SOURCE APPORTIONMENT OF AEROSOLS BY ^{14}C MEASUREMENTS IN DIFFERENT CARBONACEOUS PARTICLE FRACTIONS

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ABSTRACT. Radiocarbon enables a distinction between contemporary and fossil carbon, which can be used for the apportionment of biogenic and anthropogenic sources in environmental studies. In order to apply this approach to carbonaceous atmospheric aerosols, it is necessary to adapt pretreatment procedures to the requirements of ^{14}C measurements. In this work, we followed an approach in which total carbon (TC) is subdivided into fractions of different chemical and physical properties. [14]C data of ambient aerosols from Zürich (Switzerland) are presented for the 2 sub-fractions of TC, organic carbon (OC) and elemental carbon (EC). Furthermore, OC is separated into water-insoluble OC (WINSOC) and water-soluble OC (WSOC). Results demonstrate the importance to differentiate between these fractions for ^{14}C-deduced source apportionment, as the contributions can range between both extremes, nearly exclusively biogenic and anthropogenic.

INTRODUCTION

Atmospheric carbonaceous particles include a huge variety of organic substances, which can sum up to half of the mass of the fine urban aerosol (Jacobson et al. 2000; Turpin et al. 2000). For their source apportionment, 2 different strategies are often employed, which can be classified as the "bottom" and "top" approach. The bottom approach pursues a complete identification of every single organic compound (Zheng et al. 1997; Kubátová et al. 2002). The top approach considers the carbonaceous particles as a whole with a given total carbon (TC) content, followed by a more specific division into the sub-groups organic carbon (OC) and elemental carbon (EC) with different physical and chemical properties (Krivácsy et al. 2001; Kleefeld et al. 2002). Moreover, OC can be separated into water-insoluble OC (WINSOC) and water-soluble OC (WSOC). Some classes of organic compounds that are found in these sub-groups are n-alkanes, aromatic compounds (e.g. PAHs), and long-chained carboxylic acids for WINSOC; polyols, polyethers, mono-, di-, and poly-carboxylic acids for WSOC; and a complex mixture of graphitic and high molecular weight refractory organic species for EC (Rogge et al. 1993; Jacobson et al. 2000; Turpin et al. 2000; Decesari et al. 2001). Whereas the bottom approach involves very extensive analytical procedures and allows only an identification of typically less than 10% of the organic mass at present (Rogge et al. 1993; Kubátová et al. 2002), the top approach leads to method-dependent sum parameters (Schmid et al. 2001; Currie et al. 2002).

Concerning the process of formation in the atmosphere, carbonaceous particles are often classified into primary organic aerosol, which is directly emitted as particles, and secondary organic aerosol (SOA), which is generated from gaseous precursors by atmospheric oxidation (Pun et al. 2000). During this process, less volatile compounds are formed, which then partition to the aerosol phase. This exposure to atmospheric oxidants introduces oxygenated groups to organic aerosol compounds, which enhances water solubility of SOA. Therefore, WSOC mainly consists of secondary aerosol.

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Radiocarbon measurements of carbonaceous particles bear the potential to distinguish between fossil carbon and contemporary carbon and, consequently, between anthropogenic and biogenic emission sources of aerosols (Currie et al. 1989; Klinedinst and Currie 1999; Currie 2000; Lemire et al. 2002). Whereas first studies were restricted to the analysis of TC (see Currie 2000 for a review), recent work also focused on ^{14}C analysis in specific fractions of the carbonaceous aerosol. On the one hand, preparative chromatography made it possible to perform compound specific studies of different PAHs (Currie et al. 1997; Currie et al. 2002; Reddy et al. 2002) and fatty acids (Matsumoto et al. 2001) according to the bottom approach. However, a large amount of aerosol had to be collected for these studies to achieve enough material for ^{14}C determination, resulting in a poor time resolution. On the other hand, ^{14}C measurements in EC (Slater et al. 2002; Currie et al. 2002; Reddy et al. 2002) and OC (Szidat et al. 2004a) followed the top approach.

Furthermore, the determination of ^{13}C has a potential to trace the extent of atmospheric photochemical processing. Rudolph et al. (2003) observed for the gas phase that isoprene is enriched in ^{13}C with increasing average lifetime, which suggests for the particulate phase that SOA is depleted in ^{13}C compared to the gaseous precursors.

In a previous work, we presented a separation scheme for the determination of ^{14}C in TC, OC, and EC and demonstrated its potential as an environmental tracer by investigation of Standard Reference Material (SRM) 1649a, Urban Dust (Szidat et al. 2004a). For this study, this separation scheme is extended to water-insoluble OC (WINSOC) and applied to ambient aerosol samples collected in Zürich, Switzerland.

METHODS

Sampling of Aerosols

Between 16 August and 8 September 2002, 4 aerosol samples were collected on pre-baked quartz fiber filters (D = 150 mm, QF 20, Schleicher and Schuell) with a high-volume sampler (Digitel DA80) and a PM_{10} inlet at the Swiss National Air Pollution Monitoring Network (NABEL) station in the city center of Zürich, Switzerland (47°22′42″N, 8°31′52″E, 410 m asl). After collection, samples were wrapped in aluminum foil, packed into air-tight plastic bags, and stored at –20 °C. For the ^{14}C analysis of EC and WINSOC, a long sampling duration (3–5 days) was necessary to get the carbon mass of approximately 20 µg required (Szidat et al. 2004a). The NABEL station Zürich represents an "urban background site", as primary emissions from traffic or industries have only a small impact (EMPA 2000). Meteorological parameters and concentrations of PM_{10} (half-hourly values using a betameter) as well as ozone were routinely determined at this station by the Swiss Federal Laboratories for Materials Testing and Research, Dübendorf.

Separation of Carbon Fractions for ^{14}C AMS Measurements

Seven sub-samples of 16 mm each of the air filters were used to perform the analysis of the different carbon fractions (1 for TC, OC, and WINSOC, 2 for total and water-insoluble EC). With the device *THEODORE* (Two-step heating system for the EC/OC determination of radiocarbon in the environment) (Szidat et al. 2004a), different carbonaceous particle fractions were separated within 10 min in a stream of oxygen under the following conditions and as illustrated in Figure 1.

TC was combusted at 650 °C; a previous acidification was not necessary because carbonates can be neglected in mid-latitude aerosols (Chow and Watson 2002). OC was separated from other carbon fractions at 340 °C. For WINSOC analysis, a water-extracted filter was obtained by soaking in
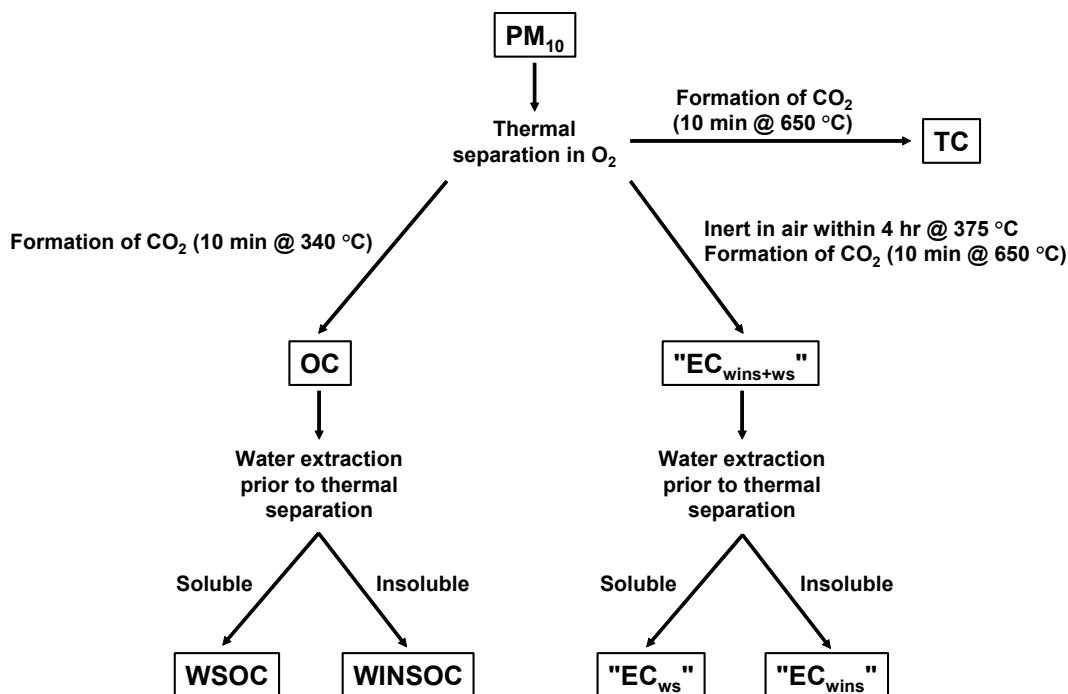
Figure 1 Separation scheme of the different carbon fractions

10 mL of high-purity water overnight (Gelencsér et al. 2000). Filters were dried and OC separation was conducted as described above. Determination of WSOC was performed by subtraction (WSOC = OC – WINSOC). For the analysis of EC, 2 methods were used: For the determination of EC according to Szidat et al. (2004a), OC was eliminated for 4 hr at 375 °C in a muffle furnace and EC was then combusted at 650 °C. This EC fraction represented a sum of 2 fractions and is named $EC_{wins+ws}$. In order to remove high-molecular polyacidic species, which rapidly form EC by pyrolysis on heating, a water extraction pretreatment as described above was carried out prior to the elimination of OC at 375 °C. The remaining fraction represented water-insoluble EC (i.e. EC_{wins}). The water-soluble fraction (EC_{ws}) was determined by subtraction ($EC_{ws} = EC_{wins+ws} - EC_{wins}$).

In order to achieve a highly efficient separation and isolation of OC and EC, an average total recovery of 60–80% was accepted. The residual OC included large polymeric polar molecules such as humic-like substances, which may hinder the separation of OC and EC and, therefore, were disregarded. These losses during the thermal treatment are tolerable for isotopic ratio measurements assuming identical $^{14}C/^{12}C$ ratios of the measured and the neglected fraction, which was shown to be valid for SRM 1649a, Urban Dust (Szidat et al. 2004a).

Sample Analyses

TC concentrations were determined by manometrical measurements of the produced carbon dioxide using the system *THEODORE* (Szidat et al. 2004a). $EC_{wins+ws}$ and EC_{wins} concentrations were measured with nearly quantitative yields using a longer combustion time of 42 min (Lavanchy et al. 1999). OC was calculated as the difference of TC and EC_{wins}, which was regarded as the best proxy for EC as described below.

Concentrations of water-soluble inorganic ionic species were analyzed in the water extract with standard ion chromatography (IC). Filter debris and suspended insoluble particles were removed using a 0.45-μm PTFE syringe filter. Uncertainties of IC analyses were less than 10%.

[14]C measurements were performed at the PSI/ETH compact AMS system, which is based on a 500-kV pelletron accelerator (Synal et al. 2000). For details of measurement parameters and data evaluation of sub-mg samples, see Szidat et al. (2004a). Using both the isotopic ratio and the carbon concentration, data were corrected for an overall blank, which was dominated by the filter blank but also included the blank of storage and chemical pretreatment of the samples. In this paper, ^{14}C results are presented as the fraction of contemporary carbon (f_C), which equals the biogenic contribution according to a simple ^{14}C model (Currie et al. 1989; Klinedinst and Currie 1999; Currie 2000; Lemire et al. 2002; Reddy et al. 2002; Szidat et al. 2004a). The correction factor for the residual nuclear bomb excess for mid-Europe was extrapolated as 1.077 ± 0.002 for August/September 2002 using atmospheric [14]CO_2 data from the Schauinsland and Jungfraujoch stations (Levin and Kromer 1997 and 2002; Levin, personal communication).

$\delta^{13}C$ measurements of the different carbon fractions were performed with the AMS target material using an isotope ratio mass spectrometer (IRMS) with an on-line elemental analyzer injection (Saurer et al. 1997; Szidat et al. 2004a).

RESULTS AND DISCUSSION

Aerosol Composition

Details of aerosol sampling, meteorological parameters, and concentrations of different chemical species are given in Table 1 and Figure 2. PM_{10} concentrations and temperature as well as ozone maxima show rather constant values due to the time resolution of 3–5 days. The lengths of the dry period before sampling (t_{dry}) differed significantly and the samples were classified accordingly. For samples II and IV, sampling started 15.5 hr and 5 hr after a rainfall, respectively; thus, these samples represent aerosol of relatively short average lifetime. On the other hand, t_{dry} amounted to several days for samples I and III, indicating aerosol of longer average lifetime. The different lifetimes had an influence on concentrations of all chemical species and carbon fractions. Rainfall leads to wet deposition of airborne particles. Thus, the fraction of fresh primary particles is increased immediately after a precipitation event. During dry days, aged aerosols accumulate and mix continuously with new primary and secondary particles. As a consequence, aerosol with a longer average lifetime shows higher concentrations of all parameters. This also includes the secondary inorganic compounds SO_4^{2-}, NO_3^-, and NH_4^+. Sea salt and mineral dust only contributed <6% to SO_4^{2-} according to the method of Schwikowski et al. (1999), indicating that observed concentrations originated nearly exclusively from oxidation of SO_2, which is predominantly emitted anthropogenically in a present urban environment. K^+ concentrations were low for all samples and in the range of typical values for Swiss urban and rural locations in summer (Hüglin et al., forthcoming). Sea salt contributed to less than 5%, assuming constant Na^+/K^+ ratios (Keene et al. 1986), but the fraction of K^+ originating from mineral dust is quite uncertain. Following the concept of Andreae (1983), who used crustal average K^+/Ca^{2+} ratios for the correction, a contribution to K^+ from mineral dust between 36% and >100% resulted. Because of this large uncertainty, an estimation of the fraction of EC derived from biomass burning using K^+/EC ratios was not possible, but ^{14}C analyses of EC as discussed below indicate that this fraction was 6% at most.

Table 1 Meteorological conditions, aerosol sampling parameters, and concentrations of carbonaceous particle fractions as well as some inorganic ions for the campaign in Zürich in summer 2002. Concentrations of carbonaceous particle fractions are presented with combined standard uncertainties (ISO 1995).

Sample	I	II	III	IV
Sampling period	16 Aug, 19:00–21 Aug, 19:00	21 Aug, 20:00–26 Aug, 20:00	30 Aug, 09:00–02 Sep, 09:00	03 Sep, 20:00–08 Sep, 20:00
Air volume (m^3)	3600	3600	2160	3600
PM_{10} ($\mu g\ m^{-3}$)	26.3	25.8	25.4	23.3
T_{max} (°C)[a]	26.9	23.9	23.2	22.5
$Ozone_{max}$ (ppbv)[a]	57	46	44	46
h_P (mm)[b]	3.3	0.0	45.6	1.0
t_{dry} (d)[b]	4.3	0.6	(3.0) 9.2[c]	0.2
TC ($\mu g\ m^{-3}$)	7.2 ± 0.3	3.6 ± 0.1	6.2 ± 0.2	2.5 ± 0.1
OC ($\mu g\ m^{-3}$)	5.7 ± 0.3	2.9 ± 0.2	5.0 ± 0.3	2.1 ± 0.1
WINSOC ($\mu g\ m^{-3}$)	2.0 ± 0.4	1.1 ± 0.2	2.0 ± 0.4	0.8 ± 0.2
WSOC ($\mu g\ m^{-3}$)	3.1 ± 0.4	1.5 ± 0.2	2.5 ± 0.4	1.0 ± 0.2
$EC_{wins+ws}$ ($\mu g\ m^{-3}$)	2.1 ± 0.1	1.0 ± 0.1	1.7 ± 0.1	0.6 ± 0.1
EC_{wins} ($\mu g\ m^{-3}$)	1.5 ± 0.2	0.7 ± 0.1	1.2 ± 0.2	0.4 ± 0.1
EC_{ws} ($\mu g\ m^{-3}$)	0.6 ± 0.2	0.3 ± 0.1	0.5 ± 0.2	0.2 ± 0.1
EC/TC	0.20 ± 0.03	0.19 ± 0.03	0.19 ± 0.03	0.18 ± 0.03
SO_4^{2-} ($\mu g\ m^{-3}$)	3.5	2.1	4.8	1.6
NO_3^- ($\mu g\ m^{-3}$)	0.5	1.0	2.0	0.5
NH_4^+ ($\mu g\ m^{-3}$)	1.1	1.0	2.3	0.7
K^+ ($\mu g\ m^{-3}$)	0.16	0.07	0.13	0.02

[a]= As means of daily maxima for the period of aerosol sampling.
[b]= Precipitation depth (h_P) during sampling, dry period before beginning of sampling (t_{dry}).
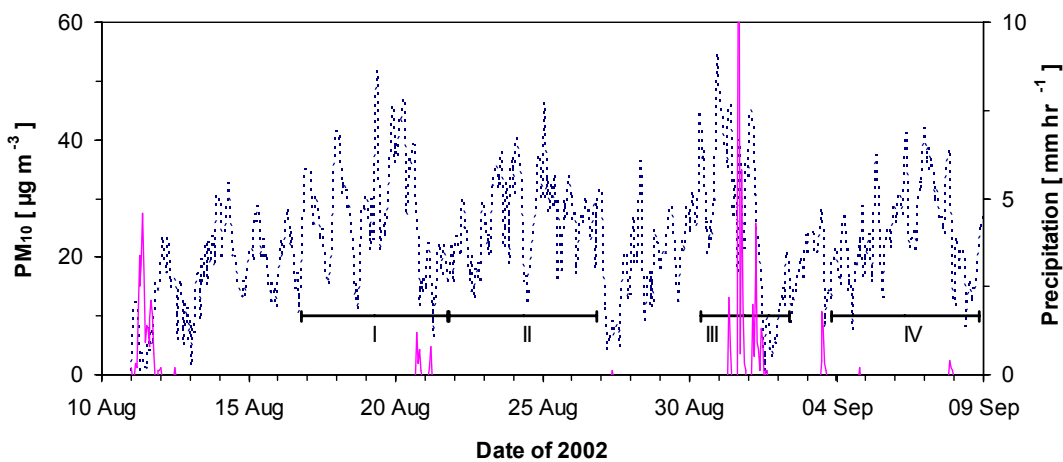[c]= 3.0 days before sampling, only a minor event with a precipitation depth of 0.1 mm occurred.

Figure 2 Hourly data of PM_{10} concentrations (dashed lines) and precipitation intensities (solid lines) during collection of aerosol samples I–IV.

Isotopic Signals of Carbonaceous Particle Fractions

Table 2 gives isotopic results for the different carbon fractions. Whereas f_C(TC) was rather constant at a level of 0.60–0.67, f_C(OC) indicated a significantly higher biogenic contribution for aerosol with a longer average lifetime (samples I and III). On the average, 82% of OC originated from biogenic sources in these samples compared to 69% in aerosol with shorter average lifetime. Equivalent results were observed for the sub-fractions of OC, WINSOC and WSOC. Similar to TC, f_C values were quite constant for all EC fractions at 0.30, 0.06, and 0.84 for $EC_{wins+ws}$, EC_{wins}, and EC_{ws}, respectively. $\delta^{13}C$ of all fractions ranged from –25.7‰ to –28.6‰. Mean values showed slightly more negative $\delta^{13}C$ for WINSOC (–27.9 ± 0.6‰) than for OC (–27.0 ± 0.2‰) and TC (–26.3 ± 0.3‰). However, this effect is not significant due to the high uncertainties; thus, a possible response of $\delta^{13}C$ to the influence of atmospheric processes (Rudolph et al. 2003) could not be detected.

Table 2 Carbon isotope results of different carbon fractions for the campaign in Zürich in summer 2002 with combined standard uncertainties (ISO 1995). "n.d." means "not determined."

Sample	I	II	III	IV
Sampling period	16 Aug, 19:00– 21 Aug, 19:00	21 Aug, 20:00– 26 Aug, 20:00	30 Aug, 09:00– 02 Sep, 09:00	03 Sep, 20:00– 08 Sep, 20:00
f_C (TC)	0.67 ± 0.02	0.60 ± 0.02	0.62 ± 0.03	n.d.
f_C (OC)	0.80 ± 0.02	0.67 ± 0.06	0.84 ± 0.03	0.71 ± 0.03
f_C (WINSOC)	0.63 ± 0.02	0.55 ± 0.04	0.68 ± 0.03	0.58 ± 0.04
f_C (WSOC)	0.91 ± 0.14	0.76 ± 0.16	0.96 ± 0.17	0.82 ± 0.15
f_C (EC$_{wins+ws}$)	0.30 ± 0.02	0.30 ± 0.02	0.30 ± 0.02	0.31 ± 0.02
f_C (EC$_{wins}$)	0.062 ± 0.020	0.064 ± 0.015	n.d.	n.d.
f_C (EC$_{ws}$)	0.84 ± 0.30	0.83 ± 0.29	n.d.	n.d.
$\delta^{13}C$ (TC) [‰]	–25.7 ± 0.4	–26.5 ± 0.6	–26.6 ± 0.6	n.d.
$\delta^{13}C$ (OC) [‰]	–26.9 ± 0.9	–27.4 ± 1.2	–26.5 ± 0.4	–27.0 ± 2.6
$\delta^{13}C$ (WINSOC) [‰]	–26.2 ± 0.5	–28.4 ± 0.5	–28.5 ± 0.8	–28.6 ± 1.0
$\delta^{13}C$ (EC$_{wins+ws}$) [‰]	n.d.	–26.9 ± 0.9	–25.7 ± 0.5	n.d.
$\delta^{13}C$ (EC$_{wins}$) [‰]	–27.3 ± 0.7	–26.1 ± 0.9	n.d.	n.d.

As stated above, the fraction of secondary aerosol increases with increasing aerosol lifetime. f_C(OC) also increased with increasing t_{dry}, indicating that SOA is to a significant fraction biogenic. This effect is even more pronounced for WSOC, and the highest f_C value was observed for f_C(WSOC) of sample III, which was preceded by the longest dry period. Thus, WSOC might be viewed as a proxy for SOA, which has a high content of water-soluble compounds (Kalberer et al. 2004), and the biogenic contribution of 96 ± 17% to WSOC of sample III indicates that SOA was mainly of biogenic origin.

Origin of Different EC Fractions

In Tables 1 and 2, two different methods for the separation of EC are considered. EC_{wins} resulted from the thermal EC separation with water extraction prior to combustion and $EC_{wins+ws}$ without this extraction (Figure 1). EC_{ws} (the difference between both) amounted to 30% of $EC_{wins+ws}$ on average. This value is surprisingly high because EC is supposed to be completely insoluble in water.

Measurements of the urban model aerosol SRM 1649a (see Table 3) apportioned EC as about 95% anthropogenic (Currie et al. 2002; Reddy et al. 2002; Szidat et al. 2004a). This value was confirmed to be the best estimate for EC sources at present by snow samples from Summit, Greenland (Slater

et al. 2002). $f_C(EC_{wins})$ was close to this value, whereas $f_C(EC_{wins+ws})$ was much higher and $f_C(EC_{ws})$ corresponds to results of f_C(WSOC). This implies that actually EC_{wins} represents EC correctly due to the f_C value and the water insolubility so that $f_C(EC_{wins})$ was set as f_C(EC) in Figures 3a and b as well as in Table 3. Furthermore, EC_{ws} seems to belong to the WSOC fraction as indicated by $f_C(EC_{ws})$ and to be artificially transformed into EC during analysis by pyrolysis. Obviously, this fraction is enriched with polymeric polar OC (e.g. polyacidic, humic-like substances), which is soluble in water and often interferes with OC/EC separations (Lavanchy et al. 1999; Kalberer et al. 2004). This suggests that $EC_{wins+ws}$ accounts for a mixture of EC and polymeric polar OC.

Table 3 Comparison of ^{14}C measurements in different carbonaceous particle fractions with results from Standard Reference Material SRM 1649a, Urban Dust (NIST 2001; Currie et al. 2002), and 2 American studies of ambient urban aerosols. Results are given as mean values with the whole range of values in parentheses, except for SRM 1649a (weighted mean of 3–5 repeated measurements with standard uncertainties of the mean). "n.d." means "not determined."

Source/site	NABEL Zürich	NABEL Zürich	SRM 1649a	Aldine	Welby (summer)	Welby (winter)
Date	Aug/Sep 2002	Aug 2002	1976/1977	Aug 2000	Aug 1996	Dec 96/Jan 97
Location	Zürich	Zürich	Washington, DC	Houston, Texas	Denver, Colorado	Denver, Colorado
f_C (TC)	0.63 (0.60–0.67)	n.d.	0.39 ± 0.01	0.48 (0.25–0.68)	0.42 (0.09–0.68)	0.26 (0.13–0.69)
f_C (OC)	0.75 (0.67–0.84)	0.69 (0.51–0.80)	0.52 ± 0.03	0.49 (0.14–0.74)[a]	n.d.	n.d.
f_C (EC)	~0.06	n.d.	0.05 ± 0.01	n.d.	n.d.	n.d.
Particle size	PM_{10}	PM_{10}	100 μm (sieved)	$PM_{2.5}$	$PM_{2.5}$	$PM_{2.5}$
Sampling time [d]	3–5	0.5–1.5	~365	0.25–1	0.25	0.25
Individual samples	4	13	1	9	24	18
Reference	This work	Szidat et al. 2004b	Szidat et al. 2004a	Lemire et al. 2002	Klinedinst and Currie 1999	Klinedinst and Currie 1999

[a]Estimated values based on determinations of f_C(TC) and OC/TC; for details, see Lemire et al. (2002).
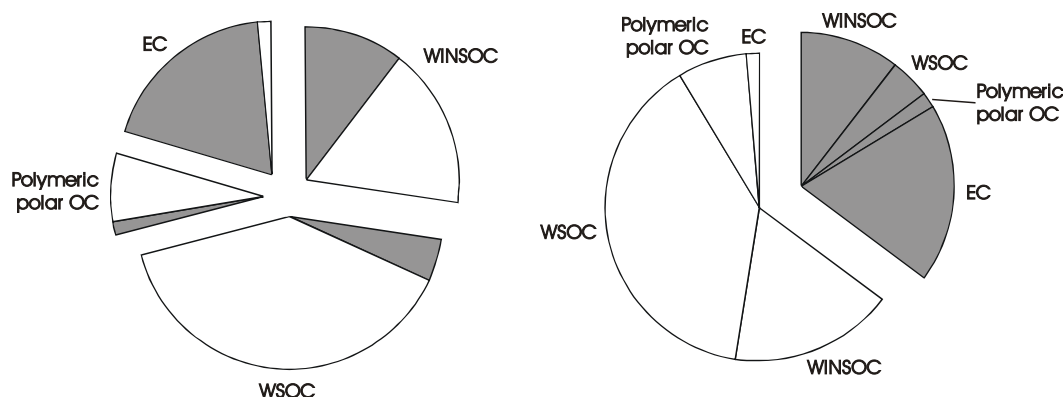

Figure 3a Biogenic (white) and anthropogenic (gray) contributions to different carbonaceous particle fractions of sample I representing aerosol of longer average lifetime, arranged by carbon fractions (left) and biogenic/anthropogenic contributions (right). Note that the fraction EC_{ws} is renamed "polymeric polar OC" (see "Sources of Different EC Fractions").

Source Apportionment Information

Figures 3a and b illustrate the source apportionment information for samples I and II. Results underline that measurements of f_C(TC) alone cannot provide a reliable identification of emission sources
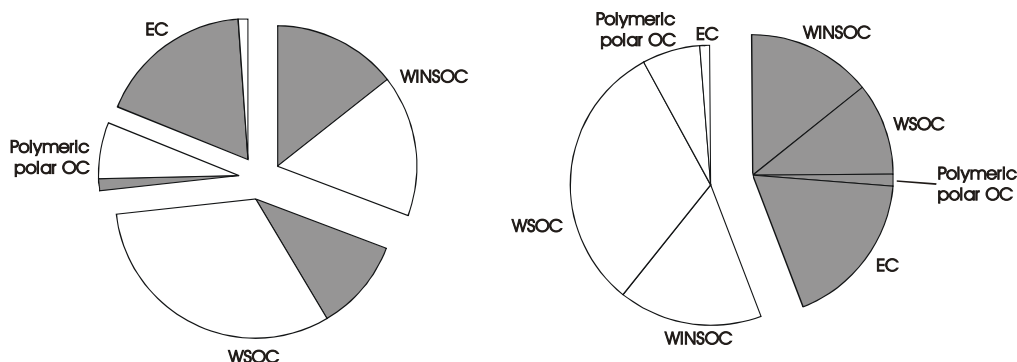
Figure 3b Same as Figure 3a but for sample II representing aerosol of shorter average lifetime

of carbonaceous aerosol, and that at least a separation of OC and EC is required, as these fractions may differ in physical and chemical properties as well as their origin. Moreover, the distinction between WSOC and WINSOC exposed a significantly higher anthropogenic contribution for the water-insoluble fraction.

Comparison of Results

f_C(TC), f_C(OC), and f_C(EC) values are compared with data from other studies in Table 3. Within a parallel campaign (Szidat et al. 2004b), we measured samples for f_C(OC) at the same site separated for day and night conditions with a higher time resolution. Both studies yielded similar f_C(OC) values. Some samples of the parallel campaign, which were collected immediately after a precipitation event and represented aerosol of very short average lifetime, showed slightly lower f_C(OC) values, which was caused by a higher fraction of fresh primary particles. A lower average of f_C(TC) was observed for cities in the US compared to Zürich. Some samples within the studies at Houston and Denver reached biogenic contributions of nearly 70%, similar to this work. In contrast to that, high anthropogenic emissions of up to 91% were also determined, which indicates completely different sources for those samples compared to Zürich. Moreover, f_C(OC) values are lower for SRM 1649a and Houston than for Zürich. However, as SRM 1649a represents an annual average and f_C(OC) values for Houston only give an estimate, a reliable comparison of ^{14}C results for OC is not possible. Finally, EC was nearly exclusively influenced by anthropogenic emissions in this work and in SRM 1649a as discussed above.

CONCLUSIONS

^{14}C measurements of different carbon fractions of airborne particulate matter according to the top approach enable an insight into emission sources of carbonaceous aerosols. Results from an urban background site in Zürich demonstrate that OC was derived from biogenic emissions to 75% of the average, whereas EC originated to 94% from anthropogenic sources. Furthermore, WSOC was determined as up to 96% biogenic, which suggests that SOA may be formed nearly exclusively from biogenic precursor gases even in an urban environment.

ACKNOWLEDGEMENTS

measurements is also acknowledged. We are grateful to the Paul Scherrer Institut (PSI) and the Swiss Federal Institute of Technology (ETH), who jointly operate the Zürich AMS facilities.

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