Our responses to the Reviewer are organized as: Reviewer comment in italic and response in blue regular font. The changes made in the manuscript refer to the new version (Page, Line), in bold.

Anonymous Referee #3 Received and published: 20 December 2019 "Seasonal source variability of carbonaceous aerosols at the Rwanda climate Observatory" by Andersson et al. The manuscript reports results of ground-based observations of carbonaceous aerosol at a mountain site in Rwanda, sub-Saharan Africa. Fine airborne particulate matter (PM2.5) was collected weekly basis on quartz fibre filters, then total carbon, organic carbon, elemental carbon, water-soluble organic carbon contents and their radio and stable isotopes were analyzed. Major inorganic ions (nitrate, sulfate, ammonium, and potassium ions) were also analyzed. Mass balance approach was applied to the isotopic data to identify the origins of the carbonaceous aerosols. The results were also compared with wild fire information provided by NASA and with back trajectories of air masses arriving at the sampling site using HYSPLIT provided by NOAA to better understand the origins. Studies of origins of airborne particulate organic matter are one of the hottest themes in atmospheric science, but the origins are complex and not easy to be untangled. Application of isotopes measurements will provide additional dimension in the scientific information, thus, ideal for such studies. I have been aware of the authors' previous work, the dual isotope analysis, and the analysis provides insight into the origins of organic carbons, particularly differentiation between biogenic and fossil fuel origins using 14C. Compared to 14C, the method of 13C fingerprinting is week due to its large variation of the end members, depending on source types. Here, the authors attempted estimation of carbonaceous aerosols derived from C3 and C4 plants, which are known to have discrete compositions in 13C from each other. Papers reporting those fingerprints of organic aerosols are not many (Mkoma et al., 2014, TellusB; Irei et al., EST, 2014). The 13C fingerprinting approach to the carbonaceous aerosols that contain secondary organic aerosols would not be as simple as the authors describe here, but the studied location may be close enough to capture primary carbons. As I read this manuscript, the analysis was relatively straightforward, and gained results sound reasonable.

We thank Reviewer 3 for this overall positive assessment of our work, and for constructive feedback, based on which we think the manuscript is significantly improved.

New/changed figures and tables:

Figure 1: We have updated Figure 1, now with back-trajectory arrival heights at 100 m.a.g.l., and 500 m.a.g.l. as a new Figure S1. In the submitted version the arrival heights were (by mistake) 10 m.a.g.l, and the latitude was slightly offset. We think 100 and 500 are more representative, while they also in good agreement.

Figure 4: We moved the $\Delta^{14}C$ vs TC plot to a new **Figure 5,** in which we also added a $\delta^{13}C$ vs TC plot.

The previous **Figure 5** (2D isotope plot) is the new **Figure 6**.

We have updated the previous **Figure 6** with the results from the new MCMC approach, and this is the new **Figure 7**.

New Figure S1: back trajectories at arrival height 500 m.a.g.l.

New Figure S2: $\Delta^{14}C$ vs TC and $\delta^{13}C$ vs TC from the new Bayesian MCMC source apportionment method,

New Figure S3: A sensitivity analysis of the new Bayesian MCMC source apportionment strategy w.r.t. number of data points.

New Figures S4-S6: computed fractional source contributions from 3 alternative endmember scenarios; sensitivity tests.

New Table S2 with updated fractional source contributions from the new MCMC approach.

New Tables, S3-S5: results from the MCMC-based source apportionment from the 3 alternative endmember scenarios.

However, I also had impression that they could go into a fairer evaluation that considers the possible variation in the 13C compositions of endmembers. For example, according to L177-179, they performed Monte Carlo simulation to estimate the uncertainties of fC3, fC4, and ffossil propagated from the variability of fingerprinting 13C compositions. The gained uncertainties were small enough to capture significant values of source contributions and then plotted in Figure 6. At the same time Figure 5 shows wide ranges of the 13C compositions for the end members, C3, C4 plants and fossil fuel. Are those variations reflected to the uncertainties of the source apportionment? Such large variations do not seem to end with the uncertainties in Figure 6. If not, I recommend the authors to work on more objective evaluation by providing a several scenarios with the combinations of different 13C compositions of the three endmembers, together with the most feasible apportions (probably those currently described in the manuscript). This will raise the quality of this manuscript, I believe.

We agree with the over-arching comments on the treatment of the endmember variability, and in response to both reviewer 3 and reviewer 4 we now implement a more advanced Bayesian MCMC

methodology and explore different endmember scenarios. We have updated sections 2.5 and 3.5 accordingly.

New description of the MCMC technique in M&M Section 2.5:

'The vegetation in SSA may be divided into two main photosynthetic classes: C_3-plants and C_4-plants, see discussion in Section 3.5. These two groups have distinct $\delta^{13}C$-signatures, allowing isotope-based separation. We may then resolve three source classes by combining $\Delta^{14}C$ and $\delta^{13}C$: C_3-plants, C_4- plants and fossil, through isotopic mass-balance (Andersson et al., 2015):

$$\begin{pmatrix} \Delta^{14}C(i) \\ \delta^{13}C(i) \\ 1 \end{pmatrix} = \begin{pmatrix} \Delta^{14}C_{C3} & \Delta^{14}C_{fossil} & \Delta^{14}C_{C4} \\ \delta^{13}C_{C3} & \delta^{13}C_{fossil} & \delta^{13}C_{C4} \\ 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} f_{C3}(i) \\ f_{fossil}(i) \\ f_{C4}(i) \end{pmatrix} \quad (2)$$

Endmember variability may significantly influence the calculated source fractional contributions (Andersson, 2011). For a discussion on the specific endmember ranges used here, see Section 3.5.

In Eq. (2) the isotopic data is treated as independent. However, here we find that there is a dependence between the isotope ratios and the TC concentrations, such that $\Delta^{14}C(i) \sim A/TC(i) + B$, where A and B are constants, and i is the sample index (Fig. 5). This is known as a Keeling relation, and is discussed in more detail in Section 3.4. The relation holds for both $\Delta^{14}C$ (R^2=0.85, $p<0.01$) and $\delta^{13}C$, while the correlation is weaker for $\delta^{13}C$ (R^2=0.55, $p<0.1$). A method for using correlations within the framework Bayesian source apportionment has recently been developed (Martens et al., 2019). The rationale is based on both statistical concepts and the averaging expected from atmospheric mixing. The endmember ranges used in the calculations are from isolated sources, but during long-range transport the variability within a given source, e.g., savanna fires, will be reduced. Using correlations between data points, a means for accounting for the mixing is obtained, and more realistic source fraction estimates are obtained. When using the estimated source fractions to back-calculate the isotope signatures, the agreement is good compared with direct fits (Fig. 5 and Fig. S2). A sensitivity analysis is discussed in section 3.5 (Fig. S3)

To account for the correlations in the data-set we therefore add a second constraint in the source apportionment calculations, based on the relation to the TC concentrations:

$$\begin{pmatrix} f_{C3}(i) \\ f_{fossil}(i) \\ f_{C4}(i) \end{pmatrix} = \frac{1}{[TC(i)]} \cdot \begin{pmatrix} f_{C3,slope} \\ f_{fossil,slope} \\ f_{C4,slope} \end{pmatrix} + \begin{pmatrix} f_{C3,intercept} \\ f_{fossil,intercept} \\ f_{C4,intercept} \end{pmatrix} \quad (3)$$

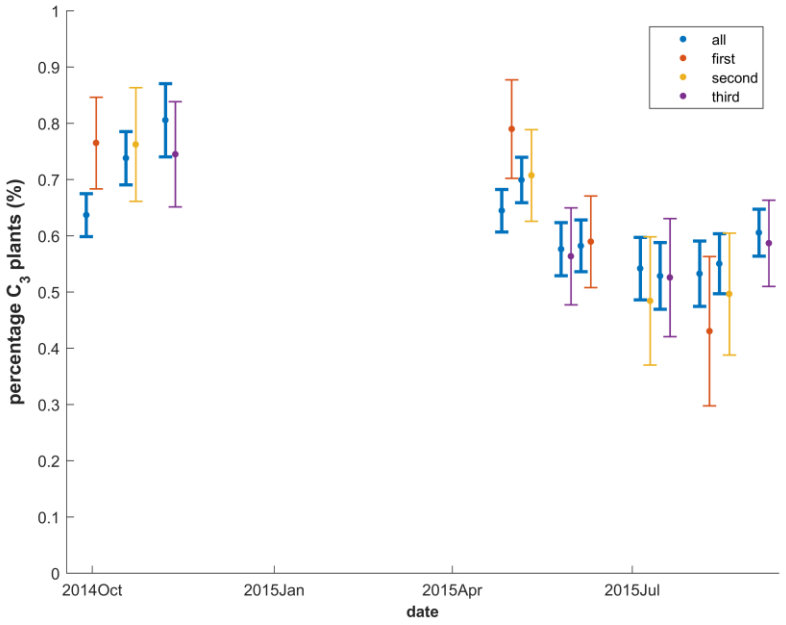
Where we, instead of fitting a source vector (f_{C3}, f_{fossil}, f_{C4}) for each individual data pair, fit two vectors: a slope and an intercept of the line, to all data points. This clearly holds the advantage of have fewer fitting parameters. We emphasize that the strength of the correlation of the isotope signatures relative to 1/TC is naturally incorporated into this relation, such that lower correlation of $\delta^{13}C$ w.r.t 1/TC impose weaker constraints on the calculated source fractions, compared to $\Delta^{14}C$.'

Pages 8-9, Lines 178-206.

New text on the sensitivity of the new MCMC approach w.r.t. number of data points in R&D Section 3.5:

'Back-calculating the isotope signatures from the computed source fractions from the MCMC-simulations essentially reproduce the Keeling relations relative to 1/TC (Figs. 5 and S2). To check influence of the number of data points used in the Keeling-based MCMC, we computed comparative scenarios where every third data point was used (starting at data point 1, 2 and 3 respectively) (Fig S3). The standard deviations for the calculated f_{C3} are on average doubled when only every third point are used (5% vs 10%), showing how correlations between multiple data points aids in constraining the sources.'

Page 15 Lines 388-394



NEW Figure S3 Sensitivity of the Keeling-based Bayesian MCMC source apportionment approach w.r.t. number of data points in the calculation. The fraction C_3-plants is plotted vs time. In blue, the results from using all 12 data pairs (errorbars: mean ± stdev). The orange, yellow and purple lines show calculations using every third data point, starting from data point 1, 2 and 3, respectively. The results from every third data points are shifted slightly in time (to the right) for visual clarity.'

Discussion on estimating the influence on KIE on the C_4 $\delta^{13}C$ endmember:

'Accounting for such effects in source apportionment is a challenge, especially since the reported values are ranges and not mean and variability, and thus are highly influenced by potential outliers. We here use a method discussed in Andersson et al. (2015) to address the issue of statistical analysis of ranges by assuming that the total range corresponds to the 95% confidence intervals of a normal distribution. This corresponds to the range of 4 times the standard deviation, yielding σ = 7/4‰, while the mean is -7/2‰. Combining this with the variability of the of pure C_4-plants we obtain: $\delta^{13}C_{C4}$: -16.6 ± 2.2‰, where $\sigma^2 = 1.2^2 + (7/4)^2$ ‰^{2}. These values are also what is obtained by numerical estimation of the convolution of a normal distribution (μ = -16.6, σ = 1.2‰) with a uniform distribution ([-7, 0] ‰), adding to the strength of statistical representation.'

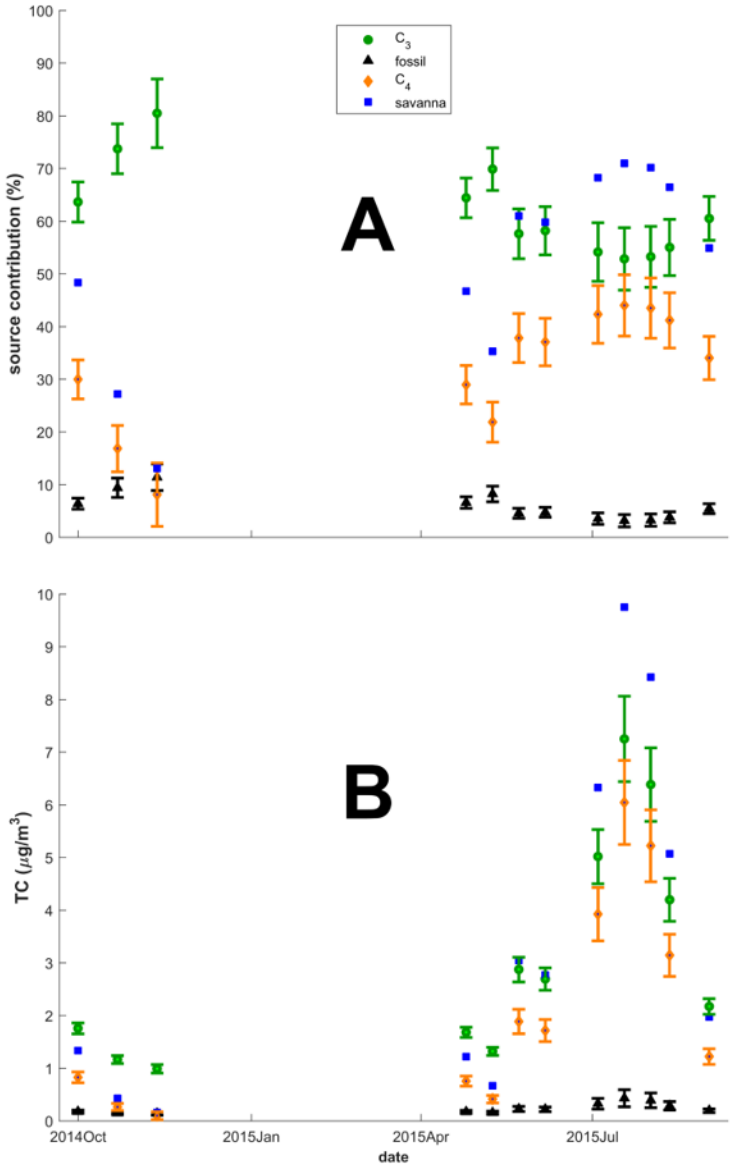
Pages 14-15 Lines 369-377

Discussion on endmember sensitivity scenarios:

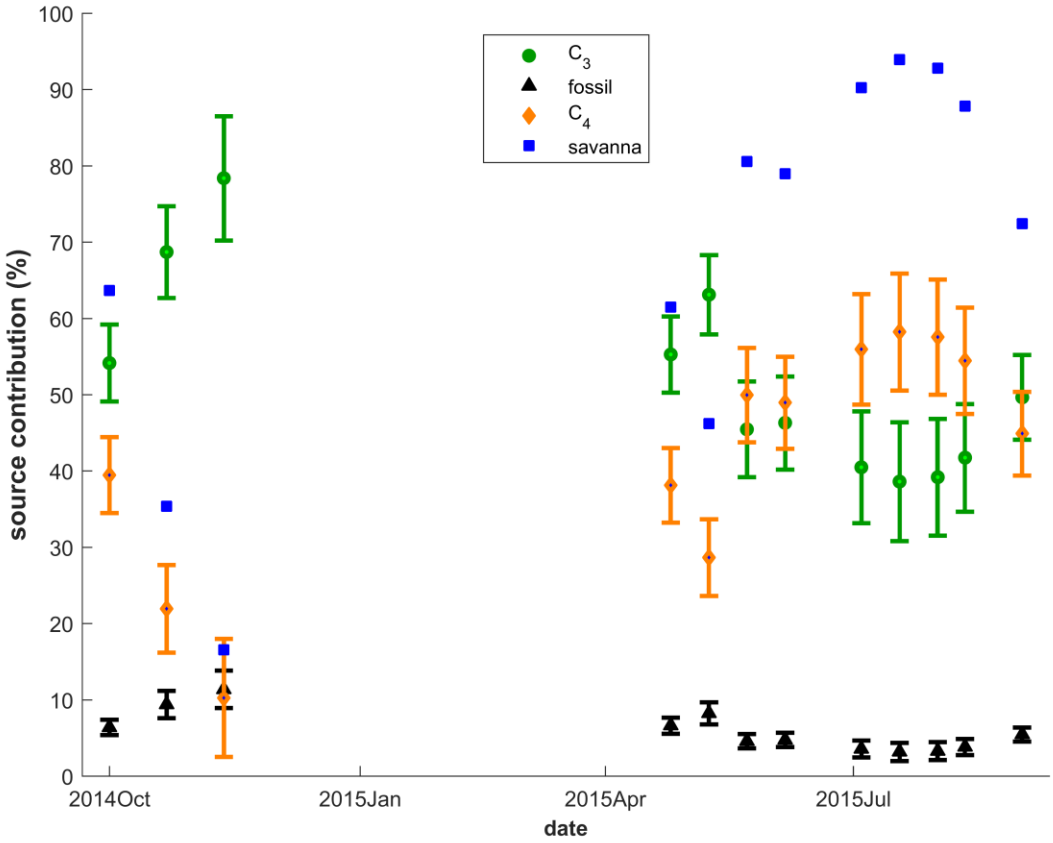
'Since the $\delta^{13}C$ endmembers for, in particularly C_4-plants, are not well-constrained, we also employed a sensitivity analysis w.r.t. endmembers and the potential influence of KIE (Tables S2 – S5 and Figs. S4 – S6). In addition to the above discussed best estimate scenario, we tested two $\delta^{13}C_{C4}$ scenarios: a 'minimum KIE scenario' with zero KIE ($\delta^{13}C_{C4}$ -13.1±1.2‰) and a 'maximum KIE scenario', with a depletion by 5.9‰ ($\delta^{13}C_{C4}$ -19.0±2.2‰). The maximum KIE scenario was established such as the $f_{C4}/(f_{C4}+f_{C3})$-ratio would be 62% as TC approach infinity, and thus 100% savanna contributions, see Eq. (4). As expected, these scenarios significantly shift the estimated relative C_4 contributions, resulting in a total range of the sample period averages of 24% (min-KIE; min 6% max 32%) to 42% (max-KIE; min 10%, max 58%), thus providing lower and upper bounds (Figs. S4 and S5 and Tables S3 and S4). The corresponding value for our best estimate is 32% (max 44%, min 8%). In addition, we investigated a scenario with a 3‰ depletion of the fossil endmember ($\delta^{13}C_{fossil}$ -28.5±1.3‰). Since the fossil contribution is overall low as determined by $\Delta^{14}C$, and since $\Delta^{14}C$ constrains the fossil contribution independently of the $\delta^{13}C$ data, this shift has no significant influence on the computed source fractions 6% (max 11%, min 3%) (Fig. S6 and Table S5). Overall, we stress that these three sensitivity test scenarios represent extreme limits, and the a priori least biased scenario is the initially outlined best scenario.'

Pages 14-15, Lines 395-410.

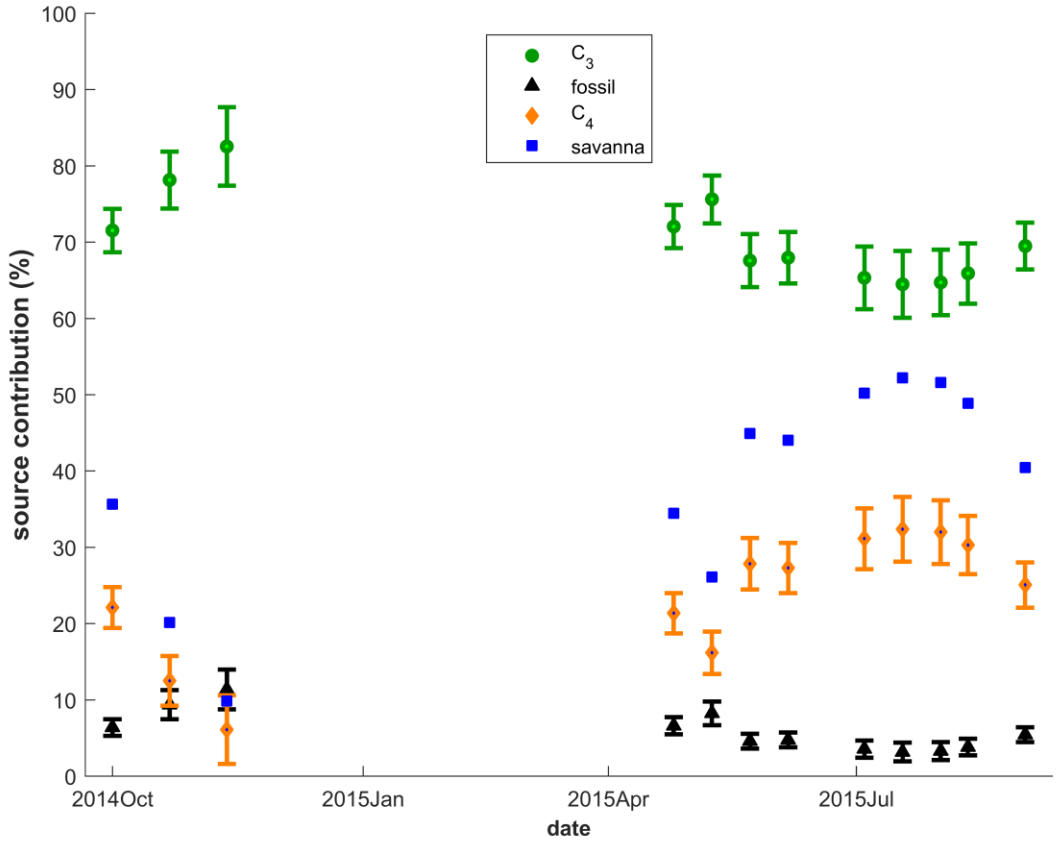
We have also updated related Figures, 5 and 7, and added Figures S3 – S6 and Tables S3 to S5 in the supplementary information, see also Figures below.



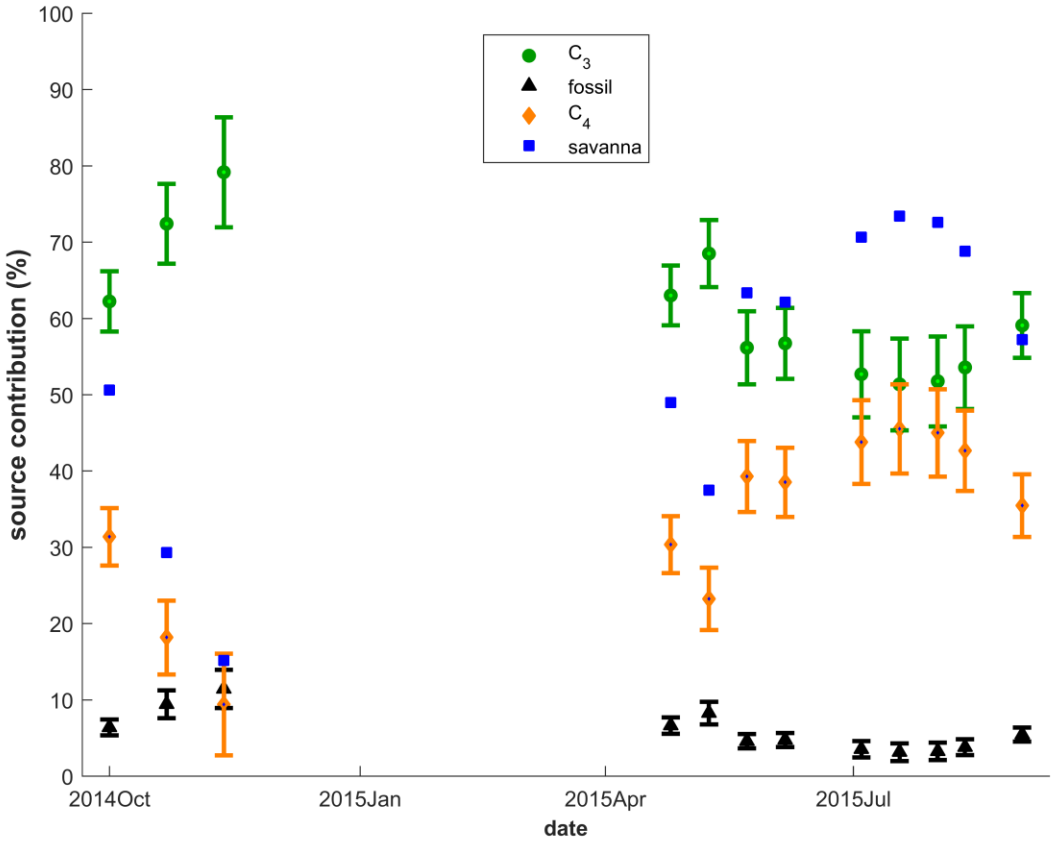
NEW Figure 7: Carbon isotope source-segregated fractions and concentrations of TC vs time computed with the 'best endmember scenario'. Panel A. Relative source contributions (%) of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles). Estimated savanna contributions are shown as blue squares. Panel B. Source segregated concentrations of TC of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles). The error bars (standard deviations) were calculated using Markov chain Monte Carlo simulations.



NEW Figure S4: Carbon isotope-source segregated fractions and concentrations of TC vs time computed with the 'maximum C_4 scenario'. Panel A. Relative source contributions (%) of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles). Estimated savanna contributions shown as blue squares. The error bars (standard deviations) were constrained using Markov chain Monte Carlo simulations. Panel B. Source segregated concentrations of TC of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles).



NEW Figure S5: Carbon isotope-source segregated fractions and concentrations of TC vs time computed with the 'minimum C_4 KIE scenario'. Panel A. Relative source contributions (%) of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles). Estimated savanna contributions shown as blue squares. The error bars (standard deviations) were constrained using Markov chain Monte Carlo simulations. Panel B. Source segregated concentrations of TC of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles).



NEW Figure S6: Carbon isotope-source segregated fractions and concentrations of TC vs time computed with the 'depleted fossil scenario'. Panel A. Relative source contributions (%) of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles). Estimated savanna contributions shown as blue squares. The error bars (standard deviations) were constrained using Markov chain Monte Carlo simulations. Panel B. Source segregated concentrations of TC of C_3-plants (green circles), C_4-plants (orange diamonds) and fossil (black triangles).

My comments on specific parts of the manuscript are provided below.

Abstract: Remove "(PM2.5)" because the abbreviation is not repeated in the abstract.

Yes, removed.

L98: Add the manufacturer information for PM2.5 inlet. Please provide the information of sampling frequency and duration.

The manufacturer for the inlet is the same as for the pump. We moved the manufacturer to the end of the sentence, and added 7 days sampling.

Page 5 Line 107

L151-152: Please provide the model and manufacturer information for AMS and IRMS.

The isotope-ratio measurements were conducted by personnel at the NOSAMS facility. To our knowledge they assembled their own instruments.

https://www.whoi.edu/nosams/ams-instruments

L192: Correct JAA to JJA. L193-194: Figure 1 does not show distinct plots of wild fires for the JJA and DJF periods. The authors may want to show two plots showing two periods.

We agree that this would make sense. Unfortunately, DJF was the period when our sampler was broken due to a lightening strike so we do not have any chemical/isotope data for this period, and we therefore remove the reference to the DJF period in Figure 1,

We changed the sentence to:

'During JJA the fires mainly occur to the south of Rwanda (Fig. 1).'

Page 5, Line 99

L205: Please define "BT".

Thanks. We now spell out 'back trajectories' throughout the manuscript.

L214-215: "This variability suggests. . ." needs supporting information (i.e., references).

We disagree on this point. This is an inference.

L221: Replace "-" with commas.

We have updated accordingly.

L223: Provide references directly here instead of "Table 1 that refers references.

This point was also raised by reviewer 2. As there are 10 references to the Table, we now write:

"However, it is also typically elevated in emissions from savanna fires (Table 1; e.g., Gao et al., 2003; Formenti et al., 2003)."

Page 10 Lines 250-251

L224-226: Please explicitly state whose results have agreed with the observations here.

We have changed the sentence to read:

"The dry season concentrations of carbonaceous aerosols components and inorganic ions reported here are overall in good agreement with the concentrations observed dry season rural and aged savanna fire air masses (Table 1)."

Page 10 Lines 252-253

L227-230: I am not sure where I can find the evidence showing the decrease and effect. Please describe the location of this information specifically.

This data is presented in the referenced Table 1, where different stages of plumes are described, e.g., 'fresh', 'aged' etc.

L241-242: Both Figure 3 and Table S1 do not show OC/EC ratios. Please provide those.

This point was also brought up by reviewer 2. In figure 3 we wanted to plot EC/TC for parallel construction with all Panels. However, OC/EC is a more commonly used parameter. We now write:

"Here, the EC/TC shows a distinct seasonality (Fig. 3 and Table S1). More commonly analyzed, though, is the OC/EC ratio (=(TC-EC)/EC), with elevated levels during the wet season (11±3) compared to the dry season (7±3; Table S1)."

Page 11 Line 268-270

L246-247: There would be many possible reasons for this variation, and I do not agree with the statement of "The elevated wet-season. . .". I recommend either to remove this sentence or provide the evidence to justify this possibility.

We agree and removed this sentence.

L255: I recommend to replace "a pulse" with a different term. How about occasional input?

We agree and have changed to 'occasional input'

Page 11 Line 283

L271: Avoid symbols of arrow and infinity in the text.

We agree and now write 'as TC approaches infinity'.

Page 12 Line 300

L277-278: In my opinion, descriptions of "d13C enrichment" and "13C/12C ratio enrichment" are not correct, but enrichment in (or with) 13C is the correct description. Please consider this throughout the text.

We agree and have updated throughout.

L275-281: I am not sure the point the authors want to make in this paragraph. Occurrence of chemical reactions in the particle? Please re-write it to make the point clearer.

Thank you for allowing us to clarify. The point is that $\delta^{13}C$ influenced by KIE, while $\Delta^{14}C$ is not.

We now write:

'In contrast to $\Delta^{14}C$, the $\delta^{13}C$-value is influenced by both atmospheric processes (i.e., kinetic isotope effects, KIE) and source signatures. Here, the $\delta^{13}C$-value shows a similar pattern relative

to the $\Delta^{14}C$-value, depleted in ^{13}C (min $\delta^{13}C$ = -27‰) during wet seasons, and higher during the dry season (max $\delta^{13}C$ = -21 ‰) (Fig. 4B). The correlation w.r.t. 1/TC (R^2=0.55, p<0.1) is weaker compared to $\Delta^{14}C$ (Fig. 5B). The direct fossil vs biomass source correlation from the $\Delta^{14}C$ Keeling curve is also driving the $\delta^{13}C$-signatures, but the higher variability is explained by larger endmember variability and potential influence of KIE, see Section 3.5. An overall enrichment in ^{13}C has been found in aged air masses in South Asia, especially for WSOC (Kirillova et al., 2013; Dasari et al., 2019), but less so for TC. In fact, the enrichment of ^{13}C in WSOC often appears to be counter-acted by a decrease in water-insoluble OC (e.g., Yan et al., 2017; Fang et al., 2017).'

Page 12 Lines 304-313

L284: Please provide the degree of "shift" specifically. Also replace "around" with "∼" sign, or vise versa.

Thank you. We now write:

"However, the temporal trend appears shifted in the RCO samples from values around -25 ‰ to around 22 ‰ in mid-May

Pages 12-13 Lines 315-317

L286: Not sure what agreed in. Please make this specific.

Thank you for pointing out unclarities. The sentence now reads:

"In addition to the complications of comparing measurements conducted at different sites during different years, there is a good agreement in the $\delta^{13}C$-values, and the temporal offset may be explained by inter-tropical convergence zone position variability.'

Page 13 Line 317-320

L287 Please define "ITCZ".*

We now spell out 'inter-tropical convergence zone', see above comment.

L303: State Figure 3 when discussion the results shown somewhere.

We agree. Updated accordingly.

L330: Replace "between" with from.

We agree. Updated accordingly.

L331-334: As I mentioned earlier, I recommend to analyze possible variations in more detail, then provide this fingerprinting d13C that gives feasible results. Choice of this value without other possibilities will lead a biased interpretation.

We have significantly expanded upon this part in the new version of the manuscript. See response to the over-arching comments by the reviewer.

L340-342: I am not sure why the authors can say so. Please provide the evidence (observations or references demonstrating such characterizations).

We think this conclusion is more evident within the new MCMC source apportionment strategy.

See response to the over-arching comments by the reviewer.

L355-356: Does Figure 6 show 71% of carbonaceous aerosols from savanna fire in the dry season? I do not know where I can find this information in the figure.

We have updated this section with the results from the new MCMC source apportionment strategy and included the estimated savanna results as blue squares, in the New Figure 7, see above.

L360-390: I recommend to rewrite "Outlook" because some indirect topics, such as CO2 source and brightening stuff, are referred with many references.

We agree, and have reduced references and discussion on such topics, while still maintain that parts of the original text is relevant, as this is an outlook section (not a summary or conclusion).

Table 1: Correct "BC/EC".

In some of the references the BC was estimated by light-absorption ('BC') but in some as EC.

Figure 1: As I mentioned earlier, provide two plots for two seasons.

Please see response to earlier comment.

Figure 2: The scales of y-axes are overlapped. Please fix those.

Thank you for noting this. Now fixed.

Figure 4c: It is interesting to see such a relationship. If extrapolating the curve to zero of TC, which is originated from plant burning, what the intercept value would be? I recommend to briefly discuss this value in the text.

We definitely see how this could be of interest. However, as TC approach zero, the isotope signature approaches negative infinity; clearly non-physical. The Keeling-relation is based having a variable source and a background. But the background is not zero.

Figure 5: I recommend to refer the references for d13C of C3, C4, and fossil in the footnote.

Although we in principle agree, we think reference to Section 3.5 is sufficient, as the list is rather long.

Figure 6: Add the horizontal line of zero for panel A. By the way, all figure captions should be under the figures. Are those just the style of ACPD?

Yes, the legends are now located below the figures. We have replaced the previous Figure 6 with a corresponding novel Figure 7, see above.

Table S1: Refer inorganic components in the table heading as well

Thank you. Now done.

References

Martens, J., Wild, B., Pearce, C., Tesi. T., Andersson, A., Bröder, L., O'Regan, M., Jakonsson, M., Sköld, M., Gemery, L., Cronin, T.M., Semiletov, I., Dudarev, O.V., Gustafsson, Ö.: (2019) Remobilization of Old Permafrost Carbon to Chukchi Sea Sediments During the End of the Last Deglaciation. Glob. Biogeochem. Cyc. 33, 2-14, doi: 10.1029/2018GB005969