a.	1	129	n.a.
	D	0.771	0.015	0.011	2	176	n.a.
	E	n.r.	n.r.	n.a.	0	117	n.a.
	F	0.732	0.003	n.a.	1	121	n.a.
	G	0.732	0.004	n.a.	1	158	n.a.
	H	0.751	0.009	0.010	3	n.r.	n.a.
	I	0.732	0.003	0.005	3	130	n.a.
Filter blank Milan/Ispra	A	0.577	0.009	n.a.	1	4	n.a.
	B	n.r.	n.r.	n.a.	0	n.r.	n.a.
	C	0.474	0.003	0.001	2	4	n.a.
	D	0.422	0.016	n.a.	1	1	n.a.
	E	0.424	0.006	n.a.	1	1	n.a.
	F	0.308	0.008	n.a.	1	1	n.a.
	G	0.563	0.012	n.a.	1	4	n.a.
	H	n.r.	n.r.	n.a.	0	n.r.	n.a.
	I	n.r.	n.r.	n.a.	0	n.r.	n.a.
Milan (corrected)	A	0.534	0.005	n.a.	1	123	n.a.
	B	n.r.	n.r.	n.a.	0	n.r.	n.a.
	C	0.516	0.004	n.a.	1	122	n.a.
	D	0.560	0.014	0.010	2	116	n.a.
	E	0.505	0.007	n.a.	1	96	n.a.
	F	0.490	0.003	n.a.	1	123	n.a.
	G	0.518	0.004	n.a.	1	135	n.a.
	H	n.r.	n.r.	n.a.	0	n.r.	n.a.
	I	n.r.	n.r.	n.a.	0	n.r.	n.a.
Ispra (corrected)	A	0.760	0.007	n.a.	1	126	n.a.
	B	n.r.	n.r.	n.a.	0	n.r.	n.a.
	C	0.751	0.002	n.a.	1	125	n.a.
	D	0.774	0.015	0.012	2	175	n.a.
	E	n.r.	n.r.	n.a.	0	117	n.a.
	F	0.737	0.003	n.a.	1	120	n.a.
	G	0.742	0.008	n.a.	1	154	n.a.
	H	n.r.	n.r.	n.a.	0	n.r.	n.a.
	I	n.r.	n.r.	n.a.	0	n.r.	n.a.

Table 2a $^{14}C(TC)$ results for samples Milan, Ispra and RM 8785 (all uncorrected and corrected for filter blank) and the corresponding filter blanks (see also Figure 1). Values are given with average measurement uncertainty for single analysis as reported by the laboratories and intralaboratory deviation for single analysis from *n* repeated determinations, estimation of TC concentrations on the filters and TC/PM ratios. n.r. = not reported; n.a. = not applicable. *(Continued)*

Sample	Lab	$^{14}C(TC)$ $F^{14}C$	Uncert. $F^{14}C$	Intralab deviation $F^{14}C$	*n*	TC µg/cm^2	TC/PM
RM 8785 (uncorrected)	A	0.402	0.002	0.007	3	58	0.30
	B	0.454	0.003	n.a.	1	n.r.	n.r.
	C	0.439	0.001	0.021	6	36	0.27
	D	0.478	0.009	0.029	3	29	0.32
	E	0.514	0.003	n.a.	1	30	0.35
	F	0.386	0.003	0.032	5	47	0.25
	G	0.379	0.002	n.a.	1	91	0.40
	H	0.491	0.009	0.043	2	n.r.	n.r.
	I	0.403	0.002	0.006	5	66	0.30
Filter blank RM 8786	A	1.192	0.010	n.a.	1	5	n.a.
	B	n.r.	n.r.	n.a.	0	n.r.	n.a.
	C	0.958	0.004	0.016	2	6	n.a.
	D	1.350	0.027	0.008	2	3	n.a.
	E	1.236	0.015	n.a.	1	5	n.a.
	F	1.419	0.031	0.429	3	4	n.a.
	G	n.r.	n.r.	n.a.	0	8	n.a.
	H	1.280	n.r.	n.a.	1	n.r.	n.a.
	I	n.r.	n.r.	n.a.	0	n.r.	n.a.
RM 8785 (corrected)	A	0.301	0.012	0.005	3	51	0.27
	B	n.r.	n.r.	n.a.	0	n.r.	n.r.
	C	0.306	0.087	0.028	6	30	0.23
	D	0.356	0.084	0.060	3	26	0.29
	E	0.374	0.015	n.a.	1	25	0.29
	F	0.274	0.036	0.046	5	43	0.23
	G	n.r.	n.r.	n.a.	0	83	0.36
	H	n.r.	n.r.	n.a.	0	n.r.	n.r.
	I	n.r.	n.r.	n.a.	0	n.r.	n.r.

$^{14}C(TC)$ analyses showed a reasonable coherence of the data, especially for the ambient samples from Milan and Ispra. Here, the reported measurement uncertainties and the intralaboratory standard deviations from repeated analyses were comparable (~0.010 $F^{14}C$), which suggests that internal contributions to uncertainties and biases were largely considered appropriately. The interlaboratory standard deviations were slightly larger (by a factor of 1.5 to 2.5), however, indicating that lab-external uncertainties and biases remained underestimated as also observed in other ^{14}C intercomparisons (e.g. Scott et al. 2010). An overall variability of ~0.02 $F^{14}C$ may be evaluated as acceptable, as the reference value for pure non-fossil emissions, which has to be applied to apportion fossil vs. non-fossil sources from ^{14}C measurements, induces an uncertainty of similar extent (Hodzic et al. 2010). Subtraction of the filter blank did not alter the results for samples Milan and Ispra, as the blank-carbon contribution is small (i.e. ~2%). The large interlaboratory variabilities for the filter blank of ^{14}C value and the carbon mass of >20% and >50%, respectively, indicate that the uncertainties introduced during the blank subtraction should include a substantial additional margin allowing for a realistic variability of the blank. This margin shall comprise uncertainties from the fieldwork (e.g. inhomogeneities during sampling, variable blank contributions of different filters, and reduced representativeness of the blank for the sampling conditions) and the lab work (e.g. contamination induced during pretreatment and its variability). As a consequence of the latter, a reliable interlaboratory comparison is only possible based on the blank-corrected data, because the contamination from the lab work was not identical among the laboratories.

Table 2b ^{14}C(EC) results for samples Milan, Ispra, and RM 8785 (uncorrected and corrected for filter blank) with average measurement uncertainty for single analysis as reported by the laboratories and intralaboratory deviation for single analysis from *n* repeated determinations, estimation of EC concentrations on the filters and EC/TC ratios. Methods of OC removal are documented in Table 1. n.r. = not reported; n.a. = not applicable.

Sample	Lab	^{14}C(EC) F^{14}C	Uncert. F^{14}C	Intralab deviation F^{14}C	*n*	EC µg/cm^2	EC/TC
Milan (uncorrected)	C	0.122	0.001	0.004	2	7	0.05
	D	0.122	0.007	0.019	2	25	0.21
	E	n.r.	n.r.	n.a.	0	n.r.	n.r.
	F	0.226	0.002	n.a.	1	11	0.08
	G	0.243	0.002	n.a.	1	56	0.40
Milan (corrected)	C	0.115	0.011	0.005	2	6	0.05
	D	0.119	0.008	0.019	2	24	0.21
	E	n.r.	n.r.	n.a.	0	n.r.	n.r.
	F	n.r.	n.r.	n.a.	0	n.r.	n.r.
	G	n.r.	n.r.	n.a.	0	n.r.	n.r.
Ispra (uncorrected)	C	0.340	0.002	0.018	2	7	0.05
	D	0.299	0.007	0.013	2	19	0.11
	E	n.r.	n.r.	n.a.	0	n.r.	n.r.
	F	0.541	0.003	n.a.	1	12	0.10
	G	0.493	0.003	n.a.	1	48	0.30
Ispra (corrected)	C	0.378	0.043	0.022	2	6	0.05
	D	0.298	0.007	0.013	2	19	0.11
	E	n.r.	n.r.	n.a.	0	n.r.	n.r.
	F	n.r.	n.r.	n.a.	0	n.r.	n.r.
	G	n.r.	n.r.	n.a.	0	n.r.	n.r.
RM 8785 (uncorrected)	C	0.168[a]	0.003	0.008	2[a]	6	0.18
	D	n.r.	n.r.	n.a.	0	n.r.	n.r.
	E	0.567	0.009	n.a.	1	3	0.12
	F	0.120	0.005	0.015	2	7	0.19
	G	0.191	0.004	n.a.	1	39	0.43
RM 8785 (corrected)	C	0.085[a]	0.088	0.005	2[a]	4	0.15
	D	n.r.	n.r.	n.a.	0	n.r.	n.r.
	E	n.r.	n.r.	n.a.	0	n.r.	n.r.
	F	n.r.	n.r.	n.a.	0	n.r.	n.r.
	G	n.r.	n.r.	n.a.	0	n.r.	n.r.

[a] One ^{14}C(EC) analysis (0.305 F^{14}C uncorrected) is not included as it was considered as an outlier by the laboratory.

The ^{14}C(TC) values of RM 8785 were less reproducible than the samples Milan and Ispra in several aspects. The intralaboratory standard deviation amounted to an average of 0.023 F^{14}C and was thus more than 5 times larger than the reported measurement uncertainty. The interlaboratory variability was even more than twice as high as this. Both observations can be attributed to inhomogeneities of the material during loading of this artificial PM sample. This inhomogeneity has already been reported for the PM mass and the TC concentrations that both vary by 40% (Klouda et al. 2005; NIST 2005a). This fact necessitates that all measured components (such as TC) are related to the PM mass of each individual filter, which was specified in the RM report (NIST 2005a). As a consequence, the TC/PM ratios showed less variability between the laboratories than TC concentrations.

Table 2c ^{14}C(OC) results for samples Milan, Ispra and RM 8785 (uncorrected and corrected for filter blank) with measurement uncertainty as reported by the laboratories, estimation of OC concentrations on the filters and OC/TC ratios. *n* was 1 for all samples. n.r. = not reported.

Sample	Lab	^{14}C(OC) F^{14}C	Uncert. F^{14}C	OC μg/cm^2	OC/TC
Milan (uncorrected)	D	0.722	0.014	59	0.50
	G	0.734	0.004	57	0.41
Milan (corrected)	D	0.728	0.015	58	0.50
	G	0.741	0.008	54	0.40
Ispra (uncorrected)	D	0.891	0.017	58	0.33
	G	0.863	0.004	77	0.49
Ispra (corrected)	D	0.901	0.018	57	0.33
	G	0.872	0.007	74	0.48
RM 8785 (uncorrected)	D	0.621	0.012	18	0.60
	G	n.r.	n.r.	n.r.	n.r.
RM 8785 (corrected)	D	0.494	0.094	15	0.56
	G	n.r.	n.r.	n.r.	n.r.

Even so, the standard deviations of TC/PM ratios were higher in this study than in an earlier intercomparison (0.32 on the average compared to 0.23 from Klouda et al. 2005). The variability of the ^{14}C(TC) values shows that the inhomogeneous filter loading also affected the isotopic ratios, which unfortunately reduces the potential of RM 8785 as reference material for ^{14}C analyses of carbonaceous aerosols. Another drawback is the fact that the blank material RM 8786 carried a large carbon contribution (>10% of the carbon found on RM 8785) with a considerably different F^{14}C value (1.239 compared to 0.438 on the average). This generated a large shift of F^{14}C between the uncorrected and the blank-corrected result of >0.1 and added substantial uncertainties from the blank subtraction. The latter is documented as larger or smaller than the uncertainty of ^{14}C(TC) of RM 8785 (blank corrected) in Table 2a due to the application of the individual laboratories of more or less conservative additional margins, respectively. Although one might conclude from the large uncertainties of the blank-corrected ^{14}C(TC) of RM 8785 that only the uncorrected measurements should be chosen for establishing a reference value, we cannot recommend this procedure. Because PM loading varied between single filters while the blank stayed relatively constant, the ^{14}C(TC) of RM 8785 can only be regarded as independent of the choice of the individual filter after subtraction of the filter blank. The consensus value of ^{14}C(TC) of RM 8785 from this work was determined as the average of the 5 laboratories (Table 3) associated with the interlaboratory standard deviation of the mean, and thus amounts to 0.322 ± 0.019. (We did not use weighted averages as done in other intercomparisons [e.g. Scott et al. 2010] because the uncertainties of the laboratories were dominated by the different choices of additional margins allowing for a realistic variability of the blank as discussed above, so that these uncertainties are not suitable as weighting factors.) As RM 8785 was produced by dispersion of SRM 1649a on filters with reducing the PM size from 100 to 2.5 μm (Klouda et al. 2005), it is of interest to compare the ^{14}C(TC) for both reference materials. Also for this comparison, results of RM 8785 should be considered including blank correction in order to eliminate the influence of the filter. SRM 1649a gave somewhat higher values than RM 8785 (0.544 ± 0.057 laboratory average with standard deviation between the laboratories from Currie et al. 2002). This suggests that the coarse fraction that was removed during preparation of RM 8785 was rather non-fossil compared to the remaining fine fraction. Consequently, size segregation should be avoided when using SRM 1649a as a ^{14}C reference material.

Table 3 Summary for each sample. Reported measurement uncertainties are averaged for all laboratories. Interlaboratory deviations reflect variations between the laboratories. (Note that this standard deviation refers to the single analysis of the best estimates of *n* laboratories and does not represent the standard deviation of the mean.) n.a. = not applicable.

Sample	*n*	^{14}C F^{14}C	Uncert. F^{14}C	Interlab deviation F^{14}C	TC, OC, EC µg/cm^2	Interlab deviation µg/cm^2	Fraction[a]	Interlab deviation
Milan (uncorrected)								
TC	9	0.516	0.005	0.023	121	13	n.a.	n.a.
EC	4	0.178	0.003	0.065	24	22	0.19	0.16
OC	2	0.728	0.009	0.009	58	2	0.45	0.07
Ispra (uncorrected)								
TC	8	0.746	0.006	0.014	137	21	n.a.	n.a.
EC	4	0.418	0.004	0.117	21	18	0.14	0.11
OC	2	0.877	0.011	0.020	67	13	0.41	0.11
Filter blank Milan/Ispra								
TC	6	0.461	0.009	0.100	3	2	n.a.	n.a.
EC[b]	1	0.188	0.004	n.a.	1	n.a.	0.18	n.a.
OC[b]	2	0.518	0.015	0.135	2	1	0.84	0.22
Milan (corrected)								
TC	6	0.520	0.006	0.025	119	13	n.a.	n.a.
EC	2	0.117	0.009	0.003	15	13	0.13	0.11
OC	2	0.734	0.011	0.009	56	3	0.45	0.07
Ispra (corrected)								
TC	5	0.753	0.007	0.015	136	23	n.a.	n.a.
EC	2	0.338	0.025	0.056	13	9	0.08	0.04
OC	2	0.887	0.012	0.020	65	12	0.40	0.11
RM 8785 (uncorrected)								
TC	9	0.438	0.004	0.049	51	23	0.32	0.05
(EC)[c]	(4)	(0.262)	(0.005)	(0.206)	(14)	(17)	(0.23)	(0.14)
EC[c]	3	0.160	0.004	0.036	17	19	0.27	0.14
OC	1	0.621	0.012	n.a.	18	n.a.	0.60	n.a.
RM 8786								
TC	6	1.239	0.017	0.160	5	2	n.a.	n.a.
EC[b]	1	0.298	0.005	n.a.	2	n.a.	0.33	n.a.
OC[b]	1	1.350	0.027	n.a.	3	n.a.	1.00	n.a.
RM 8785 (corrected)								
TC	5	0.322	0.047	0.041	43	22	0.28	0.05
EC	1	0.085	0.088	n.a.	4	n.a.	0.15	n.a.
OC	1	0.494	0.094	n.a.	15	n.a.	0.56	n.a.

[a] TC/PM for TC, EC/TC for TC, OC/TC for OC.

[b] Individual data not shown in Tables 2b and 2c for reasons of space.

[c] Results are shown for all laboratories (in parentheses) and after exclusion of 1 outlier as discussed in the text.

Despite the larger than previously reported measurement uncertainties, repeated ^{14}C(EC) analyses by the individual laboratories revealed acceptable variabilities (<0.02 F^{14}C), if one takes into account that these measurements involve considerable sample preparation, which may even limit a good in-house reproducibility. However, the comparison of results between the laboratories uncovers huge discrepancies. Standard deviations of uncorrected filters amounted to 0.065, 0.117, and 0.206 F^{14}C for the samples Milan, Ispra, and RM 8785, respectively, which accounted for 28–79% of the measured ^{14}C(EC) value. Such large differences raise the question of how published ^{14}C(EC) data from different laboratories can be evaluated or compared. It is obvious that this scatter was caused by the utilization of different methods of EC isolation. For discussion of these effects, we exclude laboratory E in the following, as it analyzed only RM 8785 and found particularly large ^{14}C(EC) values compared to the other laboratories, reducing the interlaboratory variability for RM 8785 substantially (Table 3). For the remaining laboratories, the applied methods of OC removal differed in the application or omission of water extraction and acid fumigation before the oxidation step as well as the details of the thermal treatment (Table 1). On the one hand, the aqueous or acid pretreatment may reduce analytical artifacts from non-quantitative removal of water-soluble components or carbonates, respectively. On the other hand, the intensity of the thermal treatment may directly influence the characteristics of the recovered EC (i.e. rather comprehensive or restricted to the most recalcitrant fraction): whereas too-high recoveries could indicate incomplete OC removal, too-low recoveries could lead to an underestimation of wood-burning EC because of its lower thermal stability compared to diesel EC (Hammes et al. 2007). Although the EC recovery can roughly be perceived from the EC/TC ratios in Table 2b, the true EC/TC ratio unfortunately remains unknown. This also applies for RM 8785, as 2 different TOA methods in the previous intercomparison resulted in completely different values of 0.28 and 0.49 using optical transmission and reflectance, respectively (Klouda et al. 2005). Zhang et al. (2012) observed that ^{14}C(EC) may decrease by ~0.03 F^{14}C, if the EC recovery declines by 10%. The results of laboratories C, F, and G seem to corroborate the decrease of ^{14}C(EC) with declining EC recoveries, even if this trend was not very clear. Laboratory D found lower ^{14}C(EC) values than the other 3 participants taking into account its comparably high EC recoveries, which may be attributed to the exclusion of water-soluble OC by water extraction. For RM 8785, laboratory D reported problems during water extraction, as the PM was not embedded into the filter as for ambient filters, so that the aerosol was dislocated on the filter surface and was rinsed through causing large inhomogeneities of PM loading. Without laboratory E, ^{14}C(EC) results were the most reproducible for RM 8785 followed by the urban sample from Milan. This suggests a reduced susceptibility to charring and other artifacts for the reference material compared to the ambient samples and for urban compared to rural sites. As a consequence, a good interlaboratory comparability for RM 8785 does not necessarily prove an acceptable conformity for ambient samples. In conclusion, the outcome of the intercomparison of ^{14}C(EC) analyses strongly requires method improvements. It should be noted that several laboratories have already taken steps toward method optimization since the performance of the intercomparison in 2009 (e.g. Zhang et al. 2012; Bernardoni et al. 2013).

There is only limited information on the comparison of ^{14}C(OC), as only 2 laboratories participated using similar methods. Nevertheless, the results of both laboratories agreed within measurement uncertainties, although gained OC/TC ratios differed by >20% from each other. The standard deviation between both labs was slightly higher for the sample Ispra than the average internal measurement uncertainty, whereas both statistical terms were comparable for the sample Milan. This suggests that complete conformity of sample preparation techniques was not as critical for correct ^{14}C determination of OC as for EC. The ^{14}C(OC) value for RM 8785 remained practically unusable because the blank correction mainly affected the OC fraction and induced very large uncertainties.

CONCLUSIONS AND OUTLOOK

An intercomparison of ^{14}C analysis of the carbonaceous aerosol fractions TC, EC, and OC on 2 ambient PM samples from Milan and Ispra, Italy, and RM 8785 (air particulate matter dispersed on filter media) was conducted among 9 laboratories. The following findings emerged from this study:

- ^{14}C(TC) measurements of the ambient samples Milan and Ispra resulted in an acceptable agreement among the laboratories. Average F^{14}C values of the blank-corrected filters with interlaboratory standard deviations amounted to 0.520 ± 0.025 and 0.753 ± 0.015, respectively. The mean uncertainties as reported by the individual laboratories were a factor of 1.5–2.5 smaller than the variabilities between the participants.

- ^{14}C(TC) results for RM 8785 showed a larger scatter than the ambient PM samples. This was presumably caused by the inhomogeneous loading during production. The consensus value of the blank-corrected sample is 0.322 ± 0.019. The contribution of the filter blank was unusually large (>10% by carbon mass with 1.239 F^{14}C). This introduced an additional uncertainty of the blank-corrected ^{14}C result, up to 0.087 F^{14}C depending on the additional uncertainty margins applied by the laboratories allowing for a realistic variability of the blank.
- In general, RM 8785 demonstrated only limited applicability as reference material for ^{14}C analysis of carbonaceous aerosols due to the large scatter of data caused by the inhomogeneous filter loading, the substantial filter blank of RM 8786, and the adverse behavior during water extraction.
- The comparison of ^{14}C(EC) revealed considerable discrepancies between the laboratories with standard deviations of up to 79% of the measured ^{14}C(EC) value. This was caused by different methods of EC isolation, i.e. the application of water extraction or acid fumigation before the oxidation step, and details of the thermal treatment. Whereas water extraction tended to result in smaller ^{14}C(EC) values, increasing EC recoveries led to larger ^{14}C(EC).
- The measurements of ^{14}C(OC) agreed well. The relevance of this outcome is somewhat limited, however, as only 2 laboratories provided ^{14}C data for the OC fraction.

Unfortunately, it was not possible to agree on common procedures of OC and EC isolation among all participants. There is an urgent need for further discussion about this and for a second stage of this intercomparison. We assume that such a repetition will turn out better than this one, as the data of this work were produced in 2009 and substantial improvements of procedures have been performed in several laboratories since then. A second stage should also include further discussion on data treatment, e.g. regarding the choice of appropriate additional uncertainty margins allowing for a realistic variability of the blank.

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