

Response to Referees – cp-2019-94

We are extremely thankful to Murat Aydin for the time he dedicated to a second round of review, and his constructive comments on the article. We listed below our responses to the major and minor specific comments. The comments of the referee are in black, and our corresponding responses are below in blue. All the section and figure numbering included in our response to reviewers refers to the updated manuscript and SI.

Xavier Faïn on behalf of all co-authors

REVIEW FROM MURAT AYDIN

One of my general comments was about the possibility of firn processes having something to do with the production of CO spikes. I gather from their responses that the authors disagree and see this as a process happening within the ice matrix after bubble closure. It may be a good idea to include a sentence to this effect to orient the reader.

Petrenko et al. (2013) have investigated the occurrence of in situ CO production in the firn air at three Greenland sites. They cannot fully exclude such in situ production, and we already report in the manuscript that “a small contribution from in situ CO production (up to 5 ppbv) within the firn itself could not be ruled out (Petrenko et al., 2013)” (Sect 3.5.2). In our study, we did not identify any reasons that contradict this conclusion from Petrenko et al. (2013). This does mean that in situ production is a process happening in the ice matrix after bubble closure. To clarify the manuscript, we have modified Sect 3.5.2 and the conclusion to mention this.

I understand the statement about not having any direct evidence for CO production happening in the firn. However, some of the observations reported here are very difficult to explain solely with production after bubble closure. Specifically, there is no straightforward interpretation of the CO vs. the corresponding TOC data. New figures show seasonality in TOC and CO in the PLACE ice core, but the TOC in summer and winter layers appears to be within 10-20% of the mean levels and the lack of overall correlation between TOC and CO is puzzling.

The “summer” and “winter” TOC data reported on Fig. S26 are indeed within 20% of the mean levels, but we have defined summer (resp. winter) as April-September (resp. October-March). The TOC values extracted over these periods lasting 6 months are lower (resp. higher) than summer maximum (resp. winter minimum). However, extracting data at higher resolution was not possible considering the accuracy of the depth scale.

Note: the Fig. S26 has been slightly modified as we found an error in the plot.

Thinking purely from this perspective, I don't see why there would be no in situ production in the winter layers, for example.

We agree that in situ production in winter layers cannot be fully excluded, this is why we recommend to interpret our multisite CO reconstruction as an upper bound of past atmospheric CO abundance in the Arctic atmosphere.

Finally, we have additional reasons to consider that in situ CO production can occur in winter layer at the Tunu13 site (because of remobilization of TOC from summer to winter layers). Such reasons partially explain why we have not considered Tunu13 in the multisite composite.

I agree with the need to better understand the fate of TOC in the firn and snow, but does this not imply that firn processes could have a role in the production of CO?

Yes, we identify one specific firn process that can have a role in the production of CO at sites of low accumulation: TOC remobilization from summer layers to winter layers (Sect. 3.3.2). For this reason, we have conservatively excluded Tunu13 from the multisite composite.

The discussions regarding the fate of TOC and the relationship with NH₄⁺ are snow/firn processes that the readers will struggle to connect to CO production in the ice after bubble closure. Perhaps, there is more that can be said to help make this connection?

In the summary section 3.3.3, we do say that “we cannot rule out that a redistribution of organic carbon along depth driven by OC post-deposition process (shifting the ammonium-formate equilibrium with the gas phase) impacts specifically the Tunu13 CO record by providing some additional organic substrates in winter layer”. With this sentence, we explain why the fate of TOC, revealed by the TOC-NH₄⁺ relationship, can impact CO production. We have modified Section 3.3.2 to better explain this point.

In my opinion, the strongest argument for accepting the composite 5th percentile of measurements as a likely atmospheric record is the agreement between different ice core measurements and firn records. The paper should emphasize this angle in the abstract and in the conclusions.

We have modified the abstract and conclusion accordingly.

The authors chose not to include the Tunu record in the final composite history. My whole point in arguing for its inclusion was that this would not significantly alter the final composite record. The conceptual model included in the supplement (Fig. S12) is pretty helpful in demonstrating how the analytical smoothing impacts the measurements, but the average increase in CO is always less than 10 ppb and 3-4 ppb on average. The figures they included in the review also show that the composite record looks pretty much the same with or without inclusion of the Tunu record. In the end, I don't really mind leaving out the Tunu record. If they believe there is potential for recovering a long term record at Tunu, it can be pointed out somewhere that artifacts due to analytical smoothing do not seem to drive the type of large long term trends apparent in the composite record and show Fig. R4 in the supplement. We did not fully understand the point that the reviewer made in the last sentence of the previous paragraph, and thus we were not able to address it (what is Fig. R4?). Overall, the revised manuscript does not include any comments on the potential of the Tunu13 site for recovering a long term record. Such recovery would require improved analytical capability (i.e., a better resolution), and seems speculative at this point. However, the full Tunu13 CO record is provided (Fig. 17), and future studies will be able to start new investigation using this dataset.

Line by line comments/suggestions:

L13-15: This sentence gives the impression that the co-examination of CO and TOC records shows there is no CO production in winter layers. The strongest evidence for winter layers containing largely an

atmospheric signal, hence the path towards recovering an atmospheric record from 5th percentile baselines, comes from the agreement between different ice core records in my opinion. I cannot readily infer from this that TOC in the winter layers does not produce CO in the ice while it does in summer layers because no possible explanation is provided for why it should not.

We agree with the reviewer and have modified the abstract. We kept the statement that, in our study, higher accumulation eases the extraction of atmospheric history from continuous CO signal. We added that the agreement in CO baseline between different Greenland sites supports that winter layers do contain an atmospheric relevant information. The good overlap between the multisite ice core reconstruction and the firn air CO history was already reported in the abstract.

Note: we have removed the wording “conducted at Summit” in sect. 3.4, as the Greenland firn air reconstruction is based on 3 sites (as discussed in sect 3.5.2).

L85: “Burden” is commonly used to mean the total mass/moles of a gas in the atmosphere. Better to use mixing ratio, abundance, or levels instead.

“Burden” has been replaced by “levels” or “abundance” in different sections of the manuscript, including line 85.

L129: Rephrase “extracted along the sample line...”

We rephrased as follow: “the gas is recovered from the sample line...”

L291: Ice core trends are not strictly “monotonic” even after 1875, especially for some of the cores; might be better to say “steady.”

We are now using “steady” instead of “monotonic”.

L297: S17 instead of S15.

The manuscript has been corrected.

L324: Consider replacing “never expose directly freshly drilled cores to sunlight” with “never expose freshly drilled cores to direct sunlight.”

The manuscript has been corrected accordingly.

Lines 345-365, section 3.2.4: This 6 ppb appears to be a system blank. Is it subtracted from the discrete measurements? I could not see this info anywhere. It can probably be added to the caption of Fig. 3.

These 6 ppbv could indeed be considered as a system blank for the discrete CO analyses discussed in Sect. 3.2.4. However, in this section we investigate if in extractu CO production could occur during the melting process. Thus, the data were not corrected for blank as our goal was to observe is such blank would be increasing with time.

On the other hand, the CO data collected with the discrete method and used for a comparison with CFA dataset had to be corrected for the system blank. This is now clearly stated in the SI (Sect. SI 1.8.4), as follow : “Blank corrections were applied by subtracting the average of four gas free ice runs (CO mole fraction = 9.0 ± 2.1 ppbv) that were run concurrently with the five PLACE core samples. The CO mole

fraction measurement uncertainty for the five PLACE cores samples was defined as the CO mole fraction variability of the gas free ice measurements.”

Line 426-427: The hypothesis here is not easy to understand. Do you mean only a fraction of TOC converts to CO and the excess above a certain threshold does not result in more CO production?

Lines 426-427 read: “The larger analytical smoothing impacting the Tunu13 CO record means that some of the CO baseline signal likely incorporates in situ produced CO from spring/summer ice layers”. We are not sure how this statement relate to the comment from the reviewer.

Line 450: Incorporating instead of “incorporates.”

The manuscript has been corrected accordingly.

Line 453: No need for “however.”

The manuscript has been corrected accordingly.

Line 467-468: I think you should put the baseline back in the figure otherwise it is hard to see this. You can show a version with a mean in the supplement.

The CFA PLACE baseline is difficult to be included in Fig. 6. On one side this would allow a comparison with the historical Eurocore data from Haan et al. (1998). On the other hand this would be confusing as such baseline can not be compared directly to discrete PLACE record (which should be compared to the mean CFA signal). This issue was discussed in the first round of review.

To address the comment raised by the reviewer, we have added the specific figure shown below in the SI which plots only CFA PLACE and historical Eurocore CO dataset. This new figure is now referred in Sect.

3.4.

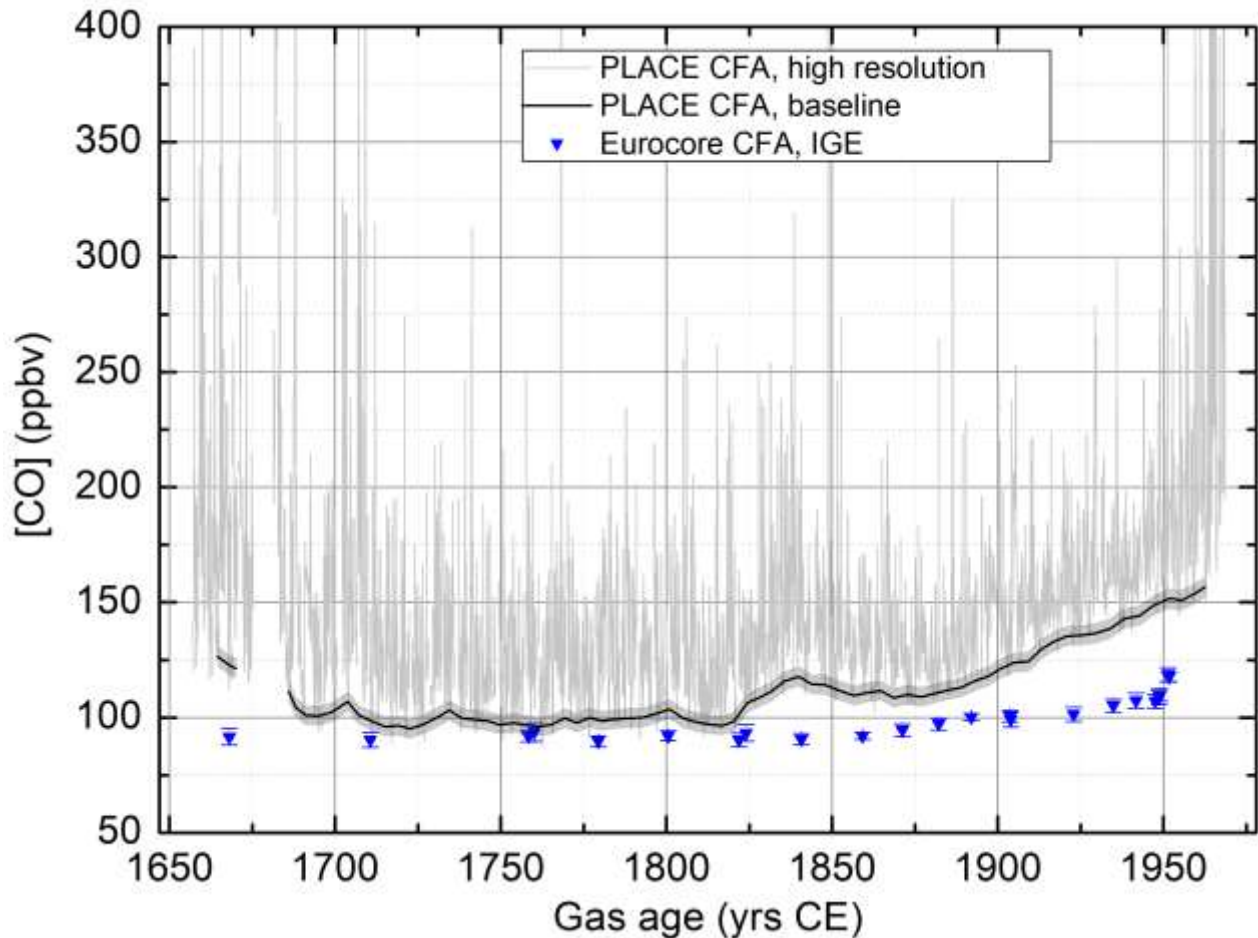


Figure S23. Continuous CO mixing ratio collected along the Place ice core (grey line) with 5th percentile baseline (black line and envelop), and historical Eurocore discrete CO data (blue dot, Haan et al 1998).

Section 3.5.1: There is too much emphasis on Fig. 1, which has already been discussed. It would be better to point out the trends in Fig. 7, which is done in the conclusions but seems out of place there.

We are now emphasizing better Fig. 7 in section 3.5.1 with the sentence “Overall, Fig. 7 reports a ~30% increase in CO concentration at high latitudes of the northern hemisphere”, which was previously referring to Fig. 1. We kept the first paragraph of Sect 3.5.1 discussing Fig. 1 as it is important to discuss the agreement between different ice core measurements and firm records (see general comments from the reviewer).