Interactive comment on "Firewood residential heating – local versus regional influence on the aerosol burden" by Clara Betancourt et al.

Response to the Referee Comments

The authors would like to express their thanks and appreciation to the valuable comments from the editor and reviewers. We address below each of the reviewer comments individually.

Anonymous Referee #1
Received and published: 19 December 2020

General comments:
This manuscript presents the simulated isotope ratios of the biomass burning tracer levoglucosan using Lagrangian Particle Dispersion Model (LPDM) FLEXPART. The authors combine the model results with observed levoglucosan concentrations and d13C to evaluate the sources of residential burning emission. The simulations indicate the aerosol is 1 to 2 days old aerosol, likely from local to regional sources. The low OH concentrations in winter likely lead to limited levoglucosan photochemical aging. The isotope analysis shows that the observed d13C is in the range of -25.3 to -21.4 ‰ , which is agreed with previous studies on levoglucosan source specific isotopic composition in biomass burning aerosol. The authors present scientific results well using FLEXPART model and isotope analysis and statistical analysis. The overall quality ofthe manuscript is good, although some areas will need improvement. I recommend that the manuscript be published after making the following revisions.

Specific comments:
1. The authors compared the difference between ECMWF and GFS dataset. However, the meteorological data (e.g., cloud fraction, low cloud cover, precipitation, temperature, wind speed) is not shown and compared with observed levoglucosan. Please provide some details for correlation between meteorological factors and observed levolucosan concentrations.
Response: For the first time, we've introduced isotopic ratios additionally to concentration in a Lagrangian model and compared simulation results to observations, with the concrete goal to differentiate between local and remote sources of biomass burning aerosol. In the preparatory sensitivity studies, we varied some of model parameters, which either are considered as main sources of uncertainties (such as meteorology as a whole), or have a strong impact on the calculated source-receptor relationships (such as emission strength or loss processes). Due to the specific cold season conditions for this study, such as higher atmospheric stability or reduced photo-chemical activity, these variations didn't induce significant differences for the simulation results. Therefore, we didn't see the necessity to deepen our investigations with such detailed correlations. We consider that these are beyond the scope of our study, which was designed to scrutinize sources by using this novel approach, and not for model development. To make this clear in the manuscript, we've introduced the following sentence in the lines 171-173:
'Following the overall goal of this study to separate local from remote sources of firewood domestic heating aerosol, changes in output depending on selected input parameter modifications were evaluated for consistency.'
We agree that isotopes might contribute to test and develop models, but we consider that a summer study would be the right framework for that in a specifically dedicated publication.

2. Line 140: Why the in-cloud scavenging is not considered? Cloud/fog scavenging might occur at lower PBL. Have you checked the cloud bottom layer height? Do you have vertical cloud data with relative humidity? Any vertical profile of in-cloud scavenging, blow-cloud scavenging?

Response: Certainly, the in-cloud scavenging was considered in the wet-deposition runs. The wet-deposition module by Grythe et al. (2017) delivered the share of below- and in-cloud scavenging in the model output. In-cloud scavenging simply did not occur in this study, even if we set the in-cloud scavenging parameters to maximum (Cloud Condensation Nucleus effectiveness = Ice Nucleus effectiveness = 1.0). We agree that the sentence 'Since anthropogenic biomass burning aerosol is emitted into the lower mixing layer, in-cloud scavenging is not likely' is misleading at this stage of the manuscript. Therefore, we've removed it in the revised manuscript. Instead, we've changed the wet-deposition paragraph (lines 227-231), now to read:
'Further, the existent simulations show that wet deposition removed minimal amounts of the emissions. This might be explained by a short exposure of aerosol to weak precipitation of less than 5mm in 6h in the investigated periods. Moreover, there were no in-cloud-scavenging events for the investigated periods. Possible explanations are absence of fog or spreading of emissions in layers lower than the cloud bottom layer height. Similarly to the low impact on concentration, wet deposition had no significant influence on the isotopic composition of the sampled aerosol either.'
A detailed analysis to justify the reason for the negligible impact of scavenging is beyond the scope of this study.

3. Line 140-141: The OH-decay rate constant of levoglucosan, 2.67 10-12 cm3 molecules -1 s-1 is one order of magnitude lower than the 1.1 10 11 cm3 molec-1 s-1 reported by Hennigan et al. (2010). Please explain why you choose 2.67 10-12 cm3 molecules -1 s-1.
Response: The comparison of model results with the observations indicates that use of the kinetic data from the isotopic study by Sang et al. 2016 (also including the kinetic isotope effect of the reaction levoglucosan + OH) is most appropriate to the purpose of this work. For the concentration, the model predominantly underestimates the sources. A four-time reduction of the lifetime would make the underestimation stronger. Conversely, much higher emissions must be considered, to explain the measured levoglucosan. As for the isotopic analyses, the lifetime reduction to two days would translate in lighter emissions by 2 to 3‰, moving to the lowest end of the hard wood source specific delta. An explanatory section is given in the lines 318-321, now to read:
'**Here is to be noted that a four-time shorter levoglucosan lifetime, when using the k_{OH} reported by (Hennigan et al., 2010) would translate in even stronger emissions, characterized by isotopic ratios 2 to 3 ‰ lighter. Then again, these are at the lowermost end of the reported $\delta^{13}C_0$.'**

4. Line 189-190: Please explain more on why higher residence time of model particles can lead to higher derived levoglucosan concentration. Wind speed, turbulence condition, levoglucosan decay rate can also affect levolucosan concentration.
Response: The term 'residence time' in the FLEXPART retro plumes designates the receptor sensitivity to a source, which is of course impacted by wind speed and turbulence conditions. To avoid confusion, we reformulated the sentence, now to read:
'For the latter case, higher GFS Hmix are derived. Lower receptor sensitivity to emissions, expressed as tres (Supporting Information, Section S5), is expected due to dilution. The tres from ECMWF runs are smaller though. A possible explanation is that due to shallow mixing layers, a large part of the emitted particles likely leaves the investigated footprint layer and does not contribute to the receptor (Hueser et al., 2017).' (lines 188-192)

5. Line 193: "vertical mixing parameterizations". Please specify which parameter.
Response: For clarification, the sentence was changed (lines 194-198), now to read:
'Differences in the modelled levoglucosan concentration and isotopic composition are expected, mainly due to the different parameterization of sub-grid processes in the atmospheric boundary

layer in the GFS and ERA5 models (Berrisford, 2011;Han, 2011). Mixing influences the concentration of a model tracer that is released in the planetary boundary layer. Yet, during the more stable cold season over Europe, the differences are expected to be small.'

6. Line 194-195: "Due to the higher vertical resolution and ability to more accurately account for topography, ECMWF meteorology was chosen to initialize the model for the future runs." Did you consider to use WRF meteorological data for comparison?

Response: For this study, we didn't consider using WRF meteorology. FLEXPARTv10 can be run with ECMWF and GFS only. For the scope of this study, we consider that the presented comparison is sufficient (q.v. response to question 1, RC#1).

7. Line 213-214: "... levoglucosan is relatively stable during winter due to the low OH concentration." Is this also due to the lower temperature in winter? What's the average temperature during sampling periods? The reference from Busby et al. (2016) seems does not point out the levoglucosan reactivity in winter is due to the low OH concentration. Please check the reference.

Response: To our knowledge, neither the temperature dependence of (levoglucosan + OH) rate constant, nor parametrizations of kinetic barriers for the heterogeneous reaction at lower temperatures were hitherto reported. The only information we could implement into FLEXPART was the levoglucosan lifetime, derived from kOH and OH average concentration. Nevertheless, while the average OH concentration in the retro plumes is prone to uncertainties, it is well accepted that the photo-chemical activity is reduced in the dark winter months. Therefore, we've revised the section (lines 270-272), now to read:

'**Simulations showed that most contributing emissions are only one day old. As a consequence, levoglucosan degradation is not expected to be significant for this study. This assumption is supported by the reduced photo-chemical activity in the dark winter months (Busby et al., 2016).'**

Additionally, Table S1.2 was included in the Supporting Information to deliver the average temperature during the sampling periods.

8. Line 255: What are the two major types of sources?

Response: Regional and near-by sources are meant here. The sentence was completed (lines 259-260), now to read:

'**According to this, there are two major categories of sources contributing to the sampled aerosol, i.e. regional and close-by sources**.'

9. Figure 4: Please explain the possible reason for the two outlier points at STYR site.
The standard deviation is also higher than others.

Response: One of our findings was that close-by sources impacted the urban area receptor. Here, weak ventilation due to presence of buildings in combination with inversion ("Street canyon situation") can lead to high pollution events. For levoglucosan concentration measurements, the error propagation analysis resulted in a 11% overall precent error for the measurement set. Therefore, the error bars at higher concentrations are bigger.

Technical corrections:

1.Line 184: Figures 6.1 and 6.2 should be Figures S6.1 and S6.2.

Response: done (180)

2.Line 258: Figure " " is Figure 4?

Response: done (262)

3.Line 264: Figure " " is Figure 5?

Response: done (267)
4.Line 302: Table 8.3 should be Table S8.3.
Response: done (312)
5.Line 307: Table 7.3 should be Table S7.3.
Response: done (317)
6.Supporting Information line 143, 146, 150, 153, 154, 157, 161, 164, 166, 169, page 9: Some equations and words are missing.
Response: equations went lost during pdf document merging. Repaired
7.Supporting Information Table S7.2: and Table S7.3: Some words are missing for the captions. Basic statistics for ": : :: : :.".
Response: equations went lost during pdf document merging. Repaired
8.Table S7.4: Some words are missing for the captions. Basic statistics for the difference between ": : :." and ": : :.".
Response: equations went lost during pdf document merging. Repaired
9.Supporting Information P.19 Table S8.3 should be Table S8.4.
Response: done
10.Figure 1: The position of tm /s legend is too close to the latitude "-30". Please move the legend to a clear region. The unit of tm can be consistent with the figures of height vs. time/h.
Response: done
11.Figure 5: The color of light green and dark green is too similar, hard to distinguish it.
Response: done

Anonymous Referee #2
Received and published: 7 January 2021

Summary:
The authors reported isotope ratios of the biomass burning tracer levoglucosan with both model simulation and measurement in two sites in Germany. The simulations indicate that the largest part of the sampled aerosol is 1 to 2 days old, and thus originates from local to regional sources. The isotopic ratios of levoglucosan showed high variability in the observation and this reported as a result of different local sources instead of aging or transportation.
Overall Comments:
The article provides new, insightful information regarding how to examine the long range transport and local influence of biomass burning emissions using both simulation and measurements of levoglucosan. The overall completeness of the manuscript is decent and the presentation is clear. I recommend publication if the authors properly address the following comments.
Specific Comments:
One of the major conclusions here is that a large fraction of biomass burning aerosols were local. However, it was only lightly discussed with several sentences in Line 197-203 simply as the result of the simulation. An in-depth justification and discussion are needed here since this is fundamental to the manuscript.
Response: the fact that a large fraction of biomass burning aerosols were local was demonstrated not only by FLEXPART simulations but also by the combination between concentration and isotopic ratio observations. Here, the best tool to interpret these measurements is the Keeling plot analysis. We

reformulated some sentences in this section to underline the additional information gained by using this approach, now to read:

'**To investigate the chemical stability of levoglucosan for this study, a Keeling plot approach was employed. The test hypothesis was that chemical decay plays here an important role. Accordingly, the Keeling plot describes the mixing of two reservoirs, in this study of fresh - 'isotopically-light', high-concentrated emissions with aged - 'heavier', low-concentrated background (Lin, 2013). For this analysis, the measured isotopic ratio was plotted vs. the inverse concentration (Figure 7). A linear regression analysis was carried out. Remarkably, according to the 95% confidence interval analysis, the yielded y-intercept range of -25.3 to -21.4 ‰, theoretically describing the sources, agrees well within error ranges with the published isotopic composition measured in aerosol from the combustion of various C3 plants (Sang et al., 2012). A y-intercept of -23.2±0.1 ‰ was derived, theoretically representing the mean isotope ratio of fresh emissions. The knowledge gained from the Keeling plot analysis was used to initialize the FLEXPART isotopic runs. Since the information on type of fuels consumed in certain regions is very scarce, a constant source specific $\delta^{13}C_0$ of -23.2 ‰ was considered to calculate the ^{13}C emissions used in the simulations (Section S5 in the Supporting information). This isotopic ratio is in the range of soft woods (conifers). Since background levoglucosan concentration data were not available, the lowest measured concentration (12.4 ng m^{-3} at the EIFE station on November 10th, 2015) was considered as constant background value. A corresponding $\delta^{13}C$ of -24.0±0.3 ‰ was derived (see Figure 7). <u>The most important outcome was that the slope of the fitted line to the experimental data was found to be slightly negative, contradicting the assumption of an aged heavy background. This analysis thus demonstrates that the initial hypothesis of levoglucosan chemical instability was false. Consequently, the variability in the observed δ-values is likely due to the contribution of local to regional sources that possess different isotopic ratios in the above-mentioned range and not due chemical processing'</u>**. (lines 284-301)

We've introduced in the conclusion section sentences that emphasize the local origin of the investigated aerosol, now to read:

'**<u>Levoglucosan isotope ratios close to emission $\delta^{13}C_0$ can be either explained by deposition, or by local to regional sources and dispersion. Since dry and wet deposition are insignificant, the latter hypothesis is the most likely.</u>**

The presented case study shows reasonable agreement between modelled and observed data within error ranges. However, the frequent underestimations, especially at STYR might indicate unidentified sources or flaws in the levoglucosan emission strength. <u>This comparison supports the fact that sources, which are very close to the receptor but not accurately described in the developed emission inventory approach, strongly influence the local aerosol burden</u>, particularly for the STYR site. <u>The Keeling plot analysis proved that an aged background was insignificant for this study, supporting the conclusion that long-range transport minimally impacted the investigated aerosol</u>. This can also explain the few overestimations of the derived concentration at EIFE which might be caused by overestimated background levels rather than underestimated removal (Grythe et al., 2017). Repeated calculations reducing the background and increasing the emissions indicated that in the initial model runs, the source strength is most likely underestimated and the background levels overestimated. The measured $\delta^{13}C$-values show by far higher variability compared with the simulated isotopic ratios. This can be explained by possible individual source-to-source variation (e.g. due to differences in the used fuel). Within the variability of $\delta^{13}C$ of emissions, the retro-plume-modelled age of levoglucosan agrees well with the age resulting from the observed isotopic ratios. This agreement demonstrates that the limitation to 7-days backwards calculations does not create any significant bias. Finally, since observations as well as the retro plume analyse show that chemical aging does not play a significant role in the cold season in Central Europe, levoglucosan can be used as a

'conservative' tracer under similar conditions. All these findings demonstrate the FLEXPART fitness to simulate aerosol processes occurring between source and receptor. The sensitivity studies revealed individual factors leading to potential biases, while the comparison between simulated and observed concentration assessed the most probable sources and loss processes for the investigated aerosol.
Both sensitivity and case studies unquestionably point out that local/regional domestic heating is the major source contributing to the biomass burning aerosol burden under the investigated conditions.' (lines 346-368)

Similarly, the lack of discussion of the source-specific isotopic composition of levoglucosan also undermines the completeness of the manuscript.

Response: At the moment, there is no accurate information on the used fuels in the domestic heating during the cold season. Therefore, a distinction of the initialized source specific isotope ratios among different categories would make no sense. We decided to use an average d13C0, which we derived from the Keeling plot. Theoretically, the y-intercept of the line fitted to the experimental data gives the isotopic ratio of the source. The negative 'isotopic' age shows yet that this might be heavier than the real mean delta value. We introduced explanatory sentences, now to read:

'**A y-intercept of -23.2±0.1 ‰ was derived, theoretically representing the mean isotope ratio of fresh emissions. The knowledge gained from the Keeling plot analysis was used to initialize the FLEXPART isotopic runs. Since the information on type of fuels consumed in certain regions is very scarce, a constant source specific $\delta^{13}C_0$ of -23.2 ‰ was considered to calculate the ^{13}C emissions used in the simulations (Section S5 in the Supporting information). This isotopic ratio is in the range of soft woods (conifers).**' (lines 290-294)

and:

'This yields a 'negative' age for the observations (Supporting Information, Table S7.3), probably a consequence of the inaccuracy of the used emission isotope ratio, which is in the upper range of source specific $\delta^{13}C_0$. Here is to be noted that a four-time shorter levoglucosan lifetime, when using the k_{OH} reported by (Hennigan et al., 2010) would translate in even stronger emissions, characterized by isotopic ratios 2 to 3 ‰ lighter. Then again, these are at the lowermost end of the reported $\delta^{13}C_0$.' (lines 317-321)

Line 26: " -25.3 to -21.4 ‰¨ . These numbers are different from " -26.3 ‰ and -21.3 ‰ in Line 265. Why are they different?

Response: The isotopic ratios in the initially submitted abstract represent the values derived from the linear regression analysis (Keeling plot section). This was not our intention therefore, we've revised the numbers, now to read:

'The high variability in the observed δ13C implies that the local levoglucosan emissions are characterized by very different isotopic ratios in the range of -26.3 to -21.3 ‰.' (lines 29-30)

Line 29: " These findings demonstrate that the aerosol burden from home heating in residential areas is not of remote origin and thus it can be mitigated by reducing local emissions. " I find this statement too general for the scope of the paper.

Response: since we don't further handle that, we've removed the sentences both from the abstract and conclusions.

Line 139: "Since anthropogenic biomass burning aerosol is emitted into the lower mixing

layer, in-cloud scavenging is not likely." More justification needed here to eliminate in-cloud scavenging. It is not rare for particles emitted in the lower mixing layer going through in-cloud scavenging.

Response: Certainly, the in-cloud scavenging was considered in the wet-deposition runs. The wet-deposition module by Grythe et al. (2017) delivered the share of below- and in-cloud scavenging in the model output. In-cloud scavenging simply did not occur in this study, even if we set the in-cloud scavenging parameters to maximum (Cloud Condensation Nucleus effectiveness = Ice Nucleus effectiveness = 1.0). We agree that the sentence 'Since anthropogenic biomass burning aerosol is emitted into the lower mixing layer, in-cloud scavenging is not likely' is misleading at this stage of the manuscript. Therefore, we've removed it in the revised manuscript. Instead, we've changed the wet-deposition paragraph, now to read:

'Further, the existent simulations show that wet deposition removed minimal amounts of the emissions. This might be explained by a short exposure of aerosol to weak precipitation of less than 5mm in 6h in the investigated periods. Moreover, there were no in-cloud-scavenging events for the investigated periods. Possible explanations are absence of fog or spreading of emissions in layers lower than the cloud bottom layer height. Similarly to the low impact on concentration, wet deposition had no significant influence on the isotopic composition of the sampled aerosol either.' (lines 227-231)

Line 204: " The simulations thus show that the major part of the sampled aerosol originates from local sources being emitted during the sampling day and the day before."
Is this a common way to define local? In figure 2, the two-day-old region are pretty far away from the measurement site.

Response: We agree. The actual goal of the study was to distinguish between local/regional and far-away sources. Therefore, we've replaced 'local' to 'local to regional' for the results throughout the manuscript. We've also changed the title from

'**Firewood residential heating – local versus regional influence on the aerosol burden**' to
'**Firewood residential heating – local versus remote influence on the aerosol burden**'

Editorial Comments:
Line 258: Please add figure number
Response: done (262)
Line 264: Please add figure number
Response: done (267)
Line 268: "rations". Typo
Response: done (300)
Line 353: "we" Why bold?
Response: no reason; changed (368)
Figure 7: The legends and the markers don't match.
Response: done

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-1133, 2020.