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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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We thank the reviewer for the comments on our paper. To guide the review process we have copied the reviewers' comments in italics. We have responded to all the referee comments and done the modifications accordingly (**in bold in the text**).

This paper is a very interesting paper that can contribute to the scope of ACP. The results are well discussed and well presented. Objectives of this paper study are to apportion sources of carbonaceous aerosols on 16 Swiss sites (Traffic, Urban back-

[Full Screen / Esc](#)

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[Interactive Discussion](#)

[Discussion Paper](#)



ground, Rural background) in the North and South of the Alps during winter-smog episodes for 5 winters (24-hours sampling, about 5 samples per winter per site between 2007 and 2012). Source apportionment is based on 14C measurements realized on Elemental and Organic Carbon separately. However, before the publication, authors must be more define or must make some corrections or provide additional information on these different points:

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

R1.1. Title: the time period reported is 2008-2012 since in the text, sampling seems to be performed also during the winter 2007-2008. Are no samples from December 2007 taken into account?

No days from December 2007 were analyzed. We therefore think that the year numbers in the title appropriately represent the time period analyzed in this study.

R1.2. Materials and methods/Aerosol sampling: dates of sampling are not reported in the paper. Could you input in this part?

A table with all the dates of the analyzed days is presented in the supporting information (SI) and we refer to this table in the main text (see page 15598 lines 12-14: “The detailed selection of all analyzed days and the distribution of PM10 concentrations on those days for every station are shown in Table S1 and Fig. 2, respectively”). In our opinion it is not necessary to move this table to the main text since it requires a lot of space, and this information is not crucial for understanding the paper: if the reader is interested in the exact dates he can refer to the supporting information.

Still, we point out more clearly now (see lines 176-177 in the revised manuscript) that the detailed dates can be found in the SI.

“The detailed selection of all analyzed days and the distribution of PM10 concentrations on those days for every station are shown in Table S1 in the **supporting information**

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

and Fig. 2, respectively.”

R1.3. Materials and methods/2.3.2: this part on data correction is very complex, it is difficult to well understand, notably due to the use of many subscript notations like “fM,EC,final”. This part must be more readable. And page 15604, line 11, is not “fNF,ref” instead of “fN,ref”?

We agree with the reviewer that there are many subscript notations in this section, however, in our opinion all these subscript notations are necessary as otherwise the different corrections cannot be separated. Concerning the readability we are aware that for readers without a strong 14C analytical background this section could be difficult. However, all the different subscript notations are defined in the text and the different corrections are numbered and have their own heading (e.g. 1) blank correction, 2) EC yield correction. . .). Therefore, we believe that it should be possible to follow the different corrections also for people not working on 14C analysis. Nevertheless, we inserted a table (**Table 2: “Summary of the different correction steps of the 14C raw data.”** showing all equations in the right order used for the corrections. In the table we have defined all subscript notations and inserted in the text the following (see line 266 in the revised manuscript):

“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**).”

We also changed fN,ref to “**fNF,ref** “ (see line 326 in the revised manuscript)

R1.4. Materials and methods/2.5: how was PM10 mass measured on the different sites: with TEOM? Equipped with a FDMS system? On which sites PM10 mass was measured gravimetrically?

Filter samples at the different stations are not collected with the same frequency which was stated in the text (see page 15597 lines 8-9: “. . .(every 2nd or 4th day or daily depending on the station). . .”). However, PM10 was not measured gravimetrically on all

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



of these filters (also stated in the text see page 15597 lines 19-20: “It should be noted that on some filters PM10 mass was measured gravimetrically. . .”). The frequency for the gravimetric PM10 determination also varies from station-to-station and therefore, PM10 data obtained from TEOM or TEOM-FDMS instruments (also this is different from station-to-station) was used in our paper. It should be noted that for all stations in Switzerland the approach presented in Gehrig et al., 2005 to correct/harmonize online and gravimetric PM10 measurements is applied.

In order to make this clearer we inserted the following in lines 378-382 in the revised manuscript:

“PM10 is measured online with beta attenuation monitors (FH62-IR, Thermo ESM Andersen) and by TEOM-FDMS (Thermo Environmental) instruments and an approach presented in Gehrig et al. (2005) to correct/harmonize online and gravimetric PM10 measurements is routinely applied to data from all stations.”

R1.5. Results and discussion/3.1: page 15609 line 7: input a “in” before Zotter et al.

We added “in” before Zotter et al. 2014 (see line 456 in the revised manuscript).

R1.6. Results and discussion/3.2.2: page 15613 line 23: what is “IQRs”?

We defined IQR as “interquartile range” which denotes the difference between 3rd and 1st quartile. This abbreviation was already defined in the main text before (“. . .interquartile ranges (IQR = 3rd – 1st quartile. . .” see page 15610 line 28).

R1.7. Results and discussion/3.3.2: in this part and in the Table 3 EC/Levo, OC/Levo, OC/EC and Levo/K+ are reported: have you compare your values with those from Herich et al., 2014 in winter? Or with values from Gianini et al. 2013 (ref: Sci.Tot.Envir. 454-455, 99-108), that reported OCWB/Levo from PMF and CMB estimations in the same Swiss sites (ZUR, BERN, MAG, PAY)? Could you more compare your ratios with those from these papers in the part 3.3.3 and discuss about differences? Particularly differences between 14C measurements and PMF or aethalometer

models estimations conducted on Swiss sites.

Gianini et al. (2013) compares different source apportionment methods and uses data from Gianini et al. (2012a) and Gianini et al. (2012b). In this study good agreement was found in winter for biomass burning OC from PMF and CMB whereas biomass burning EC obtained from CMB did not agree with PMF and the Aethalometer method. Therefore, Herich et al. (2014) used OCWB and ECWB calculated with PMF from Gianini et al. (2012b) together with additional data from Herich et al. (2011). In our paper we compare the ratios obtained from the 14C analysis with the average ratios from Herich et al. (2014) which include different approaches for each site and already discuss the differences between our results and those presented in Herich et al. (2014) and our study (see page 15619 lines 1-9)

“The differences in the ratios most likely originate from (1) uncertainties in the OCBB determination (e.g. OC/levoglucosan emission ratios have to be assumed which can be highly variable) (2) SOC from biomass burning is not taken into account in the OCBB values as presented in Herich et al. (2014) but is included in OCNF as obtained by the 14C measurement and (3) a contribution of other non-fossil sources (e.g. cooking or biogenic aerosol) to OCNF as apportioned with the 14C analysis cannot be completely ruled out although they are expected to have a minor influence during winter-smog episodes in Switzerland. . .”

Furthermore, we decided to compare our ratios with the average ones from Herich et al. (2014) as not all different approaches were applied at the different stations (e.g. no Aethalometer approach in BER and no OCWB data obtained with the Aethalometer model was reported and therefore, OCWB/Levo ratios only refer to PMF or the tracer approach).

However, we added now a sentence (see lines 702-704 in the revised manuscript) referring to Gianini et al. (2013).

“..(including 14C analysis, aethalometer model, positive matrix factorization, chemical

Full Screen / Esc

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Discussion Paper



mass balance, macro tracer approach, **see Gianini et al. (2013) and Herich et al. (2014) for a discussion about possible differences in the biomass burning marker ratios due to different approaches**) were. . .”

R1.8. Conclusions

You say page 15621 line 1 “wood burning can be the dominating source of carbonaceous aerosols during the cold season, in Europe” and during winter-smog episodes. But it is for just the carbonaceous fraction of aerosols. What is the contribution of wood burning to PM10 during these winter-smog episodes? Is the contribution higher or lower than those from Secondary Inorganic Aerosols?

With our measurements we could not directly assess the biomass burning contribution to total PM10. We only measured non-fossil OC and we could only semi-quantitatively relate a part of OCNF to biomass burning. As mentioned in the manuscript, a part of this OCNF is related to SOA and/or to primary modern emissions. Therefore, we believe that with our data an accurate estimation of a wood-burning contribution is not possible and we prefer reporting the contribution of fossil and non-fossil fractions of OC instead. Accordingly, in the conclusion we reported OM/PM10, EC/PM10, the individual secondary inorganic fractions to PM10, OCNF/OC and ECNF/EC. In our opinion this is sufficient as readers could very roughly estimate the total wood burning contributions from these numbers if they wish, but only qualitatively.

On the same page, you write “no correlation was observed between fossil OC and fossil EC and NO_x, indicating that a considerable amount of OCF is secondary OC (SOC) formed from fossil precursors emitted from traffic”. Why it could be SOC from traffic since it was no correlated with ECF or NO_x? OCF could maybe be formed from precursors emitted by other fossil sources like combustion of fossil energy for domestic heating or in the industry? Can the non-correlation between OCF and ECF and NO_x due to an analytical error on the OCF measurement, particularly is the correction of the charring well adapted?

Full Screen / Esc

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Interactive Discussion

Discussion Paper

In this statement in the conclusion we only say “a considerable amount of OCF is SOC from traffic”. We did not write that all OCF is SOC from traffic. Furthermore, in the corresponding section of the text (section 3.3.1) we also mentioned the possibility of other sources of OCF (page 15615, lines 2-7):

“Taken together these observations indicate that a considerable amount of OCF is associated with emissions or atmospheric pathways that yield fossil organic aerosol with little or no ECF and NO_x. These processes may include primary emissions from non-mobile fossil fuel combustion sources, e.g. heavy fuel combustion (e.g. crude oil, not widely used in Switzerland), or secondary organic carbon formed from fossil VOCs emitted from traffic.”

It was previously shown (e.g. Chirico et al., 2010; Platt et al., 2013) that traffic emissions form substantial amounts of fossil SOC. Furthermore, in Switzerland basically all electricity (94

“...whereas no correlation was observed between fossil OC (OCF) and the two latter components, indicating that a considerable amount of OCF is secondary OC (SOC) formed from fossil precursors **mainly** emitted from traffic.”

R1.9. General comment on the figures: Figures 3, 5, 6 and 8 are so small and it is difficult to read some characters. Could you change character and figures sizes please?

We increased the font size in these figures (axis labels, legends. . .).

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