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Supplement of

An optimised organic carbon / elemental carbon (OC / EC) fraction separation method for radiocarbon source apportionment applied to low-loaded Arctic aerosol filters

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Text S1: COMPYCALC correction workflow

In this section, the COMPYCALC correction workflow is explained. A colour code is applied on the input value Table S1 and output Table (Table S2) to highlight corresponding values. The $F^{14}C$ values from the TC and EC radiocarbon measurements (Table S1) were used to calculate F_{OC} using Eq. S1. F_{EC} is corresponding to the EC value from the radiocarbon measurement. The output from the COMPYCALC run is shown in Table S2. The output includes the input EC value (F_{EC}), the EC value correct to 100% yield ($F_{EC(corr)}$), and the EC value correct to 100% yield with 0% charring ($F_{EC(final)}$). Note that in the COMPYCALC output file the terms F14C_EC, F14C_EC100, and F14C_EC100_0_charr are used for F_{EC}, $F_{EC(corr)}$, and $F_{EC(final)}$, respectively. The workflow for $F^{14}C$(EC) correction using COMPYCALC is summarised below in Fig. S1:

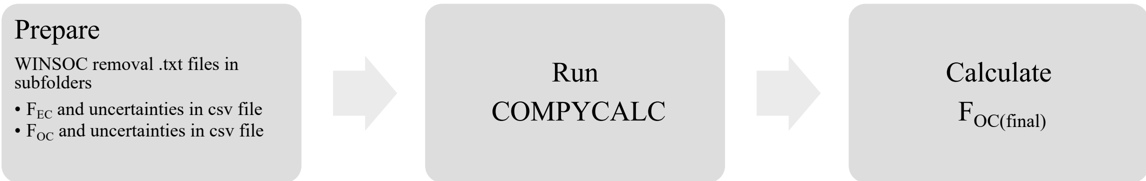

Figure S1: The workflow for corrections with COMPYCALC. The input $F^{14}C$ values F_{EC} and F_{OC} are added as csv files to the COMPYCALC folder, the COMPYCALC script run, and with the resulting $F_{EC(final)}$ the $F_{OC(final)}$ value calculated.

Input values

Table S1: COMPYCALC input values. Columns used for input are marked in colour; the F_{EC} refers to the $F^{14}C$(EC) value obtained from the radiocarbon measurement, F_{OC} was calculated using Eq. S1 from the $F^{14}C$(TC), $F^{14}C$(EC), and EC/TC ratio. TC and EC loadings are from measurements at the University of Bern. Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	TC $F^{14}C$	TC µg C cm^{-2}	F_{EC} $F^{14}C$	EC µg C cm^{-2}	EC/TC ratio	F_{OC} $F^{14}C$
23 Feb 2017	02 Mar 2017	0.770	9.5	0.881	1.47	0.15	0.749
05 May 2017	15 May 2017	1.068	7.1	0.597	1.21	0.17	1.165
31 May 2017	26 Jun 2017	0.852	2.6	0.642	0.82	0.32	0.951
*08 Sep 2017	28 Sep 2017	0.959	4.1	0.689	0.47	0.11	0.993
28 Sep 2017	06 Oct 2017	1.036	22.3	0.544	2.41	0.11	1.095
*06 Oct 2017	24 Oct 2017	0.825	3.4	0.748	0.44	0.13	0.837
*05 Dec 2017	21 Dec 2017	0.509	3.3	0.563	0.82	0.25	0.492
23 Jan 2018	31 Jan 2018	0.573	6.1	0.184	1.03	0.17	0.652
21 Mar 2018	29 Mar 2018	0.951	5.0	0.570	0.71	0.14	1.014
06 Apr 2018	16 Apr 2018	0.957	6.0	0.527	0.84	0.14	1.027
*12 Jul 2018	30 Jul 2018	0.786	2.8	0.677	0.34	0.12	0.802
*30 Jul 2018	15 Aug 2018	0.997	9.5	0.767	0.55	0.06	1.011
23 Nov 2018	03 Dec 2018	0.727	3.9	0.554	0.56	0.14	0.756

*Pooled filters

$$F_{OC} = \frac{F_{TC} - F_{EC} * \frac{EC}{TC}}{1 - \frac{EC}{TC}} \tag{S1}$$

Text S2: COMPYCALC Output

In the main folder with the compycalc.R script, a summary pdf file and a summary csv are generated by COMPYCALC. In the csv file (see Table S2), the first COMPYCALC output column is called filter_name_short and defined by the last letter of the folder name, in which the Sunset raw data files for each filter are placed. Self-descriptive are the following five columns: EC_yield, charring_S1, charring_S2, charring_S3, and charring_total are the mean EC yields obtained by OC removal, the charring for each step in the Swiss_4S protocol, and the toal charring (sum of charring S1-S3), respectively. F14C_EC is the initial uncorrected EC value (F_{EC}), F14C_EC100 corresponds to the $F^{14}C$ value for EC extrapolated to 100% EC yield ($F_{EC(corr)}$), F14C_EC100_0_charr to the $F^{14}C$ value for EC extrapolated to 100% EC yield with 0% charring ($F_{EC(final)}$). The corresponding columns with a _u-suffix estimate the uncertainty by error propagation. The corrected OC value ($F_{OC(final)}$) was calculated with Eq. S1 and the F14C_EC100_0_charr value. As shown in Fig. S2, the summary pdf gives a visual overview of the $F^{14}C$ results, the EC yield, and the charring for each step.

Table S2: Summary output of COMPYCALC with the filter sampling start and end date added in the first and second column. Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	COMPYCALC output						
23 Feb 2017	02 Mar 2017	filter_name_short	EC_yield	charring_S1	charring_S2	charring_S3	charring_total
05 May 2017	15 May 2017	A	0.720	0.015	-0.001	0.013	0.027
31 May 2017	26 Jun 2017	B	0.865	0.029	0.001	0.024	0.054
*08 Sep 2017	28 Sep 2017	C	0.854	0.039	0.000	0.089	0.129
28 Sep 2017	06 Oct 2017	D	0.892	0.049	0.012	0.045	0.106
*06 Oct 2017	24 Oct 2017	E	0.803	0.068	-0.005	0.030	0.093
*05 Dec 2017	21 Dec 2017	F	0.854	0.021	0.011	0.022	0.055
23 Jan 2018	31 Jan 2018	G	0.930	0.016	0.006	0.022	0.045
21 Mar 2018	29 Mar 2018	H	0.921	0.012	0.003	0.014	0.030
06 Apr 2018	16 Apr 2018	I	0.919	0.020	0.002	0.017	0.039
*12 Jul 2018	30 Jul 2018	J	0.859	0.025	0.004	0.035	0.064
*30 Jul 2018	15 Aug 2018	K	0.941	0.028	0.014	0.021	0.062
23 Nov 2018	03 Dec 2018	L	0.951	0.037	0.024	0.054	0.115
Start date	End date	M	0.818	0.010	0.002	0.014	0.026

*Pooled filters

Table S2 continued:

COMPYCALC output						
F_{EC}		$F_{EC(corr).}$			$F_{EC(final)}$	
F14C_EC	F14C_EC_u	F14C_EC100	F14C_EC100_u	linear_slope	F14C_EC100_0_charr	F14C_EC100_0_charr_u
0.881	0.043	0.925	0.044	0.157	0.917	0.077
0.597	0.027	0.714	0.038	0.867	0.656	0.055
0.642	0.047	0.756	0.051	0.787	0.699	0.086
0.689	0.044	0.782	0.048	0.863	0.735	0.086
0.544	0.021	0.694	0.036	0.760	0.620	0.049
0.748	0.047	0.841	0.049	0.632	0.801	0.085
0.563	0.039	0.653	0.052	1.301	0.612	0.077
0.184	0.030	0.267	0.123	1.058	0.226	0.132
0.570	0.040	0.665	0.052	1.185	0.618	0.079
0.527	0.035	0.654	0.049	0.903	0.591	0.072
0.677	0.052	0.754	0.056	1.301	0.717	0.094
0.767	0.042	0.826	0.045	1.206	0.794	0.078
0.554	0.051	0.696	0.059	0.782	0.633	0.094

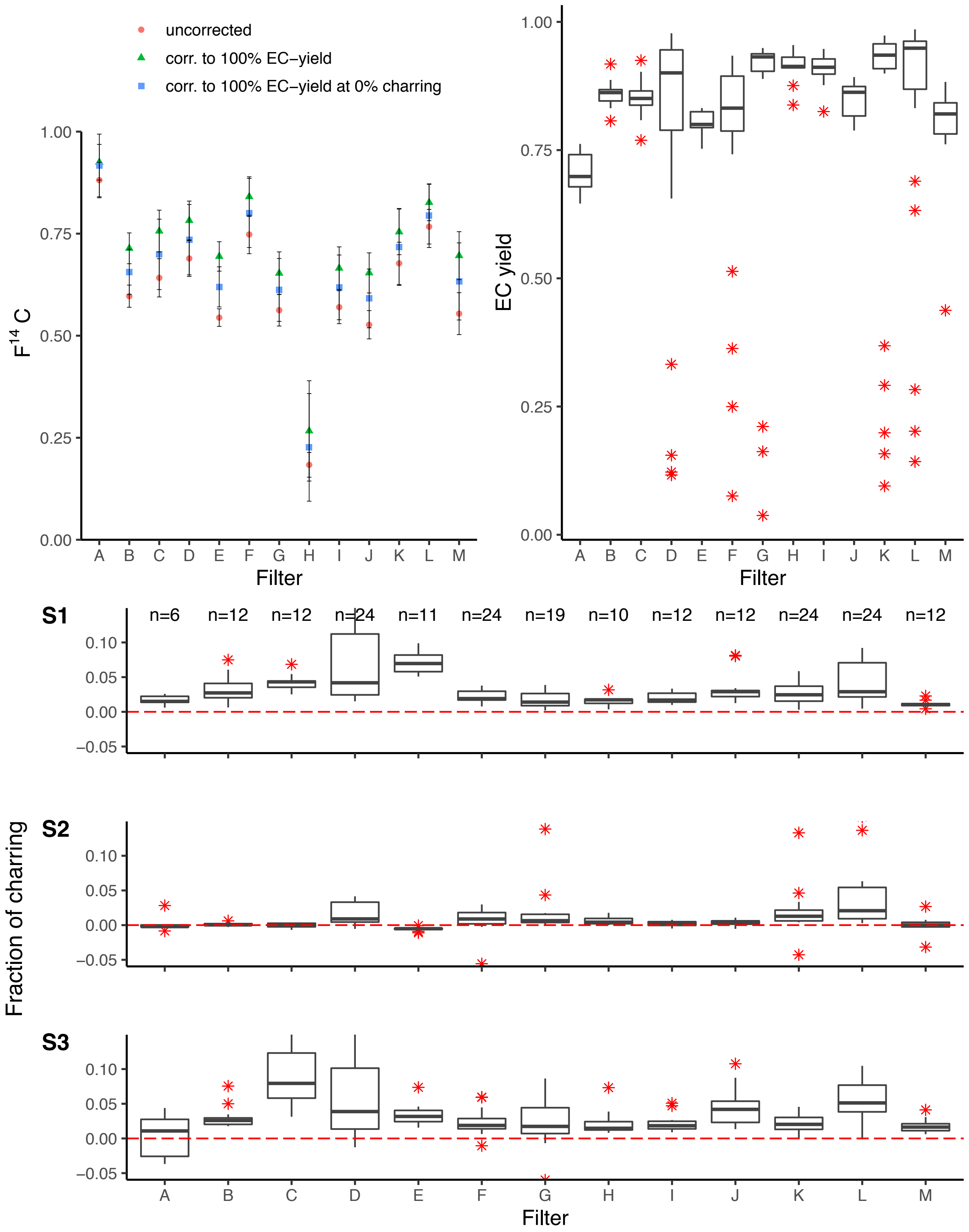

Figure S2: Summary pdf generated by COMPYCALC. The filter names correspond to the filter sampling start and end dates outlined in Table S2.

Text S3: COMPYCALC file and folder structure

The COMPYCALC (COMprehensive Yield CALCulation) script (compycalc.R) consists of three subscripts in the zsrc folder (see Fig. S3) for data input and output (yields_calc_io.R), EC yield and charring (yields_calc_ext.R), as well as an extrapolation of the $F^{14}C$(EC) values to 100% EC yield (corr_100_EC.R). Additionally, the folder contains a generic 4th step file corresponding to the S4 step in the Swiss_4S protocol (cooldown_data.csv). For each sample, the OC/EC analyser raw data files containing the laser transmission signal for each OC removal run need to be in a designated subfolder. When multiple Sunset WINSOC removal runs have been recorded to a single (txt) file, they must be split to individual files, e.g., using the 'file splitter' tool from Sunset-calc (see Chapter 3.10). Additionally, the script requires two input files in the csv format in the main folder (i.e., where the compycalc.R script is located). The first file contains two columns: the first column with the uncorrected $F^{14}C$(EC) and the second column with the measurement uncertainties. The second csv file contains a single column with the $F^{14}C$(OC) data. The data input and output script (yields_calc_io.R) loads the OC/EC analyser raw data (txt) files for each sample folder and initiates the calculation with the EC yield and charring script (yields_calc_ext.R). The results written in each sample folder is then read by the main script and forwarded to the second calculation script for the correction to 100% EC yield (corr_100_EC.R). Finally, the $F^{14}C$(EC) value extrapolated to 100% EC yield corrects for charring in the main script (compycalc.R). After all calculations, a summary data file (csv format) with overall EC yield, the fraction of charring for each OC removal step (S1, S2, S3), the total fraction of charring as well as the raw $F^{14}C$(EC) (F14C_EC), F14C(EC) extrapolated to 100% EC yield (F14C_EC100), and $F^{14}C$(EC) extrapolated to 100% EC yield and corrected for charring (F14C_EC100_0_charr) is generated as an output. Additionally, a summary pdf is generated with plots for all $F^{14}C$ results, EC yields, and the fraction of charring for each step (S1, S2, S3). Figure S4 provides an overview scheme of COMPYCALC.

```
compycalc/
├─ compycalc.R
├─ Filter-A
│   ├ — — Filter-A-WINSOC-removal-1.txt
│   ├ — — Filter-A-WINSOC-removal-2.txt
│   ├ — — Filter-A-WINSOC-removal-3.txt
│   ├ — — Filter-A-WINSOC-removal-4.txt
│   ├ — — Filter-A-WINSOC-removal-5.txt
│   └ — — Filter-A-WINSOC-removal-6.txt
├─ Filter-B
│   ├ — — Filter-B-WINSOC-removal-1.txt
│   ├ — — Filter-B-WINSOC-removal-2.txt
│   ├ — — Filter-B-WINSOC-removal-3.txt
│   └ — — Filter-B-WINSOC-removal-4.txt
└─ zsrc/
    ├ — — yields_calc_io.R
    ├ — — yields_calc_ext.R
    ├ — — corr_100_EC.R
    └ — — cooldown_data.csv
```

Figure S3: Example of the COMPYCALC folder structure with two filters (A, B). 6 individual WINSOC removal run text files are in the folder for filter A and 4 text files for filter B as an example. The COMPYCALC folder must not contain any other file(s), including hidden files.

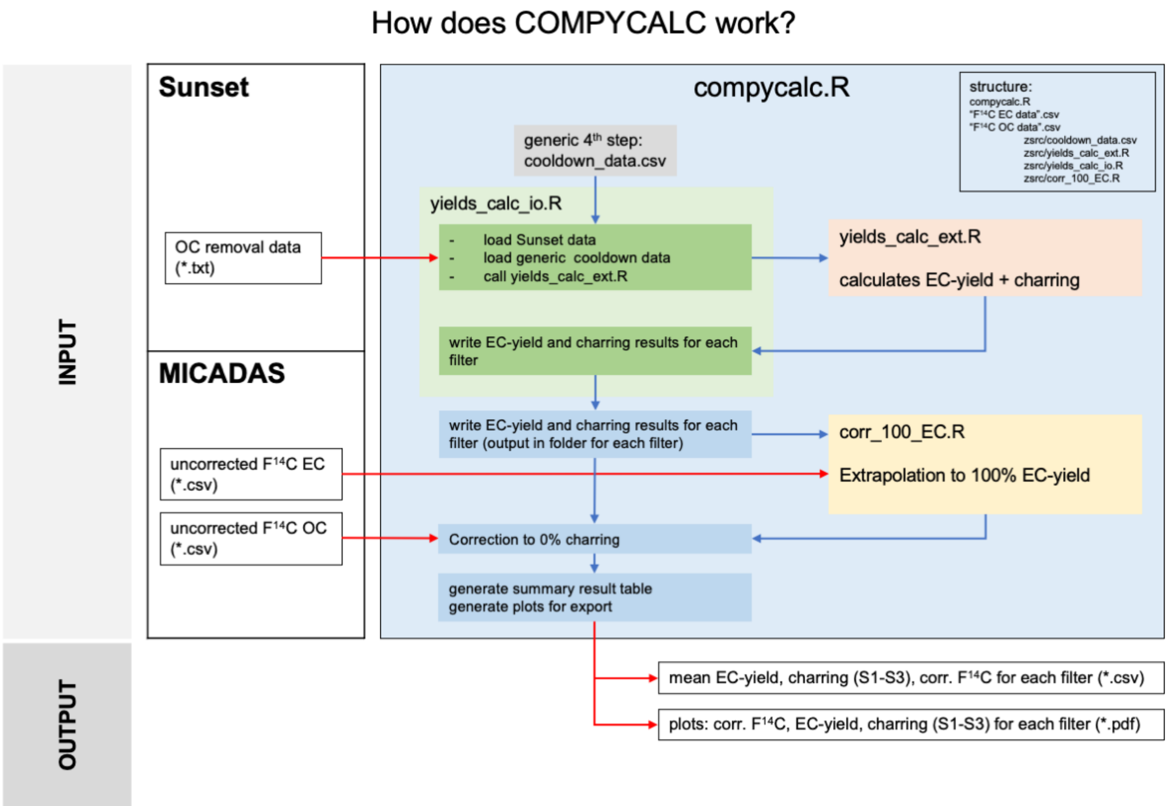

Figure S4: Scheme on how COMPYCALC loads raw data from the Sunset OC/EC analyser and from radiocarbon measurement (e.g., MICADAS AMS) data and performs the EC yield and charring calculation and extrapolation.

Text S4: Additional result tables and figures

Table S4 summarises the filter loadings for each fraction measured at the University of Bern. The circular water-extracted filters were cut in quarters before they were subjected to individual WINSOC removal. Although all filters after WINSOC removal were used for radiocarbon EC measurement, some filters were outliers and not used for EC yield and charring calculation. Table S5 summarises the total number of filters cuts used for WINSOC removal, the number of filters used for calculation, and the outliers. Table S6 and S7 summarise the EC yield and charring for S1, S2, and S3 values before and after filtering (i.e., outliers removed for EC yield and charring calculation). Figure S5 shows the $F^{14}C$ values of EC before and after EC yield and charring corrections were applied.

Table S4: Filter loadings measured in Bern using the Swiss_4S protocol. EC uncorrected denotes the total measured EC including charred OC. The EC corrected value corrects for the losses during WINSOC removal. WINSOC corrected denotes the calculated WINSOC amount without EC loss during WINSOC removal and charring. WSOC was calculated as WSOC = TC – EC_{corr} – $WINSOC_{corr}$. Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	EC uncorr. ng C m^{-3}	EC corr. ng C m^{-3}	WINSOC + EC loss ng C m^{-3}	WINSOC corr. ng C m^{-3}	WSOC ng C m^{-3}	OC ng C m^{-3}
23 Feb 2017	02 Mar 2017	27	39	70	58	92	150
05 May 2017	15 May 2017	20	23	31	28	70	98
31 May 2017	26 Jun 2017	17	20	93	90	4	93
*08 Sep 2017	28 Sep 2017	8	8	16	12	19	31
28 Sep 2017	06 Oct 2017	53	67	164	151	283	435
*06 Oct 2017	24 Oct 2017	8	5	12	11	19	30
*05 Dec 2017	21 Dec 2017	18	9	18	12	15	27
23 Jan 2018	31 Jan 2018	23	25	54	51	59	110
21 Mar 2018	29 Mar 2018	15	16	38	36	57	93
06 Apr 2018	16 Apr 2018	14	16	37	35	54	89
*12 Jul 2018	30 Jul 2018	6	4	13	13	9	23
*30 Jul 2018	15 Aug 2018	11	8	28	26	70	97
23 Nov 2018	03 Dec 2018	9	12	32	29	26	55

*Pooled filters

Table S5: Total number of filters for each sampling period used for WINSOC removal, the number of filters used by COMPYCALC for calculation after filtering, and the number of outlier filters removed for calculation (total filters – filters used for calculation). Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	Total filters	Filters used for calculation	Outliers
23 Feb 2017	02 Mar 2017	6	4	2
05 May 2017	15 May 2017	12	6	6
31 May 2017	26 Jun 2017	12	9	3
*08 Sep 2017	28 Sep 2017	24	20	4
28 Sep 2017	06 Oct 2017	11	8	3
*06 Oct 2017	24 Oct 2017	24	17	7
*05 Dec 2017	21 Dec 2017	19	14	5
23 Jan 2018	31 Jan 2018	10	6	4
21 Mar 2018	29 Mar 2018	12	10	2
06 Apr 2018	16 Apr 2018	12	10	2
*12 Jul 2018	30 Jul 2018	24	18	6
*30 Jul 2018	15 Aug 2018	24	18	6
23 Nov 2018	03 Dec 2018	12	7	5

*Pooled filters

Table S6: EC yield and charring for S1, S2, S3, and the total charring before filtering, i.e., including outliers Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	EC yield	charring S1	charring S2	charring S3	charring total
23 Feb 2017	02 Mar 2017	0.705	0.017	0.002	-0.013	0.006
05 May 2017	15 May 2017	0.860	0.033	0.001	0.020	0.054
31 May 2017	26 Jun 2017	0.852	0.042	0.000	0.114	0.156
*08 Sep 2017	28 Sep 2017	0.774	0.148	0.055	0.817	1.020
28 Sep 2017	06 Oct 2017	0.803	0.072	-0.006	0.034	0.100
*06 Oct 2017	24 Oct 2017	0.757	0.028	0.008	0.094	0.130
*05 Dec 2017	21 Dec 2017	0.803	0.094	0.112	1.323	1.529
23 Jan 2018	31 Jan 2018	0.911	0.016	0.006	0.023	0.045
21 Mar 2018	29 Mar 2018	0.908	0.020	0.002	0.023	0.045
06 Apr 2018	16 Apr 2018	0.849	0.034	0.003	0.046	0.083
*12 Jul 2018	30 Jul 2018	0.792	0.140	0.039	0.151	0.329
*30 Jul 2018	15 Aug 2018	0.829	0.172	0.074	0.334	0.580
23 Nov 2018	03 Dec 2018	0.788	0.011	0.000	0.018	0.029

*Pooled filters

Table S7: EC yield and charring for S1, S2, S3, and the total charring after filtering, i.e., without outliers as defined in COMPYCALC. Filters that were pooled for ^{14}C analysis are marked with an asterisk.

Start date	End date	EC yield	charring S1	charring S2	charring S3	charring total
23 Feb 2017	02 Mar 2017	0.720	0.015	-0.001	0.013	0.027
05 May 2017	15 May 2017	0.865	0.029	0.001	0.024	0.054
31 May 2017	26 Jun 2017	0.854	0.039	0.000	0.089	0.129
*08 Sep 2017	28 Sep 2017	0.892	0.049	0.012	0.045	0.106
28 Sep 2017	06 Oct 2017	0.803	0.068	-0.005	0.030	0.093
*06 Oct 2017	24 Oct 2017	0.854	0.021	0.011	0.022	0.055
*05 Dec 2017	21 Dec 2017	0.930	0.016	0.006	0.022	0.045
23 Jan 2018	31 Jan 2018	0.921	0.012	0.003	0.014	0.030
21 Mar 2018	29 Mar 2018	0.919	0.020	0.002	0.017	0.039
06 Apr 2018	16 Apr 2018	0.859	0.025	0.004	0.035	0.064
*12 Jul 2018	30 Jul 2018	0.941	0.028	0.014	0.021	0.062
*30 Jul 2018	15 Aug 2018	0.951	0.037	0.024	0.054	0.115
23 Nov 2018	03 Dec 2018	0.818	0.010	0.002	0.014	0.026

*Pooled filters

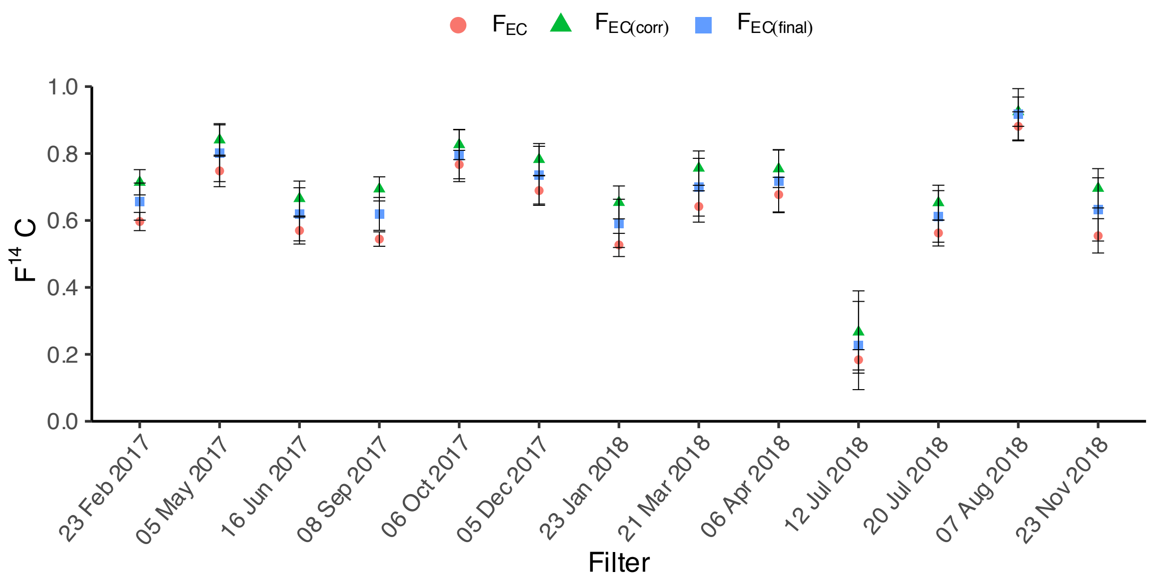

Figure S5: $F^{14}C(EC)$ values for the EC yield and charring correction. Starting from the initial EC value (F_{EC}), COMPYCALC computes the yield extrapolated EC value ($F_{EC(corr)}$) and with the charring correction, the final corrected EC value is calculated ($F_{EC(final)}$).

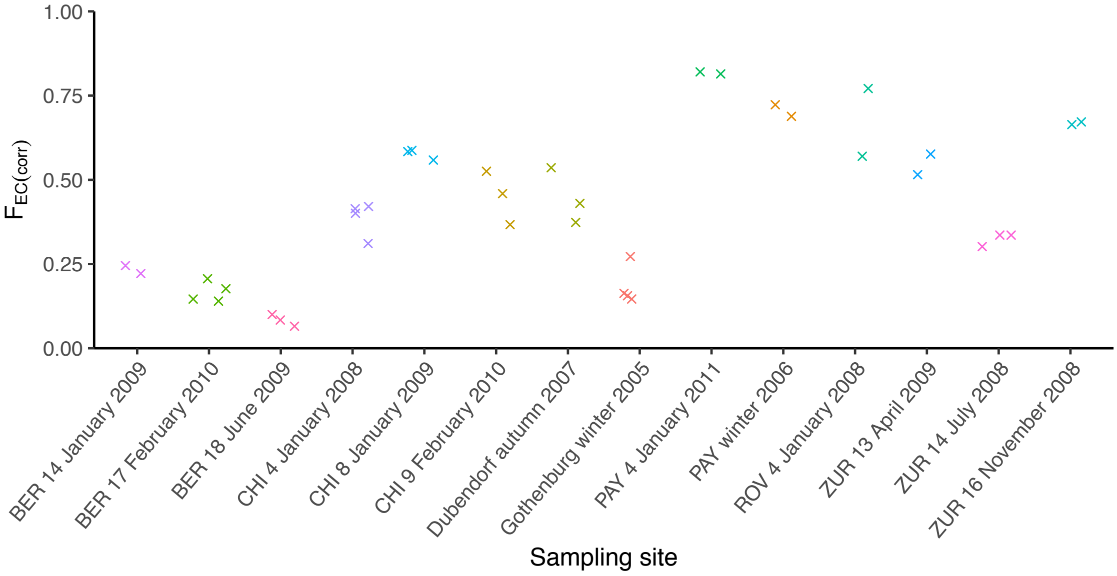

Figure S6: Extrapolation and correction jitter plot of the data from Zotter et al. (2014) with the Arrhenius approach. Figure S2 of Zotter et al. (2014) shows the Fraction Modern of EC as a function of the EC yield from multiple sites. Here the thermal desorption model corrected Fraction Modern for each site is shown. In an optimal case, the $F_{EC(corr)}$ should be independent of the EC yield and lead to the same $F_{EC(corr)}$ value. We estimate an uncertainty of 0.1. The abbreviation BER refers to the sampling station in Bern, Switzerland, CHI to Chiasso, Switzerland, PAY to Payerne, Switzerland, ROV to Roveredo, Switzerland, and ZUR to Zurich, Switzerland. Sampling site details can be found in Zotter et al. (2014) Table 1.

Text S5: Constant contamination chemical wet oxidation

OxII (SRM 4990 C) and fossil NaAc (Szidat et al., 2014) standards were used to prepare ~1000 ppm stock solutions in ultrapure water. An aliquot of the standard stock solutions equivalent to 3.5–57.0 µg C and 5.0–50.0 µg C for OxII and NaAc, respectively were added to an Exetainer vial (12 mL) containing ultrapure water (5.0 ± 0.2 mL). Inorganic carbonaceous impurities were removed by purging with helium. The chemical wet oxidation was performed as described in Chapter 2.4. The constant contamination of 0.9 ± 0.2 µg C with $F^{14}C$ = 0.20 ± 0.08 was determined by a drift model (Salazar et al., 2015; Hanke et al., 2017) and shown in Fig. S7. Constrains 0 to 1 for the Fraction Modern (R_S) and of 0.1–6 µg C for the mass of the contaminant (m_k) were made, then the drift correction minimised for both m_k and R_S within the given constrains.

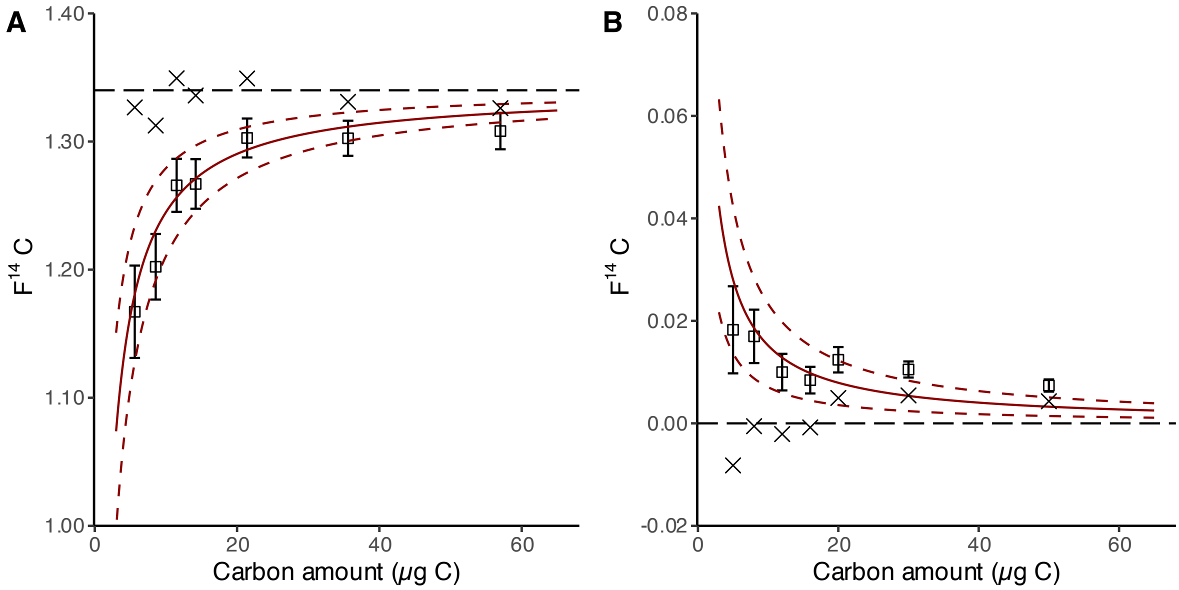

Figure S7: Constant contamination of the chemical wet oxidation (procedural blank). Measured radiocarbon data plotted as $F^{14}C$ with measurement uncertainty versus sample size (µg C) for modern OxII standard (A) and fossil NaAc standard (B). The solid dark red lines with the 1σ uncertainty ranges (dashed) are the drift model curves, the crosses the drift corrected $F^{14}C$ values.

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