

General comments:

Please note: Upon revising the manuscript we discovered that there was a small error in equation 4, which is now corrected. The numbers calculated with the correct formula changed only in the insignificant digits compared to the previous version. Moreover, the standard deviation of the modern contamination was not correct and is actually larger than reported in the first version of the manuscript.

Reviewer 1

We thank the reviewer for the thorough reading of the manuscript and the thoughtful comments. Addressing these points helped improve and clarify the manuscript. We hope that the revised version is now suitable for publication.

1) Most tests were carried out at 340 °C whereas the final choice for aerosol samples seems to be 360 °C. Can the authors comment on this?

We initially tested at 340 °C, since this was the temperature most commonly used in the literature and by us in previous experiments. However, we also tested $F^{14}C(OC)$ as a function of temperature. We found no change in $F^{14}C(OC)$ up to 400 °C, even though we extracted more OC at the higher temperatures (stated in the manuscript, but not presented in a figure). This indicated that raising the temperature in the first temperature step does not result in considerable EC combustion and therefore should not strongly affect the EC yield.

For the actual ambient samples that were sometimes highly loaded, we saw that 360 °C was often better suited to combust sufficient amounts of OC. Eventually, we decided that using 360 °C in the first temperature step would have the advantage of getting more OC for analysis, and lead to a lower fraction of ‘not analyzed’ carbon, without making the tests done here at 340 °C here invalid. The defined test substances were all removed at 340 °C, except for the fraction that was charred. We don’t expect the already small charred fraction to considerably further decrease by a 20 °C increase in temperature. This is also supported by the fact that our assessment of charring is similar to the one measured by Zhang et al., 2012, at 360 °C. Moreover, the tests on the ambient filters CA30, CA59, CA85, which were analyzed with $T1 = 360$ °C, show that the recovery is still around 80%, in the same range as for the test filters with $T1 = 340$ °C.

We will make this clearer in the manuscript, by inserting the following paragraph before the description of the final filter tests:

“The final decision was to use a S2 temperature step of 2 minutes at 450 °C, because this combines reasonable BC recovery rates with removal of most refractory OC. For $T1$ we decided to use a temperature of 360 °C, since this gives a higher recovery rate of OC on some highly loaded samples. Varying the temperature of step 1 did not change $F^{14}C_{(OC)}$ and showed only minimal loss of carbon black material, which both indicates that this slightly higher temperature should not strongly affect EC recovery and consequently $F^{14}C_{(ECr)}$.”

2) Page 139, lines 8-16: if the referee is right, HOxII and graphite are used as “check” standards. But what is the standard used for F14C determination? (i.e. the “normalisation” standard to use in eq.1?). It should not be the HOxII commonly used, as it cannot be used both for normalisation and check

In principle this is true, if exactly the same samples are used for normalization and check. However, the normalization is done using HOxII targets derived from large quantities of the standard, where the small contaminations mentioned here do not change the nominal $F^{14}C$ value appreciably. To assess the contamination, very small HOxII standards are introduced into the AMS, and are treated as samples, i.e. normalized to the big HOxII standards. The measured deviation in $F^{14}C$ from the nominal value for small samples is caused by contamination and can thus be used to assess the contamination (de Rooi et al., 2010).

3) Page 147, line 6: unclear. Do the authors mean that the F14C overestimation can be up to $0.05 \cdot F^{14}C(RC)$ or 0.05 absolute? Please clarify.

Absolute, we will clarify this in the text, by inserting the following sentences:

“In the extreme case of completely fossil EC ($F^{14}C_{(EC)} = 0$) and biogenic OC ($F^{14}C_{(OC)} \sim 1$), this would increase $F^{14}C_{(EC)}$ by 0.05 (absolute). If $F^{14}C_{(OC)}$ is lower and $F^{14}C_{(EC)}$ is higher than in this extreme case, the overestimate is smaller (e.g. 0.03 for $F^{14}C_{(OC)} \sim 0.8$ and $F^{14}C_{(EC)} \sim 0.2$).”

4) Page 149, lines 15-19: here the authors state that a coincident decrease in the recovered mass and F14C(RC) can be considered as an indirect indication of residual OC removal (see line 1-2). However, the authors also state (page 148, line 16) that biomass burning soot is less refractory than liquid fuel soot. The removal of biomass burning soot would give the same effect as the removal of organic material. The optical analysis can help discriminating the two situations.

The optical method is a very good tool to distinguish between removal of OC and biomass burning EC, if available. However, most EC/OC extraction systems do not have this option. This is why we also explore some other methods to estimate the removal of OC.

In principle, if biomass burning EC is strongly separated from fossil EC during combustion, it would not be possible to distinguish between OC and biomass burning EC removal without the help of optical methods. In practice, as shown by Zhang et al, (2012) the selective removal of biomass burning EC is relatively gradual, and does not lead to a strong decrease in ^{14}C with moderate changes in the recovered EC.

For example, Zhang et al., (2012) show in the supporting material that decreasing the mass EC yield by 0.1 results in a change in $F^{14}C$ of only around 0.02 – 0.025. For filter CA12 we show that raising S2 temperature from 450 to 500°C, EC mass recovery drops by 0.2 and $F^{14}C$ changes by 0.05, quite comparable to the data by Zhang et al., (2012).

This is roughly the effect that can be expected from preferential removal of BB EC. A strong dependence of $F^{14}\text{C}(\text{EC})$ on recovered mass, such as for filter CA2 is therefore still a sign of residual OC removal.

In hindsight, we think the term ‘selective removal’ of biomass burning carbon is a bit unfortunate, since it implies much stronger separation biomass burning and fossil fuel EC than actually occurs.

We will therefore replace the term ‘selective’ removal by “preferential” removal in the revised manuscript. On page 149 after line 19, we will also add the sentence:

“Preferential removal of biomass burning EC is usually associated with a much more gradual decrease in $F^{14}\text{C}_{(\text{EC})}$ ”.

5) Figure 3 is not understandable. Some bars appear missing. Please check and modify

Indeed, we now realize the description of Figure 3 needs clarification to be completely understandable. We now add a detailed description of the individual bars and what they represent and describe the figure as follows in the revised manuscript:

“Figure 3 shows the handling blank in $\mu\text{g C}/\text{cm}^2$ filter material for TC, OC and EC as white bars. For EC the two white bars represent the lower limit of $\sim 0.1 \mu\text{g}/\text{cm}^2$, if 3 filter pieces are used for EC extraction and the upper limit of $\sim 0.3 \mu\text{g}/\text{cm}^2$, if one filter piece is used. This is compared to the concentration of carbon on a typical small sample, which is shown in black bars. Using materials with known ^{14}C content, the contamination of TC was divided into modern contamination (Mmc) and fossil contamination (Mfc) as detailed in Eq (2) – (5). These are shown as additional grey bars for TC only.”

We hope this clarifies the data shown in Figure 3.

References 1) Manuscript by Yu et al. is reported in the reference list, but it is not present in the text 2) Poeschl, 1996 is cited in the text, but it is not present in the reference list 3) Sometimes Bernadoni et al. 2013 and some others Bernardoni et al., 2013 is cited in the text. Please check. 4) Wonaschütz et al. is cited in the text, but Wonaschuetz is reported in the reference list. Please use the same umlaut representation

These are all corrected, thank you!

Reviewer 2

Thank you, Sönke Szidat, for the interesting and helpful comments. We tried to address all of them carefully and this was really a big help to improve the manuscript.

General comments:

1. I cannot comprehend the reason, why the authors chose the term “refractory carbon (RC)”. At the end of page 134, they refer to the convention paper of Petzold et al. (2013), which in fact recommends not to use new terms in studies of carbonaceous particulate matter. As a consequence of this, “EC” is still the correct term to me, even if EC cannot be recovered quantitatively and the rather refractory fraction of it is analyzed. If the authors like to stress this point, the usage of an index (e.g. EC_{ref}) may be acceptable, which still seems to be more elegant than the usage of RC_{ex} (extracted RC). This would omit confusions as on page 135, line 27, where refractory organic material (ROM) is introduced, which is a fraction of OC, whereas refractory carbon (RC) should be a fraction of EC. The similarity between ROM and RC is too close and may remind the quick reader of the fractions OM and OC, which represent the same portion of the carbonaceous aerosol, whereas ROM and RC do not. Furthermore, the authors themselves come back to the term EC, e.g. on page 136, lines 10 and 17.

Thanks for this point of view, we will use EC and EC_{ref} (or maybe EC_r, because “ref” is very often used as abbreviation for “reference”) in the revised version of the manuscript. We were thinking of using the term “RC” as a distinction from “EC” analyzed by conventional thermal-optical methods, but since we do not use such data in the manuscript, this is actually superfluous.

2. In the context of the previous comment, I recommend reporting $\delta^{14}\text{C}$ measurements of EC a) as the measured value together with b) the EC recovery for the sample and c) the extrapolated $\delta^{14}\text{C}(\text{EC})$ for 100% recovery according to Zhang et al. (2012). c) is necessary, as the measured $\delta^{14}\text{C}(\text{EC})$ strongly depends on the extraction recovery with a trend to more fossil values for lower recovery as indicated in Fig. 7. For interpretation of the radiocarbon analysis of EC, however, the total EC is relevant and not the occasionally extracted fraction of it.

Yes, we think this is a good suggestion. We did not measure the dependence of $\delta^{14}\text{C}(\text{EC})$ on recovery directly, but our slope of $\delta^{14}\text{C}$ vs. EC mass loss agrees well with the data presented in Zhang et al. (2012), see response to reviewer 1, comment 4. Therefore, we will use the relationship that Zhang et al. suggest in the appendix to extrapolate the values presented in Table 1 to 100% recovery. We will present this in an additional column in the Table.

Specific comments:

3. Page 133, lines 4-6: This sentence needs improvement.

We hope the sentence is clearer in the revised manuscript, after splitting it in two sentences and making the phrasing more exact:

“Aerosols from wood combustion have by a variable $F^{14}\text{C} > 1.04$, depending on the age and origin of the wood. Most of the wood burned today was grown over the last 20 – 60 years, when ^{14}C levels were elevated in the atmosphere following the nuclear bomb tests.”

4. Page 135, lines 4-5: “refractory and organic carbon” in line 5 should be substituted by “these fractions”.

Done

Line 8: “organic carbon” and “refractory carbon” should be removed.

Done

5. Page 136, lines 22-24: How easily can these pressure conditions be adjusted and kept constant? Which kind of needle valve do you use?

We use a normal 1/8 Swagelok needle valve. The oxygen and He are fed to the reaction tube via pressure regulators. The pressure in the reaction tube depends on the pressure set in the regulator and the flow set in the needle valve. The dependence on the flow is not very strong, since the flow is small and the reaction tube has a relatively big volume. If the flow is changed, the pressure takes some time to adjust, but stays very constant after that. The pressure in the purification line is more strongly affected by the flow, e.g., for 70 ml/min we get roughly 17 mbar; for 40 ml/min around 10 mbar, while pumping with a low vacuum oil pump.

6. Page 140, lines 5-9: We had bad experience with soaking the filters. Particulate matter was dislocated on the filter surface leading to inhomogeneous loading after the procedure. We even observed statistically significant losses. Therefore, we applied the dynamical water extraction as described in Zhang et al. (2012) instead of soaking. How did you evaluate that only a small fraction of insoluble material was lost (line 8)?

We evaluated it by measuring the absorption of the material on selected filter before and after water extraction using an Ulbricht sphere. This is admittedly not an extremely accurate method. In some cases we got slight decreases (~10% in BC), but also sometimes an increase was measured. We never observed that the filters were inhomogeneous after water extraction. We do not expect that moderate losses should have a strong impact on $F^{14}\text{C}(\text{ECr})$, but it could skew the recovered fraction. Moreover, losses during water extraction could have an impact, if the amount of total EC is estimated from TC concentration and $F^{14}\text{C}(\text{EC})$, $F^{14}\text{C}(\text{OC})$. We therefore decided to monitor the change in absorption for all water extracted samples and if necessary correct accordingly. This will now be stated in the manuscript.

Maybe the relatively good results with the water extraction come from the fact that we use PM_{2.5} samples. I think I remember that water extraction of PM₁₀ samples was more difficult, which might be related to larger particles being more easily removed from the

filter.

For the future we also plan to switch to the dynamical water extraction, which is clearly the better solution, also for PM2.5 filters.

7. Page 140, line 25 to page 141, line 2 and page 144, lines 12-15: How did you transfer the HOxII and the graphite standards onto the filter – as dry material or as solution/suspension?

If you used a solution/suspension, did you perform the blank subtraction described on 144 for the standards as well? What was the F14C value of the water and ethanol blank? How can you assess the blank from water extraction using HOxII and graphite, as both substances will be removed during water extraction (HOxII by dissolution, graphite by dislocation during soaking)?

The standards were applied as very small grains of the dry material, even though this made it difficult to control the exact amount of material applied. However, using a solution can introduce additional contamination, which we tried to avoid.

8. Equation 4: I assume that you determined measurement uncertainties for this calculation using error propagation. These should be shown in Fig. 3 and discussed in the text.

Actually upon addressing this comment, I realize now that in the text it is not clearly stated that the +/- ranges refer to the standard deviation of the mean values. The propagated uncertainties for the modern contamination are quite small (<5%), using reported uncertainties in F14C from AMS measurements (around 0.01 for HOxII and 0.001 – 0.005 for graphite, absolute) and uncertainties in measured carbon mass (around 3%). The propagated uncertainties for the individual fossil contaminations are larger, and for the average fossil contamination it is still around +/- 0.4 ug or 30%.

However, the variability in the calculated modern and fossil contamination is still larger than that, because the introduced contamination can be quite variable from sample to sample. This is in our opinion the more interesting point scientifically, therefore we decided to show the standard deviation of the contamination, to demonstrate how variable it is. We will clarify this in the text and also state the propagated measurement uncertainties. We will also include the standard deviations in the figure.

Please note that the standard deviation of the fossil contamination was not correct in the original manuscript.

9. Page 146, line 7: I propose to add at the end of this sentence: “, especially after water extraction (Bernardoni et al., 2013; Zhang et al., 2012).”

Done

10. Page 149, line 5: It should read “Poeschl, 2005”.

Corrected

11. Page 151, lines 1-2: Are the filters CA2 and CA18 specified in the methods section? I could not find it.

We realize now that we did not specify them and did not describe very clearly which filters were used for what tests. There were actually three test filters used.

We will add the following description in beginning of section 2.5:

“Ambient aerosol samples were also used as test filters. Three filter samples (CA 2, CA12, and CA 18) were used as test filters for EC recovery. They were collected at the Cabauw observatory, a regional field site in the Netherlands in the following time periods: Filter CA2 - 11 to 14 Feb 2011; Filter CA12 - 27 Feb to 1 Mar 2011; Filter CA18 - 6 to 12 Apr 2011. Other samples were used to evaluate the final combustion procedure and are more closely described in Table 1.”

It is now clearly stated in the text which filter was used for what tests.

12. Tables 2-4 should be moved to the Supplementary Material or removed completely.

We tried to put them into the supplementary material in the original submission, but this was not allowed by the journal, so we had to put it in the text. I think removing them altogether might be a good idea, because they can be readily found on the internet. We will try to add the link to the supplier site instead.

13. Caption Fig. 3: It should read “HOxII”.

corrected

14. Caption Fig. 7: It should read “/TC) of”. The explanation of the last sentence is misleading and should be improved. The difference between Fig. 7a and 7b should be explained including the usage of the two different filters.

Corrected

References:

de Rooij, M., van der Plicht, J., Meijer, H.A.J.: Porous iron pellets for AMS C-14 analysis of small samples down to ultra-microscale size (10-25 mgC), Nuc. Instr. Meth. B 268, 947-951, 2010.

Zhang, Y. L., Perron, N., Ciobanu, V. G., Zotter, P., Minguillon, M. C., Wacker, L., Prevot, A. S. H., Baltensperger, U. and Szidat, S.: On the isolation of OC and EC and the optimal strategy of radiocarbon-based source apportionment of carbonaceous aerosols, Atmos. Chem. Phys., 12, doi.: 10841-10856, 10.5194/acp-12-10841-2012, 2012.