

Interactive comment on “Radiocarbon analysis of elemental and organic carbon in Switzerland during winter-smog episodes from 2008 to 2012 – Part 1: Source apportionment and spatial variability” by P. Zotter et al.

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Received and published: 4 September 2014

We thank the reviewers for their comments on our paper. To guide the review process we have copied the reviewers' comments in italics. Our responses are in blue, regular font. We have responded to all the referee comments and done the modifications accordingly (**in bold in the text**).

General comments:

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This is an important study that presents what is in many ways a unique data set. It is a long-term (5 years), multi-site study (16 stations) focusing on winter-smogs. As pointed out; “The duration of this project together with the large number of stations results in one of the world’s largest aerosol 14C datasets available.” Impressive! I only recommend minor changes and clarifications. The results are also important in that they clearly show the importance of wood combustion in Switzerland. The same is most likely true also elsewhere around the globe. The separation of OC from EC prior to aerosol 14C analysis also show that wood burning emissions account for a large fraction of EC during winter-smog episodes in Switzerland. This result is highly relevant considering the current interest in the so called Short-Lived Climate Pollutant (SLCP), focusing on Black Carbon (BC) as a strong climate forcer and also causing severe health effects.

We thank the reviewer for the positive comments. In the following we will respond to each comment separately.

R3.1. The authors use mostly the term “biomass burning”, while their results clearly indicate that these winter-time smog episodes are caused mainly by residential wood combustion. To me, “biomass burning” means open fires, for instance forest fires. Perhaps the authors could be bold enough to more clearly point out residential wood combustion as the source. This would certainly help policy-makers aiming to improve local air quality.

We agree with the reviewer that it is important to point out that we are talking about wood burning emissions from residential heating. Therefore, we replaced “biomass burning” with “**wood burning**” several time (see lines 42, 80-81, 485, 516, 523, 624, 648, 728-729, 772, 777 in the revised manuscript) and also inserted “**residential wood burning**” at numerous positions, especially in the abstract and conclusions (see lines 48, 765, 770, 774, 779 in the revised manuscript).

R3.2. Also, there is some confusion in the text as to the importance of SOC formation

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versus primary OC from the wood combustion source. Again, the authors could be somewhat clearer on how much is primary versus secondary OCBB. To me, it appears to be mostly POC. I agree with the conclusion that, in contrast to OCBB, fossil OC is to large extent secondary in nature, but maybe this could also be somewhat more clarified in the text.

Since this comment is closely linked to comment R3.17 we combine our answer to both comments and here refer to our answer to comment R3.17.

Specific comments:

R3.3. Page 15597, line 14: “Since a more complex sampling (e.g. using 2 sampling lines in parallel, one with and the other without a denuder system for volatile OC removal or using 2 filters in series) is not carried out at regular air pollution monitoring stations, artefacts could not be quantified. However, due to the high filter loadings in winter such sampling artefacts are not expected to be large and we assume that they will not significantly influence the results presented in this study.” I agree, but are there any previous studies that could be referenced to back this up?

We added the following reference accordingly with the reviewer comment (see lines 151-153 in the revised manuscript):

“However, due to the high filter loadings in winter such sampling artefacts are not expected to have a large contribution (e.g. **Viana et al. (2007) found a 5% and 7% contribution of OC from positive sampling artifacts for winter samples in Amsterdam and Ghent**) and we assume that they will not significantly influence the results presented in this study.”

R3.4. Page 15597, line 23: “. . .none of the samples were pre-heated to remove any OC or EC present on the filters prior to sampling. . .” This is otherwise standard procedure in most OC/EC sampling networks and is recommended. The TC blanks are somewhat high in this study, and would be lower if the quartz filters were pre-fired. (Page 15599,

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line 4: “. . .the average TC filter loading ($2.5 \pm 0.8 \mu\text{gCcm}^{-2}$) of all measured blank filters ($n = 47$). . .”

We agree with the reviewer that the blanks would be much lower if filters would be heated prior sampling and that the blank loadings are very high compared to many other studies. However, we had no influence on how the filters were treated as the sampling was carried out by the regular air quality monitoring networks of Switzerland on a regular basis and they chose to not pre-heat. Nevertheless, as we knew this fact and saw that the blanks are high, we analyzed a large number of blanks and performed blank corrections in order to remove any influence of these high blank values on our results.

R3.5. Page 15600: Comment only: Separation of OC and EC prior to 14C analysis is tricky, and note many groups do it on regular basis. While it is certainly very important to remove as much OC (and pyrolyzed OC) from the EC fraction, it is also important not to be too aggressive and end up with only the very toughest EC fraction. Nevertheless, the Swiss 4S method being used here has been extensively tested and seems to give reasonable results.

We thank the reviewer for acknowledging this.

R3.6. Page 15603, Eq 1: There appears to be a “minus” sign too many.

One of the minus signs was removed.

R3.7. Page 15604, line 11: “Hence, $f_{N,ref}$ equals. . .” Should this not be $f_{NF,ref}$?

We changed $f_{N,ref}$ to “ **$f_{NF,ref}$** ” (see line 326 in the revised manuscript)

R3.8. Section 2.3.2: After reading this section, it feels as if it would be good to have all 14C correction equations written out clearly somewhere, for instance in the supplement. Now, the reader easily gets confused after a while.

Following the reviewers’ comment we added **Table 2: “Summary of the different**

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correction steps of the 14C raw data.”, showing all equations in the right order used for the corrections and defining all abbreviations and insert the following (see line 266 in the revised manuscript) to refer to the table:

“As discussed in the following, several corrections have to be applied to the fM values obtained from the 14C measurement (**see also Table 2 for a summary**).”

R3.9. Page 15604, line 10: “EC is only emitted from fossil sources or biomass burning.” I just switched from driving an ethanol-fuelled car to one that runs on gas. In my country, these are both biofuels. Surely, my car will still emit EC, now as non-fossil EC. We can expect more EC from non-fossil sources in the near future, and your statement will gradually lose validity, unless of course you classify as biogas and bio-ethanol fuels as “biomass burning”.

We agree with the reviewer that any carbonaceous emissions from ethanol and biogas-fuelled cars would be modern and that maybe in the future the number of these cars will increase. However, gas and ethanol-fuelled cars emit basically no or only very little EC (compared for example to diesel) and in Switzerland their contribution to total vehicles is <1% (Swiss Federal Office for Statistics: <http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/03/blank/02/01/01.html>). To clarify this issue we added the following in the revised manuscript (see lines 325-326 in the revised manuscript)

“EC is only emitted from fossil sources or biomass burning (**neglecting any EC emissions from biofuels as their contribution to the total fuel use is low**). . .”

R3.10. Section 2.5: Maybe the list of which additional data is available from the various sites could also be included in Table 1. This would provide an overview. The table might get too crowded, though.

From the additional data mentioned in Section 2.5 we only use the NO_x measurements in our paper (see Fig. 5) and as the reviewer points out including all the additional data

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in Table 1 would make this table very large and crowded (note that the information Table 1 was already increased in the revised manuscript due to comment R3.13 from this reviewer). Therefore, we decided not to include the additional data in Table 1 as NO_x data is available for all stations except SCH which is clearly stated in the text (see page 15606 lines 8-9)

“...PM10 and nitrogen oxides (NO_x = NO and NO₂) data are available from all stations (except SCH),. . .”

R3.11. Page 15606, line 18: “In all networks (NABEL, Cantons and MeteoSwiss) data sets undergo an automatic and a manual quality check. . .” I guess the list of quality checks only refers to the network data and not the OC/EC, 14C and HPAEC data. This could be clarified.

In order to clarify this, we added the following (see lines 388-390 in the revised manuscript)

“In all networks (NABEL, Cantons and MeteoSwiss) data sets (**except results obtained offline from filter samples, i.e. EC/OC and levoglucosan concentrations as well as 14C data**) undergo an automatic and a manual quality check”

R3.12. Page 15607, line 3: “One aim of this study was the source apportionment of winter smog episodes in Switzerland.” What are then the other aims? They are not written out specifically anywhere. On page 15597, it says “. . .winter-smog episodes, which were the objective of our study”. In the Introduction, it says: “This paper is devoted to the comparison of different techniques used to apportion carbonaceous aerosol sources and the investigation of the spatial variability of these sources.” Maybe the specific scientific aim(s) of this particular study (paper) could be clarified further, preferably as early as possible in the text, and not in section 3.1.

The main aim of this paper is to present the 14C based source apportionment results of winter smog episodes from 5 years and their spatial variability. In our opinion, it

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is already clear from the title and the introduction (“This paper is the first paper of a two-part series investigating the spatial and temporal variability in the fossil and non-fossil sources of the organic and elemental carbon during high pollution events in Switzerland.”, see page 15596 lines 9-12) that the main aim was to investigate winter-smog episodes in Switzerland.

Following the reviewers’ comment, we now clarify the aims in the introduction (see lines 119-122 in the revised manuscript)

“This paper **presents the 14C-based source apportionment results of** carbonaceous aerosols and investigates their spatial variability.”

and also slightly change lines 3-6 on page 15607 (see lines 398-402 in the revised manuscript) as follows:

“As **we were interested in winter-smog episodes** only days with high PM10 concentrations at all stations were analyzed. As shown in Fig. 2a the selected days from almost all locations **exhibited on average values 50 $\mu\text{g m}^{-3}$ (European and Swiss daily limit) or above.**”

R3.13. Table 2: This table is confusing me. From Table S1, and the text, I get the impression that you analysed samples from all station during the selected days (Table S1). What is then the meaning of the column “Stations and time period” in Table 2? For instance, when only reading this table, I would get the impression that 14C in EC/OC are only analysed for stations BER and MAS, which is obviously not the case.

We agree with the reviewer and incorporated the most important information of Table 2 (which stations was analyzed in which winter) into Table 1 and removed Table 2.

R3.14. Table 3: Why is the station Schächental (SCH) left out of this table?

For Schächental (SCH) only 3 filters were analyzed for EC, OC and 14C in both fractions. Since this is a very low number and in addition no levoglucosan was measured we initially did not include this station in Table 3. However, in the revised version of the

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paper we now included the OCNF/ECNF ratio for SCH and explain in the table caption that no levoglucosan was measured in SCH.

R3.15. Page 15607, line 25: ...“uncertainties of the different measurement methods and OM:OC ratio used to convert OC to OM.” The Aerosol Mass Spectrometer (AMS) can provide information on the OM/OC ratio. In other publications by some of the authors, AMS data are presented from sites also included in this study. Has that data not been used here to constrain the OM/OC ratio, rather than using the value from Turpin and Lim, 2001?

OM:OC ratios from previous studies in Switzerland could not be used since 1) in previous papers (e.g. Lanz et al., 2008 and Alfarrá et al., 2007) no high-resolution analysis of the organic mass spectra was performed or 2) no OM:OC ratios are reported (e.g. Mohr et al., 2011). Furthermore, we did not focus on OM in our paper. We only use OM to show the chemical composition of PM10. In addition, changing OM:OC from 1.6 to 1.8 only increases OM/PM10 on average by 4%.

However, we agree with the reviewer that Turpin and Lim (2001) is an old reference. We therefore used now OM:OC of 1.8 as reported in Favez et al. (2010) for winter measurements in Grenoble with similar conditions and sources.

Hence the OM/PM10, OM:OC and (OM+EC+water soluble ions)/PM10 numbers in the text were changed (see line 39, 418, 422, 423, 751, 1242 in the revised manuscript).

R3.16. Page 15609, line 18: “BAS is the base for two of the world’s largest pharmaceutical enterprises, Roche and Novartis, and in addition an incinerator for medical waste is located in the vicinity of the station.” More of a comment: It seems as if the fNF,EC values for BAS are not affected by the medical waste incinerator, since these values are realistic, while the fNF,OC values are elevated. Nevertheless, one should be careful when interpreting urban aerosol 14C data.

We agree with the reviewer that in areas where possible sources of anthropogenic 14C

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could exist, great care has to be taken and especially the analysis of blank filters becomes more important. However, in many cases an influence of such sources can be clearly identified since anthropogenic sources of ^{14}C (nuclear power plants, pharmaceutical industry, biochemical laboratories...) lead to f_{NF} values clearly above 1. In addition since such sources are point sources with usually high temporal variability a constant bias is not expected. Publications about sources of anthropogenic ^{14}C and their influence on aerosols, except about the bomb peak, are very scarce and the authors are only aware of a single publication (Buchholz et al., 2012).

R3.17. The following comments address the issue on what is wood combustion POC or SOC. First two sentences from your text: Page 15610: "Furthermore, large inputs from biological and biogenic sources are also not expected under Swiss winter conditions, characterized by low biological activity. Therefore, the high $f_{\text{NF,OC}}$ values indicate that wood burning POC and SOC are most probably the main source of OC during winter-smog episodes in Switzerland." Page 15613, line 25: "Together with the low station-to-station differences, this suggests on the one hand that non-fossil sources very consistently influence stations on the Swiss Plateau and that the degree of atmospheric processing and SOC formation for the chosen days were very similar and on the other hand that the different stations on the Swiss Plateau are rather influenced by regional (still mainly within Switzerland) air pollution." You state later in the text that the non-fossil OC from wood combustion is no really SOC, but mostly primary OC. Figure 6a (scatter plot of OCNF vs. levoglucosan) and Figure 7 points to primary wood combustion OC being the major source of OC, not secondary. Also on the same topic, you write: Page 15616, line 19: "However, under winter-smog conditions in Switzerland (low temperatures and photochemical activity) rapid levoglucosan degradation is not expected and no large systematic differences in the photochemical activity and SOC formation between locations south and north of the Alps were found as evidenced by very similar OCNF to ECNF ratios (7.7 ± 2.1 and 8.6 ± 2.9 , see Table 3 and Fig. 7) for these two regions in Switzerland." In summary, it would be good if the authors could summarize their findings on POC vs SOC for wood combustion.

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We agree with the reviewer that this is not clear enough. Since OCNF is well correlated with levoglucosan and this regression line also shows only a small intercept, this indeed suggests that OCNF is to a large extent from primary wood burning emissions (see Fig. 6a). However, with our data set we cannot quantify how much of OCNF is SOC. First, OCNF includes other non-fossil sources besides wood burning and even though we do not expect a large influence of these sources (e.g. cooking or biogenic SOC) we cannot explicitly exclude them (especially cooking). Second, using wood burning emissions ratios to apportion OCNF into OCBB (only primary) and OCNF,SOC would yield a large range of results as these ratios are highly variable (OC and EC to levoglucosan emissions ratios for alpine regions were reported in Schmidl et al. (2008) to range from 3.7 to 12.5 and from 0.7 to 4.7, respectively). Therefore, we did not quantify primary vs. secondary contributions of wood burning.

In order to clarify our findings on primary vs. secondary derived OC we added the following (see lines 642-644 in the revised manuscript)

"Furthermore, this indicates that OCNF is to a large extent emitted as primary aerosol, however, with the data presented in this study it is not possible to quantify a primary vs. secondary fraction of wood-burning OC."

R3.18. Page 15615, line 16: "The wide variability of levoglucosan emission ratios results in significant uncertainties in estimating wood burning contributions." Levoglucosan is formed by pyrolysis of cellulose only, and is not formed during flaming conditions. This gives the large variability. It will never be a "perfect" tracer, but good enough for most applications, which your results show.

We agree with the reviewer that many studies used levoglucosan emission ratios to estimate wood burning contributions and even though these ratios are variable, acceptable results were obtained in these studies. Still, the variability in the wood burning levoglucosan emission ratios can yield a range of results spanning a factor of 2 in the calculated wood burning contributions of OC and EC (see for example Gelencsér et al.,

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2007). Therefore, we decided not to apply this methodology on our data and present the measured non-fossil contributions to OC and EC, instead of biomass burning OC and EC.

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