Referee 3 report – Zotter et al

Zotter et al, Atmos. Chem. Phys. Discuss., 14, 15591–15643, 2014, doi:10.5194/acpd-14-15591-2014

General comments:

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 ^{14}C 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 ^{14}C 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.

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.

Also, there is some confusion in the text as to the importance of SOC formation versus primary OC from the wood combustion source. Again, the authors could be somewhat clearer on how much is primary versus secondary OC_{BB}. To me, it appears to be mostly POC.

I agree with the conclusion that, in contrast to OC_{BB}, fossil OC is to large extent secondary in nature, but maybe this could also be somewhat more clarified in the text.

Specific comments:

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?

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, line 4: "…the average TC filter loading (2.5±0.8 μgCcm−2) of all 5 measured blank filters (*n* = 47)…"

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 pyrolized 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.

Page 15603, Eq 1: There appears to be a "minus" sign too many.

Page 15604, line 11: "Hence, $f_{\mathrm{N,ref}}$ equals…"
Should this not be $f_{NF,ref}$?

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

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".

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.

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, ^{14}C and HPAEC data. This could be clarified.

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.

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 ^{14}C in EC/OC are only analysed for stations BER and MAS, which is obviously not the case.

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

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?

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 $f_{\mathrm{NF,EC}}$ values for BAS are not affected by the medical waste incinerator, since these values are realistic, while the $f_{\mathrm{NF,OC}}$ values are elevated. Nevertheless, one should be careful when interpreting urban aerosol ^{14}C data.

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 $f_{\mathrm{NF,OC}}$ 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 $\mathrm{OC_{NF}}$ to $\mathrm{EC_{NF}}$ 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.

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.