

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  $^{14}\text{C}$  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.

We thank the reviewer for the positive comments. We carefully considered all the comments of the reviewer in the revision of the manuscript.

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.

We thank the reviewer for the suggestions and the careful reading and commenting on the manuscript. After rereading the manuscript in the light of the reviewer's comments, we think the manuscript will be considerably improved by making the statements in the text more quantitative. In the original manuscript we tried to avoid citing numbers in the text that can easily be found in figures and tables, but in many occasions the numbers needed (e.g., in comparisons) are not directly available and we added them to the text as suggested.

For easier tracking of the changes, we marked all the changes in response to reviewer 1 in yellow and the changes in response to reviewer in grey throughout the revised manuscript.

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.

This is true and later on in the manuscript we show that it indeed can occur. We added the following sentence to the manuscript: "Moreover, it is possible that highly refractory OC could survive the thermal treatment and combusted together with EC." (page 5, line 25-26)

- page 6: line 4: what do the authors mean with "virtually"?

> 95% (page 6, line 7)

line 35: "The concentration and F $^{14}\text{C}$  of TC on the blank filter were calculated by adding the 35 carbon concentrations of OC and EC and were 0.68  $\text{g cm}^{-2}$  and 0.67, respectively": to retrieve F $^{14}\text{C}$  of TC, F $^{14}\text{C}$  of OC and EC should not be barely summed, but combined with OC, EC, and TC concentrations:  $\text{TC F}^{14}\text{C}(\text{TC}) = \text{OC F}^{14}\text{C}(\text{OC}) + \text{EC F}^{14}\text{C}(\text{EC})$ . But I assume from the numbers presented in lines 25-32 this is what has been done, just state better in the text.

This is correct. We made the explanation more precise:

“The concentration of TC on the blank filters was calculated by adding the carbon concentrations of OC and EC and was  $0.68 \mu\text{g cm}^{-2}$ .  $\text{F}^{14}\text{C}_{(\text{TC})}$  of the blank filters was calculated as the weighted average of  $\text{F}^{14}\text{C}_{(\text{OC})}$  and  $\text{F}^{14}\text{C}_{(\text{EC})}$  and was 0.67.” (page: 6/7, lines: 37, 1-2)

-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".

The original phrasing is in principle correct, because if we assume that the recovery of WIOC is 100%, then (1) we assume that the measured WIOC equals the “real” total WIOC. If the recovery is less than 100%, then the “real” WIOC is calculated as measured WIOC/recovery, which is higher than (1). However, the way is formulated in the text is ambiguous and we see now that this is confusing. Therefore we changed the text to make this hopefully more clear: “To estimate  $M_{\text{WIOC}}$  we therefore assume two extreme cases: (1) WIOC is completely recovered: In this case  $M_{\text{WIOC}}$  is equal to the mass of WIOC that was determined by the ACS system. This is most likely results in an underestimate of WIOC, because a fraction of WIOC might not combust at  $360^\circ\text{C}$ . In this case the measured WIOC is less than the actual  $M_{\text{WIOC}}$ . (2) WIOC shows the same recovery as OC. In this case  $M_{\text{WIOC}}$  is as the measured WIOC divided by the recovery of OC. This results probably in an overestimate of  $M_{\text{WIOC}}$ , since usually less WIOC than OC is lost to charring. We therefore consider a range of possible WIOC concentrations from a minimum of  $M_{1\text{WIOC}}$  (complete recovery) to a maximum  $M_{2\text{WIOC}}$  (recovery as OC).” (page: 8, lines 17-24)

-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)"

done (page 10, lines 15-16)

- 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%)

We added: “If we shift the central value closer to  $M_{1\text{WIOC}}$ , e.g.,  $M_{1\text{WIOC}} + 1/3 * (M_{2\text{WIOC}} - M_{1\text{WIOC}})$ , the average values of  $\text{WIOC}_f$ ,  $\text{WIOC}_c$  change by less than 5%.” (page: 11, lines8-9)

- 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.

We added: “and increase the sample pressure during the manometric determination of TC amount.” (page: 12, lines 4-5)

- page 12 line 25: how was EC quantified in these samples?

Thank you for this comment. The EC was quantified as for the other samples in the original manuscript. We realize that this leads to a slight overestimation of EC and an underestimation of OC for these samples, because we should have subtracted the refractory biogenic OC from

the EC concentrations and add it to the OC. We have done this in the revised version of the manuscript. This leads to slightly adjusted numbers in table 3 for the spring and continental samples none of the concentration values change by more than 5%. Only the OC/EC ratio in the spring is now significantly higher. None of the conclusions or discussions of the manuscript are changed by this. (page: 13, line 3-4)

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?)

We added the following clarification to the manuscript:

"although cooking usually emits much more OC than EC (e.g., Chow et al., 2004) and is probably not very relevant at a regional background site. Therefore any potential contribution from cooking is subsumed under EC<sub>bb</sub> in this study." (page: 13, lines 11-13)

- 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?

Since it concerns only two data points it is obviously impossible to do a rigorous statistical test. Including these samples into the regional pollution case decreased the average TC concentration by only 0.1  $\mu\text{g}/\text{m}^3$ . This makes sense considering that our sampling site is surrounded by major urban centers and highways and probably most of the aerosol we measure originates from these Dutch sources, both in the marine and modified marine case.

lines 33-40: no data support the discussion. No a-priori assumption can be done on seasonal  $\text{^{14}C}$  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.

We decided to remove this discussion, following the suggestion of the reviewer.

- 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 \_yyy  $\text{^{14}C}$ ) in all seasons, except in spring when they were yyy% higher"

Thanks for this suggestion. We replaced the original statement with: "The average values of  $\text{^{14}C}_{(\text{OC})}$  varied by  $\pm 4\%$  percent for winter, summer and fall as well as for continental and regional air mass conditions, but the average  $\text{^{14}C}_{(\text{OC})}$  in spring (0.89) was 20% higher than the average of the rest of the seasons (0.74)." (page: 14, lines 15-17)

line 2: " $\text{^{14}C}(\text{EC})$  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  $\text{^{14}C}(\text{OC})$ , the terms "high" and "low" are nonsense unless further detail is given.

We changed this sentence to:

$\text{^{14}C}$  increased by almost 70% from summer to winter (page: 14, line 17-18)

line15: " $\text{OC}_f$  was constrained in a relatively narrow range, whereas estimates for  $\text{OC}_{bb}$  and  $\text{OC}_{c,o}$  varied over a much wider range reflecting the large uncertainty in  $r_{bb}$ ". Please specify what "relatively narrow" and "much wider" stand for.

Ok: We wrote instead: " $\text{OC}_f$  was constrained within 0.3 and 0.5  $\mu\text{g}/\text{m}^3$ , whereas estimates for  $\text{OC}_{bb}$  and  $\text{OC}_{c,o}$  varied over a much wider range of roughly 0.5  $\mu\text{g}/\text{m}^3$  each, reflecting the large uncertainty in  $r_{bb}$ ". (page 14, line 29-30)

line 25: "low":specify"

We added: "with average TC concentrations of 1.4 mg/m<sup>3</sup>, which is less than half of the averages in other seasons" (page: 15; line: 1-2)

lines 27-29: "The main sources of fossil elemental carbon (EC<sub>f</sub>) 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.

This sentence has been omitted in the revised version of the manuscript

lines 29-30: "However, there are relatively high EC<sub>f</sub> concentrations in fall": please, quantify "relatively high"

We now write: However, EC<sub>f</sub> concentrations in the fall are two times higher than in spring and winter and four times higher than in summer. (page: 15, line 6-7)

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%)".

We changed this sentence to : "The concentrations OC<sub>f</sub> are elevated in fall as well" (page: 15, line 7 - 8)

lines 31-36: please add numeric information throughout the text

This paragraph reads now: The contemporary OC fractions are elevated in spring: OC<sub>c</sub> accounts for 70% and WSOC<sub>c</sub> for 60% of TC in spring, whereas OC<sub>c</sub> accounts only for roughly 50% and WSOC<sub>c</sub> for 35-40% of TC in other seasons. EC<sub>bb</sub> is more than 4 times higher in winter and fall than in spring and summer 2011. WSOC<sub>f</sub> is lower than WSOC<sub>c</sub> in all season except for summer. The standard deviations reflect the variability of pollution levels, which in winter are higher than the mean value. In summary, there are some indications of a seasonal variation in carbon concentrations, but the variability within each season is high and strongly influenced by weather and air mass conditions. (page: 15 , line 10-14)

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.

The regional contribution cannot be assessed quantitatively by this simple comparison, because it depends on too many other variables, however we can conclude that the regional contributions are higher for OC and EC from traffic sources than for other carbon fractions (but we cannot say how much higher exactly).

Therefore we changed this sentence to: "Our data therefore indicate that the regional contribution to OC and EC from traffic sources is higher than for other carbon fractions and the influence of long-range transport less important." (page: 15, line 29-31)

line 14: "concentrations of EC<sub>bb</sub> are very low in regional pollution". How much lower compared to other conditions?

This now reads: "Especially concentrations of EC<sub>bb</sub> are eight times lower in regional than in continental pollution" (page: 15, line 33)

lines 27-29: "The rainfall duration was on average 1 hr/day for continental 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

There were not so many sampling periods with completely dry conditions, but very often the rain was only of short duration. In this case the number of rainy days might be misleading, if a lot of them contained only a short period of precipitation, but would be counted similarly as days, where it rained most of the day. In these conditions we feel that the total amount of precipitation that fell in each period (normalized by the number of days measured in each period) is a better measure for the influence of precipitation.

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.

We changed this sentence to:

"the concentrations of EC and OC are below 0.5 mg m<sup>-3</sup> for EC and below 1 mg m<sup>-3</sup> for OC<sub>f</sub>, OC<sub>bb</sub>, OC<sub>c,o</sub> respectively, with average values less than half of the average concentrations encountered during continental air mass conditions. OC and EC concentrations are also less variable in recent pollution with relative standard deviations roughly 50% of the mean value of most carbon fractions, whereas standard deviations nearly approach the mean value for many carbon fractions continental air mass conditions." (page: 17, line 13-18)

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?

We changed this sentence to:

"Carbon concentrations comparable to regional air mass conditions occur for EC<sub>f</sub>, EC<sub>bb</sub> and OC<sub>bb</sub> in 50 – 60% of the continental samples and for OC<sub>f</sub> and OC<sub>c,o</sub> in 30 – 40% of the continental samples. This shows that despite higher average concentrations, continental air mass conditions do not always carry high concentrations of carbonaceous aerosol concentrations to the Netherlands." (page: 17, line 18-22)

Page 17 line 9: "somewhat higher".

We changed this to:

"The fraction of WSOC is the sum of the blue areas, which accounts for ~ 3/4 of the total OC in spring and summer and roughly 2/3 in fall and winter." (page: 17, line: 34-35)

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".

Since the variability in the relative fossil contribution within each season is roughly 10% or more, we decided not to highlight the small variations and shortened the sentence to:  
"WIOC consists to roughly equal parts of fossil and contemporary carbon." (page: 18, line 2).

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/m<sup>3</sup> in

regional air mass to yyy ug/m<sup>3</sup> in continental air masses)

We changed this sentence to:

“The contributions of fossil and contemporary carbon fractions to OC (Figure 7b) stay within 5% (absolute) for different air mass origins, even though the average concentrations of OC increased from 1  $\mu\text{g m}^{-3}$  in regional to almost 4  $\mu\text{g m}^{-3}$  in continental air masses.” (page: 18, line 3-5)

line 26: "mg": sure?

corrected

line27: "most of the contemporary WIOC": lots of points in figure 8 have  $0.1 < \text{WIOC} < 0.2 \text{ ug/m}^3$ . In such cases, contemporary WIOC from modern sources other than bb is far from being a small fraction of total contemporary WIOC.

This is a good point. We made the sentence more precise. It reads now:

“In other words, a large part of the variability in contemporary WIOC in the Netherlands seems to be associated with biomass combustion” (page: 18, line 14-15)

Page 18 line 3-5: are the authors sure that no primary soluble organics are emitted by fossil fuel combustion?

Usually, primary fossil OC is considered largely insoluble and our own data give direct evidence for this. WSOC<sub>f</sub> does not show any correlation with EC<sub>f</sub>, especially if the highest concentration data points are omitted. These high concentration data points introduce a spurious correlation, because the concentrations of carbonaceous aerosol are generally very high for these four cases affecting most OC and EC fractions. This is now stated explicitly in text:

“In contrast, a similar linear regression of WSOC<sub>f</sub> against EC<sub>f</sub> yields an  $R^2$  of 0.01, indicating that fossil water soluble WSOC does not have a common source with EC<sub>f</sub>. If the four highest data points are included the  $R^2$  is generally higher (0.92 for WIOC<sub>f</sub> and 0.48 for WSOC<sub>f</sub>), but this is mainly due to the fact that for these four samples TC concentrations are much higher than average (ranging from 5 to 10  $\text{mg m}^{-3}$ ) and this leads to both higher OC and EC concentrations in general. It is not good practice to fit such bimodal data with a linear regression.” (page: 18, line, 24-28)

line 21: "relatively low": please, quantify; line 23: " the variability of the WSOC<sub>f</sub>/EC<sub>f</sub> ratios is large": please, quantify

We made this paragraph more quantitative:

“The ratio of WSOC<sub>f</sub>/EC<sub>f</sub> is  $0.44 \pm 0.46$  under regional air mass conditions, which sample relatively fresh emissions. It increases to  $0.6 \pm 0.4$  under continental air mass conditions, where older and more processed aerosol is sampled. The difference is significant at the 90% confidence level, but not at the 95% confidence level ( $p = 0.06$ ). In general the large variability of the WSOC<sub>f</sub>/EC<sub>f</sub> ratio indicates that WSOC<sub>f</sub> and EC<sub>f</sub> do not originate from a common source. (page: 19, line 11-16)

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

The values for spring (0.76) and summer (0.57) have been added to the text (page: 19, line: 33)

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.

This is true. We deleted the sentence "*This reflects that the main sources of modern OC, biomass burning and SOA formation, produce largely water soluble carbon.*" from the manuscript

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, longrange transport of biomass smoke is the most important source of WIOC<sub>c</sub> 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, EC<sub>bb</sub>, WIOC<sub>c</sub>, and WSOC<sub>f</sub> 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

This is a good point. We made this section of the text more specific:  
"... long-range transport of biomass smoke acts to significantly increase the rather low background concentrations of WIOC<sub>c</sub> (around 0.1 mg m<sup>-3</sup>) in the Netherlands. This can be concluded from the strong correlation of WIOC<sub>c</sub> with EC<sub>bb</sub> and that a strong increase in EC<sub>bb</sub> and WIOC<sub>c</sub> only happens during continental air mass conditions." (page: 22, line 21-24)

Together with the changed discussion with respect to the comment to page 17, line 27, this hopefully clarifies the point we wanted to make.

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)

We added the trajectory end point height (50m) and a sentence concerning the temporal stability of the trajectories to the figure caption.

Minor revisions:

- Page 6 line 7: "mg": Sure?

corrected (page: 6, line 10)

line 17: "ultra-small samples larger than 2 \_g C": larger or smaller? If "larger" is right, better to rephrase as "ultra-small samples down to 2 \_g C"

done (page: 6, line 19-20)

line 24: "mg": sure?

corrected (page: 6, line 26)

line 30: change "from the five single filter pieces" in "from the five single blank filter pieces"

done (page: 6, line 33)

Page 13 line 17: please change "last" in "previous"

done (page: 13, line 39)

line 24: please remove "also"

done (page: 14, line 5)