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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Sources and formation mechanisms of carbonaceous aerosol at a regional background site in the Netherlands: Insights from a year-long radiocarbon study" *by* Ulrike Dusek et al.

Anonymous Referee #2

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The paper "Sources and formation mechanisms of carbonaceous aerosol at a regional background site in the Netherlands: Insights from a year-long radiocarbon study" by Dusek et al. (Manuscript number ACP_2016_624) is an interesting manuscript dealing with elemental and organic carbon fractions source apportionment in the Netherlands using 14C as a tracer for modern contributions. Radiocarbon measurements on OC and EC are still relatively scarce in the literature, especially covering a relatively long period such as the one covered here (1-year). The sampling strategy (1-week sampling) was well developed for the scopes of the manuscript which were mainly devoted to an overview of the sources of carbonaceous particles throughout the year, allowing

a good time coverage limiting the number of samples to be prepared and analysed.

In my opinion, the data presented in the paper merit publication on ACP, even if major revisions are needed in the text of the Results and Discussion sections. Indeed, in both of them the text lacks of numerical support to most of the adjectives/adverbs used in the sentences (e.g. high/low/relatively higher, slightly lower etc), making the text difficult to be read and understood. Numeric information justifying sentences can be however extracted in most cases by tables or figures, but complementary information should be added in the text to help the reader and to support statements (e.g. if absolute concentration are present in the table and in the text the sentence is "x is slightly higher than y" - what's slightly? - rephrasing as "x is slightly higher (zz%) than y" is an important help for paper clarity). Only in few cases, statements seem not to be supported by data. Such comments should be removed by the text.

In the following, detailed comments separated by pages are present.

Major revisions:

- page 5, line 22: "charred organic compounds contribute at most 5% to the recovered EC". Due to the thermal protocol chosen, it cannot be excluded a residual contribution also by resilient (not charred) organics.

- page 6: line 4: what do the authors mean with "virtually"? line 35: "The concentration and F14C of TC on the blank filter were calculated by adding the 35 carbon concentrations of OC and EC and were 0.68 μg cm-2 and 0.67, respectively": to retrieve F14C of TC, F14C of OC and EC should not be barely summed, but combined with OC, EC, and TC concentrations: TC F14C(TC) = OC F14C(OC)+ EC F14C(EC). But I assume from the numbers presented in lines 25-32 this is what has been done, just state better in the text.

-page 8: line 7-10: "(1) WIOC is completely recovered, which most likely results in an underestimate of WIOC, and (2) WIOC shows the same recovery as OC, which is

probably an overestimate, since WIOC is associated with more volatile primary organic material and usually less WIOC is lost to charring". I think this has to be phrased opposite: "(1) WIOC is completely recovered, which most likely results in an OVERESTIMATE of WIOC, and (2) WIOC shows the same recovery as OC, which is probably an UNDERESTIMATE, since WIOC is associated with more volatile primary organic material and usually less WIOC is lost to charring".

-page 9 line 31-32: "0.1 (modern carbon from biofuels contributes 10% to carbon emission from other combustion sources)" please rephrase: "0.1 (emissions of modern carbon from the biofuel added to road fossil fuels contributes 10% to carbon emission from such sources)"

- page 10 line 27: "the results are not strongly sensitive": what does "strongly sensitive" means? Please quantify at least with examples (i.e. varying in the min-max range the results modify of xxx%)

- page 11 line 21: "due to traces of water vapor or other impurities that are not removed entirely by the ACS method". To help the reader, it should be recalled the ACS quantifies TC manometrically.

- page 12 line 25: how was EC quantified in these samples? line 30: what does "relatively uncertain" means? In the end, was cooking accounted for in any way or not? If not, please rephrase "possible cooking contributions were not considered in the following" (if so, is there any literature study pointing at negligible contributions from cooking?)

- page 13 line 14: "and they were therefore included into the modified marine cases". Did the authors verify in any way that the results are not biased by this decision? lines 33-40: no data support the discussion. No a-priori assumption can be done on seasonal 14C concentration, as it is affected by two sources (biogenic and wood/biomass burning) which are predominant in different seasons, thus a priori considerations are not feasible. Moreover, temperature and total precipitation are not enough to determine

the extent of SOA formation (e.g. precursor concentrations and solar radiation intensity have a major role in SOA formation). Please remove all the discussion.

- page 14 line 1: "remained relatively constant for all seasons and air mass conditions, but was highest in spring". What does "relatively constant" stands for? Please rephrase: "were within xxx% (or within $\pm$yyy F14C) in all seasons, except in spring when they were yyy% higher" line 2: "F14C(EC) varied more strongly and was low in summer and high in winter". What does "more strongly", "high", and "low" stand for? Again, please give numerically indication. It is noteworthy that if compared e.g. to F14(OC), the terms "high" and "low" are nonsense unless further detail is given. line 15: "OCf was constrained in a relatively narrow range, whereas estimates for OCbb and OCc,o varied over a much wider range reflecting the large uncertainty in rbb". Please specify what "relatively narrow" and "much wider" stand for. line 25: "low": specify lines 27-29: "The main sources of fossil elemental carbon (ECf) in the Netherlands do not show a strong seasonal variation and its concentrations should therefore be relatively constant throughout the year". This is in contrast with what is said at line 26 ("higher planetary boundary layers in summer"), where a different dispersion condition depending on the season seems to be expected. Such seasonal variation would modify absolute concentrations in air of EC emitted by constant sources. lines 29-30: "However, there are relatively high ECf concentrations in fall": please, quantify "relatively high" line 30: "all other carbon fractions are elevated as well". Untrue (see table 3). Maybe the authors meant: "the fossil contribution of all the other carbon fractions is elevated as well (on average xxx%)". lines 31-36: please add numeric information throughout the text

page 15 lines 10-12: "the regional contribution in the Netherlands is relatively strong for OC and EC from traffic sources and the influence of long-range transport less important". What does "relatively strong" means? Please, quantify. line 14: "concentrations of ECbb are very low in regional pollution". How much lower compared to other conditions? lines 27-29: "The rainfall duration was on average 1 hr/day for continen-

tal conditions and 2 hrs/day for regional conditions and the amount was 1.2 vs 3.4 mm/day". Maybe it is more interesting the indication on the number of rainy days and the maximum rate in mm/h

Page 16 lines 31-32: "the concentrations of EC and OC are less variable and rather low". "Less variable": quantify (i.e. variability within xxx%). "Rather low": quantify absolute values and relative differences with other conditions. lines 33: "carbon concentrations within this low range also occur regularly under continental air mass conditions". What does "regularly" means? In how many cases compared to the total?

Page 17 line 9: "somewhat higher". Please quantify line 12: "WIOC consists to roughly equal parts of fossil and contemporary carbon with slightly higher fossil contributions in summer and slightly higher contemporary contributions in fall and winter". line 15-17: "The contributions of fossil and contemporary carbon fractions to OC (Figure 7b) do not change strongly for different air mass origins, even though the absolute concentrations of OC increased strongly in continental air masses". Please quantify "do not change strongly" (i.e. is within xxx%) and " increased strongly" (i.e. grew from xxx ug/m3 in regional air mass to yyy ug/m3 in continental air masses) line 26: "mg": sure? line 27: "most of the contemporary WIOC": lots of points in figure 8 have 0.1<WIOC<0.2 ug/m3. In such cases, contemporary WIOC from modern sources other than bb is far from being a small fraction of total contemporary WIOC.

Page 18 line 3-5: are the authors sure that no primary soluble organics are emitted by fossil fuel combustion? line 21: "relatively low": please, quantify line 23: " the variability of the WSOCf/ECf ratios is large": please, quantify

Page 19: line 5: " was highest in spring and lowest in summer": please, quantify

Page 20 line 15-19: "In contrast, WSOC is dominated by modern sources in all regions of the globe with usually only 0 –20% contributions from fossil sources (e.g., Kirillova et al., 2010, 2013, 2014; Szidat et al., 2006, 2009; Wozniak et al., 2012) This reflects that the main sources of modern OC, biomass burning and SOA formation, produce

largely water soluble carbon. The data from the Cesar site fall in this range with a fossil fraction of WSOC below 0.2 (Fig. 7)." The first sentence has no implication on the second one. Indeed WSOC being dominated by modern sources has no implication on WSOC/WIOC ratio of modern sources. Opposite, the second sentence is proven by contemporary WSOC domination in the total contemporary OC fraction.

Page 21, lines 29-32: "One of the most interesting results of our study is that, even though a large fraction of carbon emitted by biomass burning is water soluble, long-range transport of biomass smoke is the most important source of WIOCc in the Netherlands". Where is this point discussed? Just few words are mentioned in the text (page 15, line 12-13). "On the other hand, ECbb, WIOCc, and WSOCf increase by more than a factor of 4 under continental air mass conditions". When revising, please also consider the comment to page 17, line 27

Figure 3: more details on Hysplit use should be given (e.g. trajectory height, stability of the trajectories as function of starting point or beginning time)

Minor revisions:

- Page 6 line 7: "mg": Sure? line 17: "ultra-small samples larger than 2 μg C": larger or smaller? If "larger" is right, better to rephrase as "ultra-small samples down to 2 μg C" line 24: "mg": sure? line 30: change "from the five single filter pieces" in "from the five single blank filter pieces"

-Page 13 line 17: please change "last" in "previous" line 24: please remove "also"

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