Response of the authors to comments by reviewers – “Stable carbon isotopic composition of biomass burning emissions – implications for estimating the contribution of C3 and C4 plants”

Roland Vernooij (corresponding author) on behalf of the authors:

We thank both reviewers and the editor for their time and effort in assessing our manuscript, and the detailed and constructive comments which helped to improve the quality of this paper. Please find below our point-to-point response to the reviews. The revised text and updated figures are included in the updated manuscript. A separate ‘track-changes’ document is included to emphasize the changes to the manuscript.

Reviewer # 1 detailed comments	**Author’s response, reasoning and comments**
Throughout manuscript: Use either Fig. or Figure for consistency.	We followed the ACP Manuscript preparation guidelines, which states: “The abbreviation "Fig." should be used when it appears in running text and should be followed by a number unless it comes at the beginning of a sentence, e.g.: "The results are depicted in Fig. 5. Figure 9 reveals that...".” https://www.atmospheric-chemistry-and-physics.net/submission.html#manuscriptcomposition We have checked all instances where we referred to the figures to make sure we followed those guidelines and hope this addresses the inconsistency that you referred to.
P9L26: “weighted average (WA)” should be given here. The abbreviation is given twice later in the manuscript.	Thanks, corrected
P11L7: Spell out RMSE here.	Added ‘Root mean squared error’ in the text
P11L26-L27: It is not clear to me what these sentences mean to say. Do you mean “As a consequence, $\delta^{13}C$ signatures of CH_4 and OC emitted by the combustion of C3 and C4 plants are much closer than the difference in the signatures of the fuel.”?	Thank you for the suggestion, that is indeed what is meant here. The text has now been changed to “As a consequence, the $\delta^{13}C$ signatures of CH_4 and OC emitted by the combustion of C3 and C4 plants are much closer than the difference in the signatures of the fuel. “
P12L2: Fig. 2f should be Fig. 3f	Thanks, this has been corrected
P12L12: Fig. 4b and the legend do not have the hatched red bars. NMHC is in red.	The red bars are now changed to solid red, in correspondence with the legend. The reason the NMHC bar was hatched was to accentuate that unlike with the other species, we did not measure the fractionation in NMHC directly but rather estimated it based on previous studies, as is mentioned in the text P12L11. To be more clear, we

	have now emphasized this in the caption of the figure.
P12L17-18: What is depleted? Please complete the sentence	We see why this is unclear. We have changed the sentence to (P12L17-19): "For C4 fires, both the products and the residual fraction were depleted in ^{13}C compared to the fuel, indicating that our measurements either underestimated the ^{13}C in the products or overestimated the ^{13}C in the fuel. "
P12L27-28: Define EDS and LDS here.	We have revised the text to 'early dry season (EDS) and late dry season (LDS)' and also corrected this later in the manuscript.
P14L23: "savan na" should be "savanna"	Thank you, this is now corrected
P15L1: "BB burning" should "BB".	We removed 'burning' in the revised text
P16L13: This is not clear from Fig. 5 to me. Better explanation of the figure is necessary here.	You are correct, this is an error. The reference here should be to Fig. 7. In the left plot, the measurements reflect the signature of a single subcomponent (e.g. lignin) with respect to the bulk (the combined subcomponents). We have now better explained this in the caption.
Literature: Please check the formatting of the references thoroughly	Checked and corrected, references are now be as complete as possible and formatted according to the Copernicus ACP standard reference style.
Table 3: Where does -30.82 in row "Woodland Savanna/LDS/δ13C" and column "Shrubs" come from? There is no number in %Cfuel in the table. This needs to be explained in the main manuscript.	The contribution of shrub burning to total fuel consumption was very uncertain as it was based on a count of different shrub heights and some weighted specimens. Also, a large portion of the shrubs remained unburned, which we were only able to estimate. Since we do feel confident in the Isotopic signature, we initially decided to publish only this in table 3. However, we realize that by omitting shrubs there may be an important (C3) source of carbon missing, which may explain part of the ^{13}C depletion observed in the emitted aerosols. We therefore added the Shrub data to the revised manuscript. To estimate the amount of carbon in the Niassa field plots, we used the original shrub counts for different height classes. The counts were multiplied by shrub weights measured in a similar Miombo woodland vegetation in the late dry-season of 2021, in the north of the Kafue national park in Zambia and the carbon content and isotopic signature measured in the original samples in Niassa. The shrub weights (in Kafue nationl park) were obtained by cutting down three specimens from each of the dominant species and for each height-class, drying them in an oven (70°C, >48h) and weighing leaves and stems separately. Since stems and leaves tend to be consumed at different rates (i.e. much of the stems remained intact while the leaves burned) these pools were initially treated separately and later combined

	into one ‘shrub pool’. This description is added to the methodology in section 2.2.3. In the revised text, we also modified Table 3 to include the Shrub biomass. In Section 3.2.1 we added the following text: ‘While shrubs contributed significantly to the carbon in the fuel load of the woodland vegetation, the estimated percentage of shrub biomass that was consumed in the fires was limited. For different size classes, the estimated percentage of shrub biomass consumed in the EDS was: ±20% for shrubs of 0-50 cm, ±15% for shrubs of 50-100cm, with larger shrubs being unaffected. In the LDS, the portion of shrubs burned was higher at ±30% for shrubs of 0-50 cm, ±15% for shrubs of 50-100 cm, ±8% for shrubs of 100-200 cm, and only 2% for shrubs >200 cm.’

Reviewer # 2 detailed comments	**Author’s response, reasoning and comments**
Explanation of ^{13}C-enriched in CO should be given.	The correlation of $\delta^{13}C$ with MCE was very pronounced which is in line with the one previous study on CO by Kato et al. (1999). In the manuscript we give several explanations that may explain part, though probably not all of this difference: 1) Flaming combustion is dominated by the combustion of relatively ^{13}C-rich hemicellulose and cellulose, whereas RSC combustion is dominated by ^{13}C-poor lignin. This is the effect that we also see in other carbon emissions. 2) during burning with the same substrate and the same fractionation, there is a distillation process; if for instance the lighter C reacts easier, the substrate gets gradually enriched in heavier C, and then, for the same fractionation factor, the CO produced is gradually enriched as well. According to Kato et al. (1999) the kinetic isotope effect (KIE), which can be larger during smouldering plays an important role. This would explain the ^{13}C-depleted RSC combustions but not so much the highly ^{13}C-enriched flaming combustion. Part of CO can be further oxidized to CO_2. In principle this also happens with fractionation, which could depend on temperature, oxygen availability etc. Assuming lighter CO reacts faster, then the remaining CO should get enriched by this process. This is consistent with CO being converted to CO_2 more during the FC, which makes sense. As CO is much less than CO_2, this could enrich the CO without resulting in significantly depleted CO_2.

	3) The MCE is inversely proportional to the absolute CO emissions. A third explanation would therefore be that there is another source of relatively ^{13}C-rich CO, which becomes more significant at low overall CO concentrations. The emissions are corrected for the background amount and signature of the CO in the laboratory before the fire, and even for the FC samples this background CO concentration was generally <1% of the sample CO concentration. Therefore, we feel background CO is not likely to be this source but it may be fire-related. 4) CO can be formed from VOCs emitted during burning. VOCs emitted can vary with stage of burning, temperature etc, and they can have different C isotopic composition depending on the chemical source, but also on the fractionation during the VOC emission. Then there can be like above, fractionation during CO production from VOCs and variations in VOCs isotopes due to chemical processing. We have added the following text to section 4.1: “During BB, CO is formed both directly and indirectly (through VOCs) and once emitted, it further oxidizes to CO$_2$. The strongly enriched CO, may be related to the different substrate components that break up to form CO and VOC (Sect. 4.2) or the kinetic isotope effects during the formation and destruction pathways (Sect.4.4).”
The explanation of differences of ^{13}C fractionation in C3 and C4 should be added. Is it due to fuel or combustion condition?	We have added a separate section to the discussion: **4.3 Fractionation in C3 and C4 fuels** Many studies have reported difference in fractionation between C3 and C4 vegetation (e.g. Das et al., 2010, Chanton et al., 2000) which was consistent with our findings (Figs 3 and 7). This may be explained by the fuel composition; Woody C3 fuels tend to be more lignin dominated compared to C4 grasses (Benner et al., 1987). The signature of the bulk material is thus shifted towards lignin in C3 wood, which may be why the signature of the lignin is less depleted compared to bulk (Fig. 7). In other words: If lignin is depleted by the same amount compared to hemicellulose and cellulose, but the lignin content is lower in C4 grasses, this would cause lignin, and subsequently lignin-derived BB products, to be more ^{13}C-depleted compared to the bulk signature of those grasses. This coincides with our finding that RSC-emissions from C4 fires were more depleted with respect to the bulk-fuel signature compared to fires in C3 fuels. Particularly in C3 fuels, which are much more heterogeneous in nature, the large variation in fuels also showed in the fractionation range of the fuel.

	Oxidation in C3 fuels (e.g. densely packed leaf litter and woody debris) is much less efficient compared to well-aerated and quick drying grasses and dry leaves. Therefore, C3 fires emit more CO, CH_4, NMHC and Particulates. Emissions from these species were isotopically more similar to the C3 bulk fuel compared to C4 vegetation, while the opposite was true for CO_2.
What is the reason for slightly more depleted EC compared to the previous studies?	Although this was the case for both C3 (p-value = 0.25) and C4 (p-value = 0.07) vegetation, the fractionation was within range of the fractionation found in previous studies. The overall depletion may also be related to a sampling bias. There were not many samples for EC and those included more C4 and mixed fuel samples (red, orange in Fig. 3), which had lower 13C for everything.
Please estimate the C3 and C4 ratio by considering different fractionation occurring in the different processes for different fuels.	In the revised manuscript, we have added a section at the end of the discussion where we discuss possible ways of correcting the measurements based on the fractionation trends we observed. **4.7 Correction for source identification** Now we have established some relations between fuel type, combustion conditions and isotopic fractionation, correction can be done in multiple ways. If the MCE is measured, fractionation towards CO and CO_2 can be corrected for using its correlation with MCE described in Figs. 3a and 3b. Equation 6 is an example on $\delta^{13}C_{CO_2,corrected} = \delta^{13}C_{CO_2} - (12.7MCE - 10)$ (6) Applying this correction led to a reduction of 26% for CO_2 and 29% for CO in the difference between the signatures of the product and the fuel. The relative contribution of C4 to the fuel mixture can be calculated using Eq. (7): $C4_{(\%)} = 1 - \frac{\lvert\delta^{13}C_{product} - \delta^{13}C_{\mathbf{C4}}\rvert}{\lvert\delta^{13}C_{product} - \delta^{13}C_{\mathbf{C4}}\rvert + \lvert\delta^{13}C_{product} - \delta^{13}C_{\mathbf{C3}}\rvert} \times 100\%$ (7) Where $C4_{(\%)}$ is the relative contribution of C4 to the fuel and $\delta^{13}C_{product}$ is the isotopic signature measured in the emissions. $\delta^{13}C_{\mathbf{C4}}$ and $\delta^{13}C_{\mathbf{C3}}$ are the assumed isotopic signatures for C4 and C3 vegetation. For The field measurements, we used -14.9‰ and -27.6‰, respectively based on the pre-fire fuel collections. Since both EC and OC

	fractionation were not significantly correlated with MCE (Fig. 3), a correction like Eq. (6) cannot be applied. We therefore corrected the field measurements by correcting assumed isotopic signatures for C4 and C3 vegetation with the average fractionation for C3 and C4 (+1.27‰ and -4.77‰, respectively) when measuring OC and (-1.28‰ and -2.67‰, respectively) when measuring EC. This approach reduced the error in the estimation of the C4 contribution to the Mozambican samples by 64% using EC as a tracer and by 43% using OC as a tracer. On average, the difference between the estimation of the C4 contribution to the total fuel mixture measured by ground measurements and derived from the isotopic signatures of the EC and OC particulates was 10% using EC and 21% using OC.