Authors' comments to reviews of the ACP MS No.: egusphere-2023-728

Sources and Long-term Variability of Carbon Monoxide at Mount Kenya and in Nairobi

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Overview

We thank the two Reviewers and the Editor for their in-depth assessment of our manuscript and overall supportive comments and constructive suggestions, which have helped to further improve the manuscript.

All issues raised by the Reviewers are addressed below, organized such that first the reviewer/editor comments are given in *italic*, directly followed by our response in blue color, and resulting edit in the revised manuscript are given in **bold green**. References in our responses to page and line numbers in the manuscript refer to the revised version.

Responses to Anonymous Referee #1 comments (RC1)

Overall assessment: this manuscript describes in situ- carbon monoxide measurements conducted at the Mount Kenya GAW station (first measurements in 1996), as well as in Nairobi. The manuscript determines the sources of the observed carbon monoxide by employing an isotope analysis for C13 and O18. Given the massive sources of incomplete combustion in sub-Saharan Africa (namely, biomass burning and savannah fires), this manuscript is an important addition to the observational evidence of the combustion products. Therefore, the manuscript is well suited for publication in Egusphere, given that the following major revisions (several suggestions/comments) are addressed.

We appreciate the overall supportive and thoughtful comments; detailed responses provided below

General comments: All in all, I think a little bit more could have been done with the large data set available in the study. While the title mentions both Sources and Long-term Variability of carbon monoxide, the shown results are more focused on source attribution. I feel that some of the long-term variability (such as Figure S1) could have been presented in the main article, instead of the supplementary. The authors could also consider tabulating some of these data, for the sake of quantitative, not only qualitative discussion.

We agree with this assessment and suggestion. While the primary objective of the manuscript is on source attribution of CO, we agree that a deeper assessment of the long-term CO data would strengthen the manuscript. However, such an assessment of CO concentration, seasonality and diurnal trends for an overlapping period, 2002-2006, has already in part been extensively evaluated and discussed in a cited paper by our co-authors (Henne et al., 2008). Nevertheless, we have now returned to the total long-term dataset and explored statistical time series analysis. This new part is now included in the revised ms along with an expanded discussion of the long-term trends -also pasted in here:

Abstract: 'While multi-year data gaps and differences in instrumentation complicate decadal-scale trend analysis, a small long-term increase is resolved.'

Chapter 3.1, Lines 169 – 181: 'Assessment of the long-term CO trend, following the approach by Thoning and Tans (1989), reveal a small but statistically significant positive decadal trend of 6.7 ± 0.4 ppb/10yrs. This statistical model is based on a fit function that includes a linear term, a quadratic term, as well as first and second harmonics. For comparison, simple linear regression gives a similar decadal rate of 6.2 ± 0.6 ppb/10yrs (for uncertainty estimation, see Kirago et al., 2022a). Like many types of environmental data, the present CO data display a lognormal-like concentration distribution, suggesting influence by exponential processes such as sink kinetics

(Andersson, 2021). This may influence trend analysis. Similarly to linear regression, regression of log-transformed data also gives a significant positive rate, which suggests that the skewed concentration profile has little influence on trend estimation. However, given the large data gaps and different measurement techniques, such interpretations should not be over-emphasized. Nevertheless, the observed increasing trend is qualitatively consistent with satellite retrievals and model estimates for sub-Saharan Africa (Buchholz et al., 2021; Hedelius et al., 2021; Zheng et al., 2019).''

Chapter 3.1, Lines 185-188: "The daytime and nighttime ambient flask CO concentrations were comparable, similar to observation from Picarro-measured CO measurements though with a slight daytime elevation (SI Figure S1). During the nighttime, the station stands above the atmospheric boundary layer, hence reduced influence from local sources."

Conclusions, Lines 274-277: "Although the data gaps in CO mixing ratios and mixed instrumentation complicates detailed analysis, a small decadal increase of 6.7 ± 0.4 ppb/10yrs was resolved for the Mt. Kenya GAW station, in agreement with satellite observations and emission inventories for the Sub-Saharan region (Buchholz et al., 2021; Hedelius et al., 2021; Zheng et al., 2019)."

We certainly agree that SI Figure S1 is a key figure, and have therefore followed the reviewer recommendation and **moved it to the main MS Figure 1**.

The isotope and flask-based CO concentration data are tabulated (SI Tables S1-S4) and the online measurement and NOAA flask-based concentration data are freely available on the WDCGG database (https://gaw.kishou.go.jp/), and also in the Bolin Centre Database (bolin.su.se/data/).

Similarly, while Nairobi has been mentioned in the title, only the source attribution of carbon monoxide has been presented in the manuscript. I feel it would strengthen the manuscript to at least present the concentration levels in the main text (some visualization would also be nice); as at the moment this is only discoverable in Table S1. Putting the general concentration levels (both Mt. Kenya and Nairobi) in some context (i.e. against some references) would have been valuable.

We agree also with this point. We now include a short discussion on CO concentration in Nairobi, as well as a graphical presentation of the data in SI Figure S1 and tabulation in SI Table S2.

Chapter 3.1, Lines 189-194: 'In Nairobi, the CO concentrations during August 2021 range between $200 – 700$ ppb ($\sim 0.2 – 0.8$ mg m^{-3}, assuming average weather conditions), well within the WHO recommended short-term (24-h average) air quality guideline level of 4 mg m^{-3} (WHO,

2021). While CO is not a major direct health concern in Nairobi as well as other urban settings (Chen et al., 2021), it affects the presence of health-detrimental components such as ground-level ozone and secondary aerosols.'

Specific comments:

Chapter 2.2, line 99: "Nine sample pairs" were collected at Nairobi. What does this mean – what are pairs?

All the samples were collected in duplicates. This has been clarified in the revised manuscript.

Chapter 2.2, Line 97: '…each sample was collected in duplicate.'

Chapter 2.4, Sampling of the 1996 campaign: the season or calendar months of the sampling could have been mentioned here.

The sampling was initially conducted at diverse dates between July 1996 and September 1997. The data is now presented in Figure 1 and tabulated in SI Table S4.

Chapter 2.4, Lines 129 and 131: 'High-volume air samples were collected between July and September 1996……… and later incidental samplings in 1997'

Chapter 2.5, long term data: for me it is not clear where the NOAA flask sample data for 2008-2012 are obtained from, as I cannot locate them (at least very easily) at the WDCGG site. The authors should make clear about the availability and traceability of these data. At the same time, it would be good to ensure that data ownership issues are addressed, as I do not find co-authorship or any acknowledgement for NOAA- affiliated persons.

The flask-based CO data and Picarro CO measurement data are contributed by the Swiss co-authors to the NOAA/WDCGG database (https://gaw.kishou.go.jp/search/file/0002-1005-3001-01-02-3001). One is, however, required to sign up to access the data. To promote ease access, all the data used in this manuscript will also be made available in the Bolin Centre Database (bolin.su.se/data/). The retrieval and use of (our) data from the NOAA database has been acknowledged and referenced accordingly.

Chapter 2.5, Lines 155-156: "In addition, flask-based CO data from Mt. Kenya GAW station by NOAA Global Monitoring laboratory and published in the WDCGG database was used in this study (Petron, 2023)."

Additional Information, Lines 303: "Data from this study will be available in the Bolin Centre Database (bolin.su.se/data/)."

Chapter 3.1, lines 168-170. The authors state that the seasonal variation are not pronounced, as the "intra-seasonal peak-to-peak amplitude is larger than the variations between different seasons". While looking at lower Figure 1, this is certainly true, I would still say based on Figure S1, that there is a clear seasonal cycle in the data, with peak average concentrations during Feb-Mar and Jul-Aug. It could be worthwhile to look at this in a bit more detail, for example by making a monthly statistical plot based on all data.

A good observation. We agree that the CO measurements at the Mt. Kenya GAW station reveal an annual cycle, based on monthly averages, characterized by peak concentrations during the dry periods as **shown in the revised Figure 1**, and now highlighted in the revised manuscript.

Chapter 3.1, Lines 169: 'Overall, peak CO mole fractions were observed during the dry periods.'

Chapter 3.1. Both daytime and nighttime measurements were conducted. Were there any differences in concentrations? Same could be observed from the Picarro data. What kind of conclusion could be drawn from the diurnal variability?

This is an interesting question. While the flask data didn't reveal a particular diurnal trend, our assessment of Picarro data for August 2021 reveal a daytime maxima, similar to previous observations by Henne et al. (2008), and attributable to the influence of the atmospheric boundary layer depth as well as local sources. This aspect was extensively discussed in a previous publication by our co-authors and highlighted in the revised manuscript, including in SI Figure S1.

Chapter 3.1, lines 185-186; ' The daytime and nighttime ambient flask CO concentrations were comparable, similar to observation from Picarro-measured CO measurements though with a slight daytime elevation.'

*Chapter 3.2, line 205-206. The authors write:" This implies that the CO dynamics in this system can be described by a two-component mixture; a relatively stable background fraction and a regional source."
I think this reasoning has to be elaborated a little bit more, I am not able to deduct how the authors have concluded about a presence of a stable background fraction, and what this actually means in respect to the source. Surely also background fractions are from some kind of source?*

The basic assumption of the Keeling approach is that there are two states that affect the variability of the isotope signatures: a stable background signal (well mixed from several sources) and a temporally varying source. Of course reality is more complicated, where both the background signal and the temporally varying components are mixtures of different sources. However, since the observational data fits the Keeling model to a fair extent, it can be agued that it is justified also here to make this very common simplifying argument. We now cite the original reference to Keeling (1958), where the model is outlined in more detail.

Chapter 3.2, lines 221-223: 'This implies that the CO dynamics in this system can be described by a two-component mixture; a relatively stable background fraction and a regional varying source (Dasari et al., 2021; Keeling, 1958).'

Chapter 3.2, lines 243-244. The authors state: "Therefore, the relative source contributions were estimated at 50% from C3 biomass and 50% from C4 and fossil sources at Mt. Kenya." Does this mean that C3= 50% and (C3+fossil) = 50 %? How does this relate to the previous sentence: "near-equal contributions from C3 and C4 biomass in the eastern Africa background atmosphere"?

The model estimates show biomass burning contribute 80-90% of CO emissions, similar to our previous isotope based assessment of BC- an exclusively primary emission product. It is also important to note the largely overlapping primary CO endmembers. While in our assessment we used C3= 50% and (C3+fossil) = 50 %, sensitivity analysis revealed that the Bayesian model simulations were generally insensitive to chosen priors. This is now elaborated more in the revised ms:

Chapter 3.2, lines 262-263: 'Since primary source endmembers largely overlap, the model simulations were generally insen-sitive to chosen priors, as investigated by sensitivity analysis.'

Chapter 3.2 and chapter 4. The Nairobi results are discussed with regards to air quality. The authors could discuss their results in the context of European limit value for CO (8ppm for 8 hour average), with the caveat, that their measurements have been on a shorter time scale. It seems CO is not a direct concern for Nairobi air.

This is an good addition and observation, now highlighted in the revised manuscript.

Chapter 3.1, lines 189-194: ' In Nairobi, the CO concentrations during August 2021 range between 200 – 700 ppb (~ 0.2 – 0.8 mg m^{-3}, assuming average weather conditions), well within the WHO recommended short-term (24-h average) air quality guideline level of 4 mg m^{-3} (WHO, 2021). While CO is not a major direct health concern in Nairobi as well as other urban settings (Chen et al., 2021), it affects the presence of health-detrimental components such as ground-level ozone and secondary aerosols'

Figure 1. Have the authors tried plotting also the 1996/97 data in the upper figure? Taking note that these are not from the exact location, a visual inspection could be interesting, nevertheless.

Great suggestion. We have incorporated the 1996/97 data **into Figure 1.** Overall, the 1996/97 data, collected at a lower altitude compared to Mt. Kenya GAW station, was recorded within the upper range of the reported CO concetrations, likely indicating higher local influence.

Figure 3 and others thereafter: I am not sure where the axis title abbreviations "V-PDB" and "V-SMOW" come from?

The isotopic composition is expressed as per mil (‰) enrichment or depletion of the isotope ratio in the sample relative to that of international standard materials, which in these cases are the Vienna PeeDeeBelemnite (V-PDB) standard for $\delta^{13}C$, and the Vienna Standard Mean Ocean Water (V-SMOW) for $\delta^{18}O$ measurements, **as discussed in section 2.3 (Lines 118-122).** Therefore, we believe that the measurement units and reference standard are a good addition to the scale, which is also common practice.

Table S1. Please make a division between the different campaigns, it is difficult to identify the Nairobi samples from the list.

Thank you for this suggestion. We have separated the three dataset; Mt. Kenya, Nairobi and Mt. Kenya 1996/97 campaign **(SI Tables S1-S3).**

Responses to Anonymous Referee #2 comments (RC2)

This is a clearly written and easy to understand paper showing multi year measurements of CO and its isotopes from Mount Kenya with some contrasting measurements from Nairobi also shown. The introduction is comprehensive and clear, and the methods (as far as measuring CO and it's isotopes) are also clear with details not covered referred to previous papers. The Results and Discussion section presents a nice discussion of the isotopic analyses but the ambient CO observation discussion is less clear with details put into the Supplementary section that to me seem like they belong in the main text.

Overall this study represents an important contribution in an undersampled region of the world and I reccomend that the paper is published after some revisions which I consider minor as the required extra analysis and text is not onerous or particularly time consuming.

We thank Referee #2 for the overall positive assessment of our work, and suggestions for improvements. All comments and suggestions have been considered, and especially the discussions on the ambient CO observations expanded.

Comments on this section:

- *Page 6 – "the seasonal variations are not pronounced" – This is actually hard to judge from what you present/ Why not show a combined seasonal average? Eyeballing the S1 figure upper panel I get a strong impression that there is a fairly consistent low in CO mole fraction around May with peaks around March and August. Sure there's some variability in timing but this looks like a seasonal variation not just random to me. In fact, this bimodal peak feature is explained by the back-trajectories in Figure 2 and explained by in the last paragraph of section 3.1 – with biomass burning from different areas bought by the changing meteorology in different seasons.*

We agree also that the CO measurements at the Mt. Kenya GAW station reveal an annual cycle, based on monthly averages, characterized by peak concentrations during the dry periods as shown in the **revised Figure 1**, and highlighted in the revised manuscript.

Chapter 3.1, Line 169 'Overall, peak CO mole fractions were observed during the dry periods.'

- *However these backtrajectories are presented without any explanation of the timeframe that they represent in either the text or the figure caption.*

Well noted. We have included the timeframe, December 2020 – November 2021, in the revised manuscript (**Figure 2**).

- *"no clear multi-year trend..". No details are given are what trend analysis was undertaken and on what data. Did you use daily mean values? All data or median values. What sort of trend analysis was done? A value of approximately zero is stated but with no uncertainty estimate given.*

Thank you for highlighting this omission on our part. Initially, our assessment of the long-term trend was based on simple linear regression. Further assessment following an approach by Thoning and Tans, (1989) reveal a small, but statistically significant, overall decadal positive trend of 6.7 ± 0.4 ppb/10yrs (SI Figure S). Here, a fit function that includes a linear term, a quadratic term as well first and second harmonics was applied on the the daily aggregated CO data for 2002 – 2021. However, we acknowledge that the data gaps and different measurement techniques for the different periods of data availability. We have provided more details in the revised manuscript.

Abstract: 'While multi-year data gaps and differences in instrumentation complicate decadal-scale trend analysis, a small long-term increase is resolved.'

Chapter 3.1, Lines 169-181: 'Assessment of the long-term CO trend, following the approach by Thoning and Tans (1989), reveal a small but statistically significant positive decadal trend of 6.7 ± 0.4 ppb/10yrs. This statistical model is based on a fit function that includes a linear term, a quadratic term, as well as first and second harmonics. For comparison, simple linear regression gives a similar decadal rate of 6.2 ± 0.6 ppb/10yrs (for uncertainty estimation, see Kirago et al., 2022a). Like many types of environmental data, the present CO data display a lognormal-like concentration distribution, suggesting influence by exponential processes such as sink kinetics (Andersson, 2021). This may influence trend analysis. Similarly to linear regression, regression of log-transformed data also gives a significant positive rate, which suggests that the skewed concentration profile has little influence on trend estimation. However, given the large data gaps and different measurement techniques, such interpretations should not be over-emphasized. Nevertheless, the observed increasing trend is qualitatively consistent with satellite retrievals and model estimates for sub-Saharan Africa (Buchholz et al., 2021; Hedelius et al., 2021; Zheng et al., 2019).''

Conclusions, Lines 274-276: "Although the data gaps in CO mixing ratios and mixed instrumentation complicates detailed analysis, a small decadal increase of 6.7 ± 0.4 ppb/10yrs was resolved for the Mt. Kenya GAW station, in agreement with satellite observations and emission

inventories for the Sub-Saharan region (Buchholz et al., 2021; Hedelius et al., 2021; Zheng et al., 2019)."

Page 7: "The stable isotope composition of CO ....varied temporally and inversely with CO". This is stated but not shown (perhaps point to Keeling plots as evidence?). What was the correlation factor – with CO ambient mole fractions?

The stable isotope composition of CO varied inversely to 1/CO (Keeling relation), that is, proportional to CO mole fractions (for example at Mt. Kenya, R^2 =0.67 for $\delta^{18}O$ and R^2= 0.39 for $\delta^{13}C$). This typo has been rectified. In addition, the temporal variation of CO concentrations and isotope composition in Nairobi and at Mt. Kenya is presented in **SI Figure S2**.

Chapter 3.2, lines 211-212: 'The stable isotope composition of CO ($\delta^{13}C$ and $\delta^{18}O$) for ambient samples from Mt. Kenya GAW station during August 2021 varied temporally with the CO mole fractions (SI Figure S2).'

- *Although Keeling plots are now text book stuff – I think a reference would be appropriate? Perhaps in sentence stating that the linear relation implies two-component mixture?*

Thank you for pointing out this. We have included two references describing and applying this approach, including the original reference, (Keeling, 1958)

Chapter 3.2, lines 221-223: 'This implies that the CO dynamics in this system can be described by a two-component mixture; a relatively stable background fraction and a regional varying source (Dasari et al., 2021; Keeling, 1958).'

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