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Supplement of

Radiocarbon analysis of elemental and organic carbon in Switzerland during winter-smog episodes from 2008 to 2012 – Part 1: Source apportionment and spatial variability

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Supplementary materials for: Radiocarbon Analysis of Elemental and Organic Carbon in Switzerland during Winter-Smog Episodes from 2008 to 2012 – Part I: Source Apportionment and Spatial Variability

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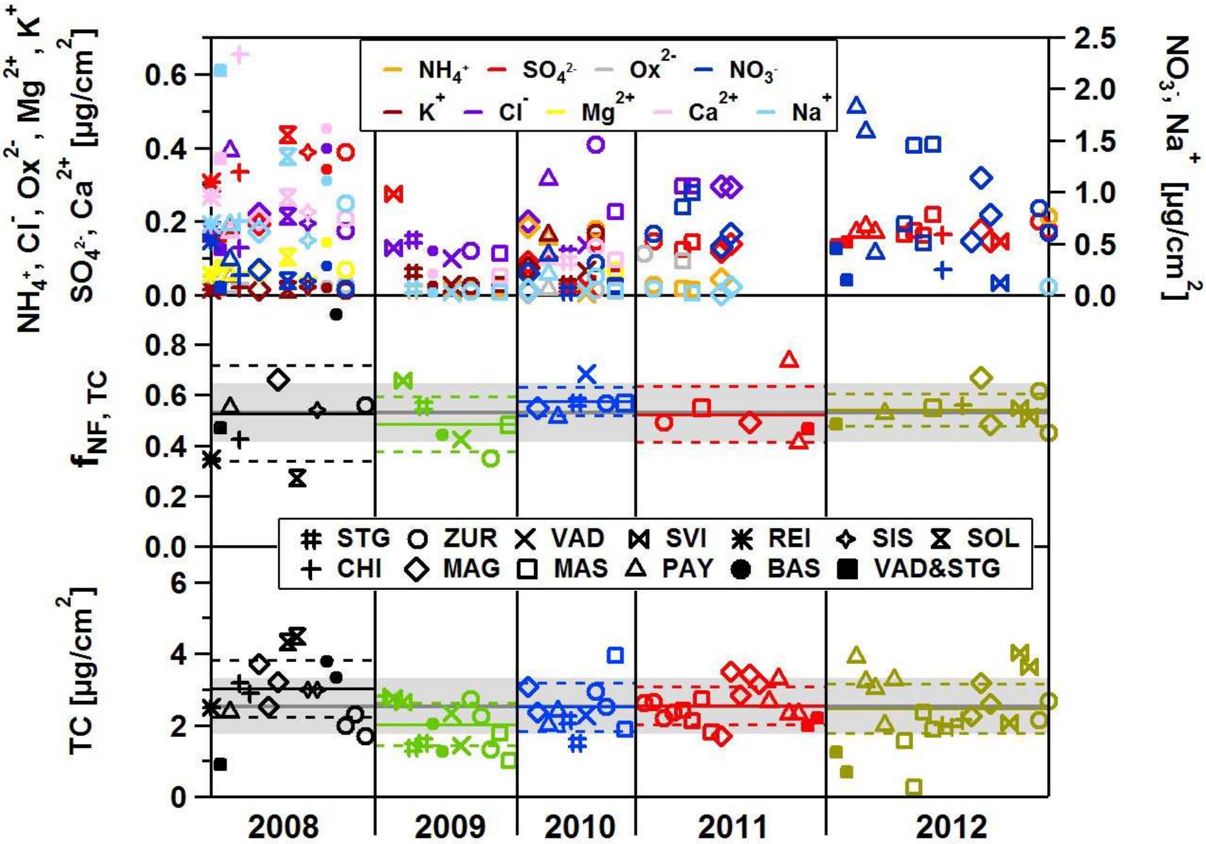

Figure S1: Results of all blank measurements. 34 blank filters were analyzed for ^{14}C in TC, 45 for major ions and 47 for the TC mass loading. Multiple results from the same station for TC represent not only different blank filters but also repeated measurements. Only for some stations (2008: two for MAG and ZUR; 2009: two for ZUR; 2011: two for MAS, ZUR and PAY as well as three for MAG; 2012: two for the combined blank of VAD and STG, MAG and SVI as well as three for PAY and MAS) TC mass was measured on more than one blank filter per year. Multiple blank results for the same station for the major ionic species refer to different blank filters, whereas multiple ^{14}C blank results represent only repeated measurements of the same blank filter. On the blank filters from the winter 2011/2012, with one exception, only nitrate and sulfate were above the detection limit. The solid and dashed colored horizontal lines in the lower and middle panel represent the annual mean and standard deviation, respectively. The solid grey line and shaded area denote the average and standard deviation over all blanks (different stations and years).

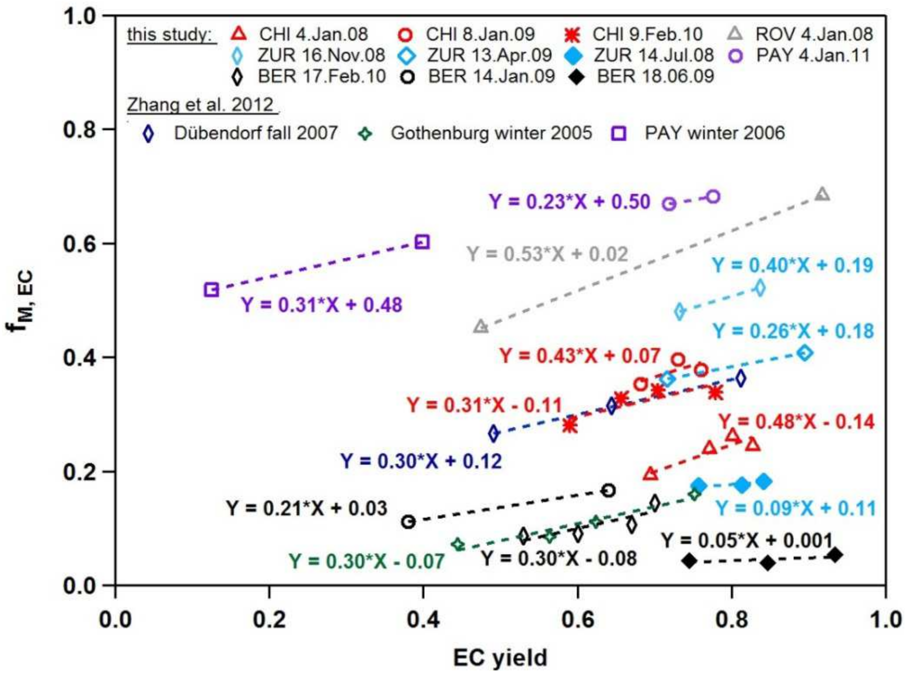

Figure S2: $f_{M,EC}$ as a function of EC yield. The open symbols represent winter samples whereas the filled ones denote filters from summer. The uncertainty for the EC yield was assumed to be 10% (see Sect. 2.3.2) and the one for $f_{M,EC}$ is on average ~2% (see Sect. 2.3.1 in the main text). An orthogonal distance regression was used to fit the data.

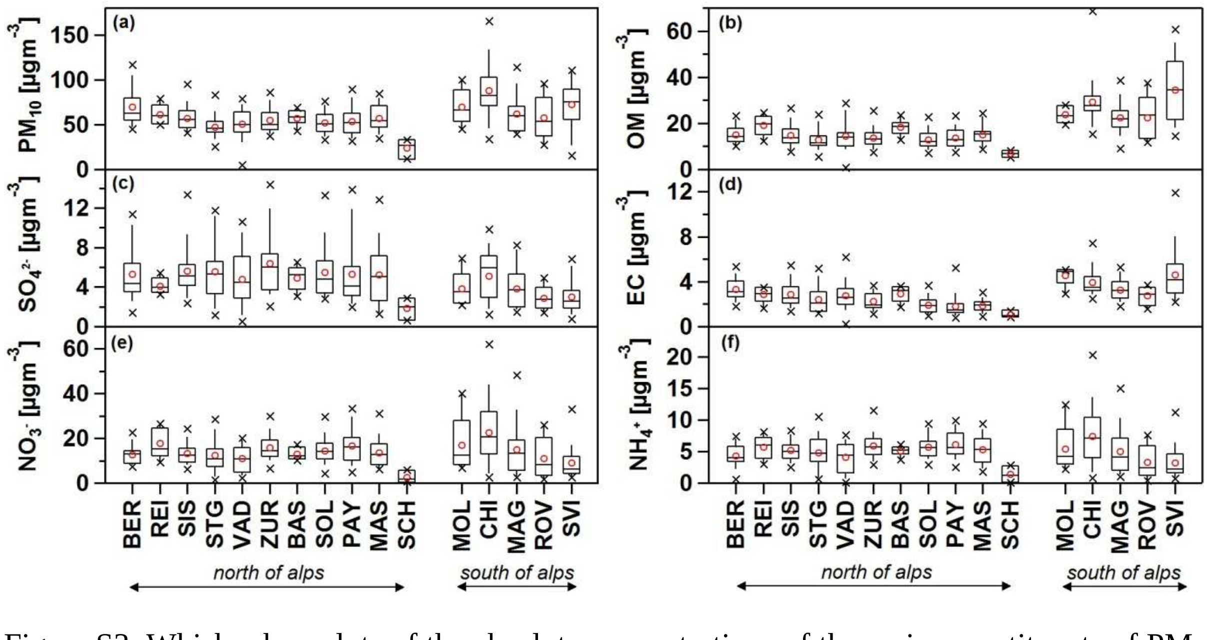

Figure S3. Whisker box plots of the absolute concentrations of the major constituents of PM_{10} from all analyzed winter samples. The open red circles represent the mean and the black crosses the max. and min. values. Stations north and south of the Alps are sorted from the left to the right from the nominal most traffic traffic-influenced station to the most rural one (see Table 1 in the main text.). Data from the yearly cycle in ZUR are excluded.

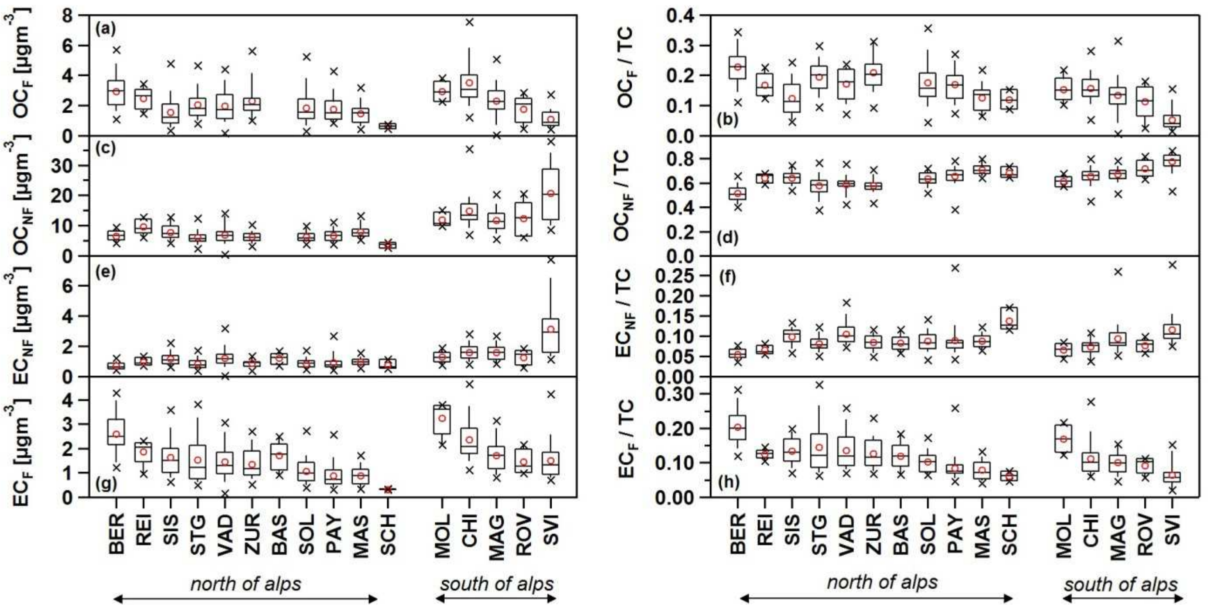

Figure S4: Whisker box plots of the fossil and non-fossil EC and OC absolute concentrations and their relative contribution to TC from all analyzed winter samples (n ~ 300). The open red circles represent the mean and the black crosses the max. and min. values. Stations north and south of the Alps are sorted from the left to the right from the nominal most traffic traffic-influenced station to the most rural one (see Table 1 in the main text.). OC_{NF} values from BAS and all data from the yearly cycle in ZUR are excluded (see Sect. 3.2.1 and Sect. 1).

Table S1: Overview of all days which were chosen for the analysis.

winter	location	day 1	day 2	day 3	day 4	day 5	Zürich yearly cycle
2007/ 2008*	north of the Alps	04.Jan. 2008	30.Jan. 2008ǂ	13.Feb. 2008	15.Feb. 2008	19.Feb. 2008	12. Aug.08; 5., 9. & 25. Sep.08; 15. Oct.08; 8. & 16. Nov.08; 18. & 29. Dec.08; 15. & 27. Jan.09; 4.Feb.09; 4. u. 16. Mar.09; 1., 13. &. 21. Apr.09; 7. & 19 May 09; 12. Jun.09; 2., 14. & 30.Jul.09
	south of the Alps	4.Jan. 2008	30.Jan. 2008	1.Feb. 2008	23.Feb. 2008	25.Feb. 2008	
2008/ 2009	north of the Alps	29.Dec. 2008	8.Jan. 2009	14.Jan. 2009	28.Jan. 2009	3.Feb. 2009	
	south of the Alps	8.Jan. 2009	14.Jan. 2009	3.Feb. 2009	23.Feb. 2009	1.Mar. 2009#	
2009/ 2010	north of the Alps	12.Jan. 2010	24.Jan. 2010	11.Feb. 2010##	13.Feb. 2010	17.Feb. 2010	
	south of the Alps	18.Jan. 2010	22.Jan. 2010	26.Jan. 2010	9.Feb. 2010	15.Feb. 2010	
2010/ 2011	north of the Alps	4.Jan. 2011	30.Jan. 2011	3.Feb. 2011	19.Feb. 2011	5.Mar. 2011**	
	south of the Alps	2.Jan. 2011	26.Jan. 2011	11.Feb. 2011	13.Feb. 2011	25.Feb. 2011	
2011/ 2012	north of the Alps	30.Jan. 2012	7.Feb. 2012	9.Feb. 2012	13.Feb. 2012	23.Feb. 2012	
	south of the Alps	11.Dec. 2011	16.Jan. 2012	18.Jan. 2012	11.Feb. 2012	13.Feb. 2012	
2012/ 2013	Bern	18.Jan. 2013	26.Jan. 2013	14.Feb. 2013	26.Feb. 2013	5.Mar. 2013	

*^{14}C in OC for all stations north of the Alps was also measured for a 6th day (11. Feb. 2008). For SVI only 2 filters, 14th & 26th December 2007 were analyzed. ^{14}C analysis in TC for 26th December 2007 from SVI and calculation of EC_{NF} (EC_{NF} = (TC_{NF} * TC – OC_{NF} *OC) / EC Szidat et al., 2004) since not enough filter material for the ^{14}C analysis of EC was left.

#Filter from 1st of March 2009 from SVI was not available and 3rd of March 2009 was analyzed instead

ǂFilter from 11th of February 2008 was used for the ^{14}C analysis of EC for STG since not enough filter material was available from 13th of February 2008

**Filter from 5th of March 2011 from VAD was not available and 3rd of March 2011 was analyzed instead

##Filter from 9th of February 2010 from BER was analyzed instead of 11th of February 2010

Table S2: Compilation of the average blank values from the different measured compounds used for the blank subtraction (see Sect. 2.3.2 in the main text). Not all major water-soluble ions were detected on all blank filters. Yearly averages were only calculated if the individual components were detected on more than two blanks.

component	**2008**	**2009**	**2010**	**2011**	**2012**
TC [µg/cm^2]	2.52 ± 0.78	2.52 ± 0.78	2.52 ± 0.78	2.52 ± 0.78	2.52 ± 0.78
$f_{M, TC}$	0.53 ± 0.12	0.53 ± 0.12	0.53 ± 0.12	0.53 ± 0.12	0.53 ± 0.12
Cl^- [ppb]	14.9 ± 6.8	8.1 ± 1.1	15.5 ± 7.4	19.6 ± 0.1	-
NO_3^- [ppb]	14.7 ± 9.8	-	12.1 ± 9.8	43.7 ± 14.7	50.5 ± 35.8
SO_4^{2-} [ppb]	20.1 ± 6.7	-	4.8 ± 3.3	8.6 ± 1.1	11.2 ± 1.4
Ox^{2-} [ppb]	1.7 ± 0.6	-	0.7 ± 0.3	-	-
Na^- [ppb]	64.4 ± 34.4	2.5 ± 1.0	7.0 ± 5.4	2.3 ± 2.2	-
NH_4^+ [ppb]	-	1.1 ± 0.1	7.7 ± 5.3	1.6 ± 0.7	-
K^+ [ppb]	1.4 ± 0.8	2.3 ± 1.0	6.2 ± 3.9	-	-
Mg^{2+} [ppb]	5.0 ± 2.0	-	-	-	-
Ca^{2+} [ppb]	20.7 ± 10.3	-	6.9 ± 1.2	-	-

Table S3: Reference f_M values ($f_{M,bio}$, $f_{M,bb}$ and $f_{NF,ref}$), which were used for correcting the elevated ^{14}C concentrations due to the above-ground thermo-nuclear bomb tests in the 1950ies and 1960ies (see Sect. 2.3.2).

year	$f_{M,bio}$	$f_{M,bb}$	$f_{NF, ref}$
2008	1.044 ± 0.015	1.127 ± 0.05	1.110 ± 0.023
2009	1.041 ± 0.015	1.123 ± 0.05	1.106 ± 0.023
2010	1.037 ± 0.015	1.119 ± 0.05	1.102 ± 0.023
2011	1.034 ± 0.015	1.114 ± 0.05	1.098 ± 0.022
2012	1.027 ± 0.015	1.106 ± 0.05	1.090 ± 0.022