

## **Interactive comment on “The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950, implications for the CO budget” by Z. Wang et al.**

**Wang et al.**

We thank referee #1 for providing very helpful suggestions and comments. Responses to the individual points are made below.

1. While this message seems quite straightforward, some complicated science is behind the firn-analysis. First of all, the seasonal cycle penetrates into the firn layer and the uppermost data points cannot be used for the analysis. In section 4.1 a rather complicated section is devoted to the air diffusion inverse and forward model. In its current form it does not shed much light on the problem at hand. I would suggest to shorten this section and refer to the references. For the isotopic part, I see e.g. a reference to Buizert et al. 2011.

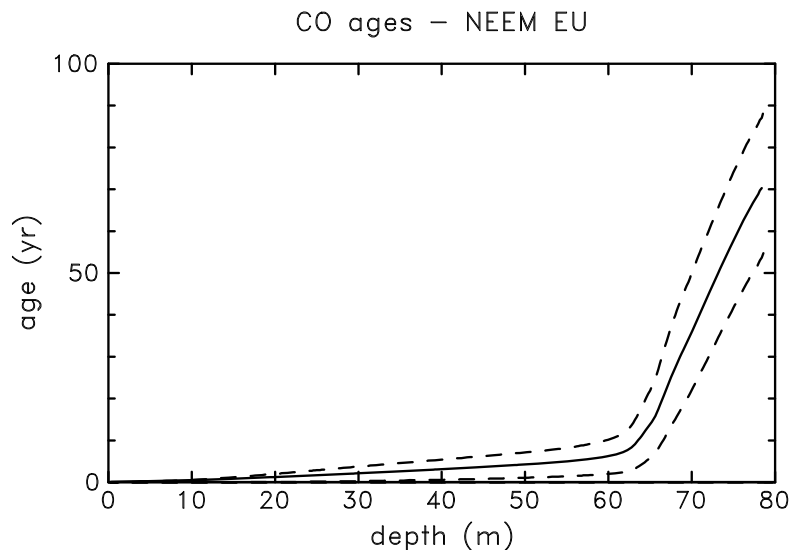
**Answer: We agree with the referee on the fact that atmospheric scenario reconstruction from firn data is complex. The seasonality issue will be discussed below. Concerning section 4.1, its first part (p30634 line 24 to p30635 line 14) dealing with the LGGE-GIPSA models setup in general terms will be shortened and refer more to publications. Its second part dealing with the methodology for isotopic scenario reconstruction has not been published elsewhere. The specific complexity of the problem for CO isotopes is related to two issues.**

**First the firn records are non-monotonous. As firn is a diffusive medium, it smooths peak-shaped signals and reconstructing the atmospheric signal requires somewhat complex methods such as those described in previous studies (Rommelaere et al., 1997;Fain et al., 2009). Second reconstructing atmospheric histories of isotopic delta values requires to simulate the behavior of both the major and minor isotope (and small variations of their ratio). Here the Rommelaere et al., 1997 method which is well adapted to non-monotonous signals is extended to isotopic ratios using principles similar to those applied in other studies (Trudinger et al., 1997;Francey et al., 1999). This will be clarified in the revised manuscript.**

2. In section 4.2 it is argued that the inverse model does not work with seasonal cycles. Although not totally clear to me, figure 2 presents the effect of seasonal cycles in the firn. I suggest to add for clarity the assumed seasonality in the atmosphere as a reference. Also the caption of this figure is hard to read. What is a "constant atmospheric trend", for instance? In the end, it is not totally clear how the barely visible green stars show the isotopic values corrected from (?) the effect of seasonality. This deserves better explanation.

**Answer: Molecular diffusion is very fast in the upper firn : above the “lock in depth”, located at 63m depth at NEEM (Buizert et al., 2011) and slows down rapidly below that depth. For example, the mean CO age is 0.5 year at 10 meters depth (first sample below surface), 1.2 year at 19.8 m depth (next sample), 7.4 years at 62 m depth and 16.5 years at 65.8 m depth (refer to the CO age-depth plot below). Moreover trace gas age in firn is not unique but undergoes a non symmetric statistical distribution (e.g. Buizert et al., 2011, Fig 6). This has the advantage of well separating**

time scales (medium/deep firn data are little or not affected by seasonality), but has the inconvenience of under sampling-seasonality. Also, the smoothed seasonal cycle in firn does not allow us to infer a 12 month periodicity. Although the reason why the inverse model cannot reconstruct seasonality (regularization term) is technically true, the seasonality issue will be presented in more physical terms in the revised manuscript. Moreover, Trudinger et al. simulated the CH<sub>4</sub> temporal evolution as seen at different depth in Law Dome firn and also found the strong vanishing of the seasonal signal with depth (Trudinger et al., 1997).



**Fig. 1. CO ages in NEEM-EU firn versus depth. Continuous line: mean ages, dashed lines: 15% and 85% accumulated probability ages.**

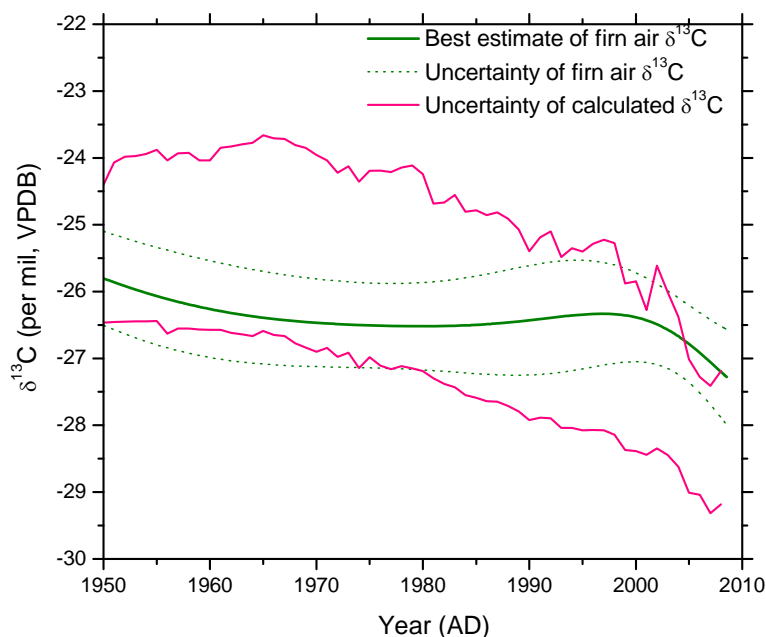
It is still possible to evaluate the impact of seasonality on depth profiles in firn by using the forward firn model. The principle we use for estimating (and correcting for) the effect of seasonality is to compare the concentrations in firn resulting from atmospheric scenarios with/without seasonality. As the recent (de-seasonalized) trend of CO isotopes over Greenland at the time scale of a few years before NEEM firn drilling is not precisely known, we use constant mean annual values for CO and its isotopes. This will be clarified in the revised manuscript. Figure 3 (not Figure 2) presenting the impact of seasonality and its caption will be improved. The assumed mean seasonalities are inferred from atmospheric data in Iceland and will be provided in the revised Supplement.

3. In section 4.3 the authors discuss the best estimated trend in figure 4. They discuss here the depth (40m), which refers, I guess to figure 5. The language of the paper is often difficult to follow, so a thorough rewriting is required, preferably by a native speaker. An example is in paragraph 4.5, "They also undergo the longest age mixing". As a non specialist, you are totally lost!

**Answer: The 40 meters depth threshold mentioned p 30637 line 12 refers to the sampling depth below which the effect of seasonality is insignificant. This will be clarified. We agree with the referee on the fact that the term “age mixing” is confusing. It refers to the fact that trace gas age at a given depth in firn undergoes a statistical age distribution (see above). This will be clarified. As for the writing, we will make an effort to generally improve the clarity of writing in the manuscript.**

4. But my major concern is with the results. The authors often claim a proper validation, while my impression is that the results are not really good. For instance, the  $\delta^{13}\text{C}$  results presented in the appendix show that none of the scenarios matches the observed maximum around 2000. One could argue that the source mix might have changed, but this would involve a very unlikely scenario.

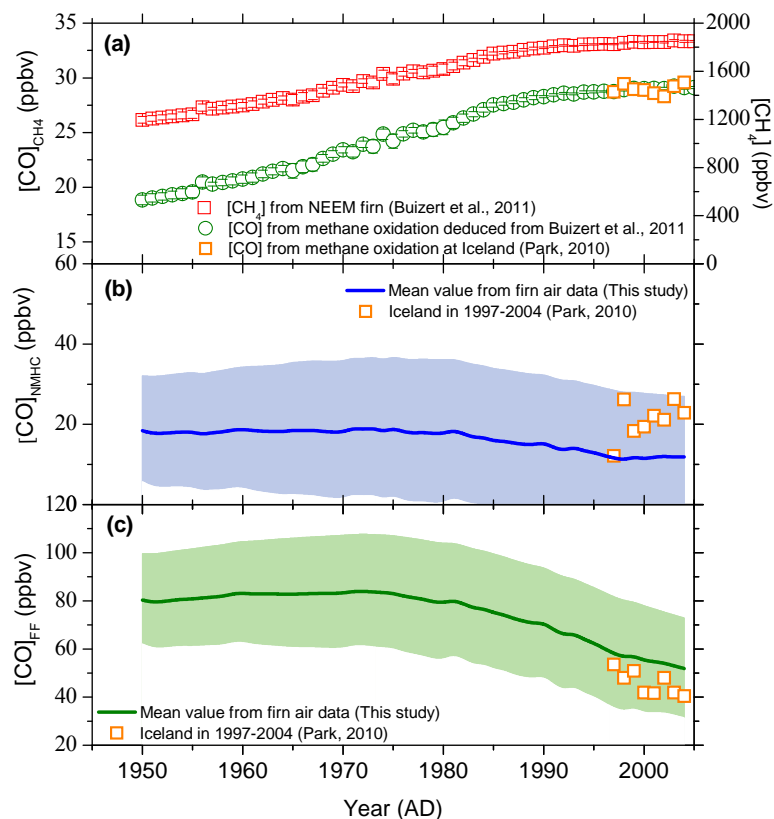
**Answer: This is a good point and it will be clarified in the revised supplement. First, new  $\delta^{13}\text{C}$  results have been calculated based on new CO source contributions (refer to the new figure. 4S below). We show the upper limit and lower limit for possible calculated  $\delta^{13}\text{C}$  trend since 1950. Large uncertainties of calculated  $\delta^{13}\text{C}$  can be observed from the figure. We have more confidence on the observation based firn air  $\delta^{13}\text{C}$  trend (green line) than on the calculated  $\delta^{13}\text{C}$  trend since our mass balance calculation is model based model simulation and just shows some most-likely scenarios based on some assumptions (e.g. steady state assumption and constant OH). We do not expect that the calculated  $\delta^{13}\text{C}$  trend perfectly reproduces the firn air  $\delta^{13}\text{C}$  trend. And many possibilities could cause the maximum of  $\delta^{13}\text{C}$  in around 2000 such as large wildfires or small NMHC oxidation.**



**Fig. 2. Comparison of calculated  $\delta^{13}\text{C}$  from mass balance calculation and the estimated  $\delta^{13}\text{C}$  in NEEM firn air by LGGE-GIPSA models. Green solid line and dotted lines are the same as those in Fig. 4. Pink lines are uncertainties of calculated  $\delta^{13}\text{C}$  derived from all the uncertainties (see text).**

5. Also, the main result in figure 7 is not very convincing. 60 ppbv CO from fossil fuel seems way to high compared to the MOZART-4 model (only 40 ppbv).

**Answer:** The results have been corrected by using *a posteriori* results of Iceland CO contributions instead of the *a priori* results (refer to the new figure for CO source partitioning below) (Park, 2010). After the correction, the calculated CO contribution from fossil fuel is between 35 ppbv to 78 ppbv in 1997-2004 (with mean CO concentration of around 56 ppbv). The *a posteriori* results of CO contribution from fossil fuel combustion based on MOZART-4 and an inverse modeling are ranging from 40 ppbv to 54 ppbv in 1997-2004, which falls within the uncertainty envelopes of the calculated CO contribution from fossil fuel. More importantly, the decreasing trend of the MOZART-4 and inverse model simulated  $[CO]_{ff}$  is consistent with that of our mass balance modeled  $[CO]_{ff}$ .



**Fig. 3. Modeled CO source partitioning based on observations and isotope mass balance model.**

6. Also the employed biomass burning scenario is way higher than GFED-3, although the resulting contribution (roughly 10 ppbv) seems reasonable.

**Answer:** Yes, the reviewer is right. The biomass burning inventory used in MOZART-4 simulation is GFED-V2. And we have already considered  $\pm 50\%$  uncertainty in our calculation, in which our employed biomass burning emissions (Ito and Penner, 2005) fall. And because both we and Ito and

**Penner 2005 used scaling method to obtain historical results, the different biomass burning emission employed did not change the resulting CO contribution significantly. Moreover, there are large discrepancies of biomass burning emissions between different inventories (Granier et al., 2011).**

7. All in all, the authors did not convince me that the final scenario really is the true story. There are to many open ends (e.g. 13C) and the modeling seems not very accurate.

**Answer: As mentioned above, after the *a posteriori* CO source contributions are used in the isotope mass balance model, the [CO]ff results seem more reasonable and the decreasing trend of the MOZART-4 and inverse model simulated [CO]ff is consistent with that of our mass balance modeled [CO]ff (refer to new figure of CO source partitioning above). It should be pointed out that there could be substantial uncertainties of our calculated  $\delta^{13}\text{C}$ . For example, even the uncertainties shown in CO source partitioning figure for the [CO]ff history allow for a scenario with constant [CO]ff through time. And there are further uncertainties that, we did not include the possible variations in OH. We have more confidence on the observation derived firn air  $\delta^{13}\text{C}$  trend (green line) than on the calculated  $\delta^{13}\text{C}$  trend since our mass balance calculation. While we are limited as far as making a 100% rock-solid statement regarding [CO]ff history, we are still able to present a most-likely scenario based on the data, which is still very valuable. This will be clarified in the revised manuscript.**

Minor points

- Figure 1 does not add anything and can be removed

**Answer: Figure 1 has been removed.**

- Table 1 misses the unit for CO

**Answer: Unit of CO has been added.**

- Page 30643: CO removal by OH has been constant over the past 50 years. This is inaccurately phrased: OH is assumed constant I guess. CO removal scales with the CO concentration, which was clearly not constant.

**Answer: This has been corrected.**

- Section 5 is named discussion, while it contains results

**Answer: The name of this section has been changed to “Isotope mass balance model and discussion”.**

- Figure 9: please indicate that the symbols refer to Pb, I guess

**Answer: This has been corrected.**

## **Interactive comment on “The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950, implications for the CO budget” by Z. Wang et al.**

**Wang et al.**

We thank referee #2 for providing very helpful suggestions and comments. Responses to the individual points are made below.

1. Authors reconstruct the fossil fuel and NMHC oxidation source history. Bottom-up inventories of both of these sources have large uncertainties so using a top-down constraint is needed. Inventories of CO emissions from biomass burning also have large uncertainties- thus there are three potential sources the authors could constrain. The limitations of the data mean only two can be solved for. Authors should motivate why they chose to solve for fossil fuels instead of biomass burning. Presumably this is because the authors believe the biomass burning is better known? If so, authors need to argue this.

**Answer: This is a very good point and we will emphasize this point in the revised manuscript. We chose to solve for fossil fuel instead of biomass burning because of the predominant impact of fossil fuel combustion source on CO isotopic ratio ( $\delta^{18}\text{O}$ ) in high northern latitudes. Model simulations show that fossil fuel combustion and biomass burning account for 34% and 10% of the total CO emission, respectively (Table 1). And fossil fuel combustion is the most enriched source for  $^{18}\text{O}$  (Table 1), which indicate fossil fuel combustion has a much larger impact on  $\delta^{18}\text{O}$  of CO. Even the fossil fuel emission is better known than biomass burning, the uncertainty of it could have much larger impact on our calculation. Therefore we chose to solve for fossil fuel instead of biomass burning.**

2. How sensitive is the trend of derived fossil fuel [CO](Fig 7c) to trends in biomass burning emissions? Since our knowledge of biomass burning trends is poor is it possible that the [CO]ff trend could become statistically insignificant with a reasonable biomass burning trend? Sensitivity tests could be performed to test this.

**Answer: The reviewer is right. The trend of biomass burning emissions could affect the fossil fuel [CO] trend but not significantly. Model simulations show that biomass burning only accounts for 10% of the total CO emissions in high northern latitudes in modern atmosphere. More importantly, its  $\delta^{18}\text{O}$  value in high northern latitudes (9‰) is very close the  $\delta^{18}\text{O}$  of our observations (7-10‰). This indicates the impact of biomass burning on [CO]ff is very small. And our calculated [CO]ff is consistent with the well known emission control policy. We believe the impact of biomass burning trend on [CO]ff is not significant. This will be clarified in the revised manuscript.**

3. Other authors have postulated that CO emissions from fossil fuel burning should have decreased when catalytic converters started to become popular but I see no mention of this literature in the paper. Authors should provide appropriate background and references.

**Answer: The references about catalytic converters (Santra and Goodman, 2002; Parrish, 2006) have been added.**

4. In addition to providing the modeled [CO] partitioning for CO sources (Fig 7) it would be useful if the authors could provide CO fossil fuel emissions consistent with the [CO]<sub>ff</sub> record. The authors' fossil fuel [CO] is about double that of [CO] derived from CO measurements and MOZART simulations (Fig 7c). This is a large difference. What is the authors' explanation as this lies outside the uncertainty envelope?

**Answer: The results have been corrected by the new method, using *a posteriori* results of Iceland CO contributions instead of the *a priori* results (Park, 2010). After the correction, the calculated CO contribution from fossil fuel is between 35 ppbv to 78 ppbv in 1997-2004 (with mean CO concentration of around 56 ppbv). The *a posteriori* results of CO contribution from fossil fuel combustion based on MOZART-4 and an inverse modeling are ranging from 40 ppbv to 54 ppbv in 1997-2004, which falls within the uncertainty envelopes of the calculated CO contribution from fossil fuel (refer to the new figure for CO source partitioning shown in the answer to referee #1). And the decreasing trend of the MOZART-4 and inverse model simulated [CO]<sub>ff</sub> is consistent with that of our mass balance modeled [CO]<sub>ff</sub>.**

5. p30635, line 15 – Regarding the inversion, how do authors define “simplest solution”? For example, continuous first and second derivatives of the temporal trend?

**Answer: The regularization term used limits the “roughness” of the scenario (Rommelaere et al., 1997; Menke, 1989). It bounds the values of the scenario's second derivative and thus the speed of variation of the scenario. This will be mentioned in the revised manuscript.**

6. p30636, line 18 – Presumably the reconstruction can capture seasonality but not seasonality with large amplitudes ?

**Answer: Mathematically, the problem is related to time scales rather than amplitude. The regularization term used to ensure the uniqueness of the solution in the inverse scenario model acts as a low-pass frequency filter. Our major aim is to infer a long term (multi decadal) time scale scenario. Due to the limited number of available firn data points to constrain the scenario (15 or 16 depth levels), it can be grasped intuitively that the time resolution of the reconstructed scenario is low. On the other hand, the age of CO (and its isotopes) in firn does not increase regularly with depth (see answer to Referee #1 on the seasonality issue). A somewhat higher time resolution is available from upper firn data. However, due to fast mixing by molecular diffusion, only one (strongly smoothed) “cycle” due to seasonality is visible in firn. This is insufficient to infer the 12 month periodicity from firn air data. This seasonality reconstruction issue will be presented in a more physical way in the revised manuscript.**

7. p 30640, line 2- Explain why source signatures are different at different latitudes. Because of differences in d18O of O<sub>2</sub>? Or do these reflect the fractionation of CO after undergoing some oxidation by OH during transport?

**Answer: Yes, the source signatures reflect the fractionation of CO after undergoing oxidation by OH during the transport (Wang et al., 2010).**

8. p 30640, line 28 – Authors state that both source d18O signatures and [CO] were calculated with MOZART, but presumably d18O source signatures are determined from measured literature values.

**Answer: Source signatures are taken from previous studies, but  $\delta^{18}\text{O}$  at the high northern latitude is calculated by the MOZART-4 with considering the oxidation by OH during transport.**

9. p30645, line 18 – Authors remark that studies by Larmarque et al. 2010 and van Aardenne et al. 2001 indicate that CO emissions from fossil fuel have increased through 1990 but authors work suggests the opposite. Authors should attempt to provide explanation. For example do these studies use constant CO emissions factors for fossil fuel burning? If so, they are not taking into account the use of catalytic converters which is an important difference.

**Answer: We realize the last paragraph of our manuscript provides inaccurate information and could cause confusion and this paragraph is not really necessary for our manuscript. So we will remove the whole paragraph in the revised manuscript.**

10. p30641, line 24 – Is this a gridded inventory? Specify spatial resolution. Have authors tested to see how sensitive their results are (i.e. [CO]<sub>ff</sub> trends to changes in the distribution of biomass burning emissions?

**Answer: Yes, it is a gridded inventory. It is based on the  $1^\circ \times 1^\circ$  spatial resolution for year 2000 and all other years are calculated by scaling factors (Ito and Penner, 2005). We use this published data to scale the CO from biomass/biofuel burning. The change of distribution of biomass burning emissions is beyond the scope of this paper.**

11. p30641, line 26 – Not clear how or why the modeled biomass burning at Iceland is scaled. Why not just use the biomass burning contribution to [CO] directly at the Greenland site? And why just for 1997-2004? Is that time of atmospheric measurements at Iceland? If so, how are measurements used to tease out the biomass burning contribution?

**Answer: These are good points and we will clarify them in the revised manuscript. For example, for year 2000, the biomass burning emission of CO in year 2000 is  $x \text{ Tg CO/yr}$  and [CO]<sub>bb</sub> in year 2000 is  $y \text{ ppbv}$ . The [CO]<sub>bb</sub> in one specific year with biomass burning emission of  $z \text{ Tg CO/yr}$  can be calculated as:  $[\text{CO}]_{\text{bb}} = x \cdot z / y \text{ ppbv}$ . We do this because we need to subtract the biomass burning contribution from the total CO to calculate the [CO]<sub>ff</sub>.**

**We do not find biomass burning contribution at Greenland is different from that at Iceland. But to compare firm model results with our observations at Iceland, we chose to use biomass burning contribution at Iceland.**

**We choose 1997-2004 because the available isotopic ratio measurement data are between 1997 and 2004. The biomass burning CO is first tagged in forward model (*a priori*) (the tracer version of MOZART-4, see Park, 2010). Then the isotopic ratio measurements are used to optimize the source contribution (*a posteriori*) in the inverse model (Park, 2010).**

12. p30643, line 12 – Since the  $\text{d}18\text{O}$  data is used to determine the fossil fuel combustion, not vice versa, the causal relation in this sentence is inverted.



**Answer: This sentence has been changed to “It clearly suggests a dominant control from fossil fuel combustion variation at high northern latitude since 1950 on the CO trend in Fig. 3.”**

13. p30643, line 17 – Not too much needs to be said, but would be good to put this finding – no change in NMHC oxidation – into some context. Is it consistent with the literature?

**Answer: Yes, we have pointed out the finding “We also find that no significant change in NMHC oxidation has occurred since 1950.” in the context. Unfortunately there has no study on the past CO from NHMC oxidation so no comparison is possible.**

14. p 30643, line 24-26 – To my eye from the graph (Fig 4) it appears that d18O is actually increasing (more enriched) from 1950 to the mid-1970s.

**Answer: No,  $\delta^{18}\text{O}$  has been decreasing since 1950. We will adjust the y-axis scales on all the panels of this figure so that the curves take up the entire panels. This would make them easier to read.**

Editorial remarks

Font size of all text in figures should be increased.

**Answer: Font size of figures has been increased.**

p30629 line 2 –Replace “frame” with “framework”

**Answer: This has been fixed.**

p30633 line 16 – Remove “in”; line 21 – Remove “to”

**Answer: This has been fixed.**

p30634 line 1 – Start sentence with “The”

**Answer: This has been fixed.**

p30636 line 15 – Replace “until” with “up to”

**Answer: This has been fixed.**

p30646 line 22 – Remove “contributing to”

**Answer: This has been fixed.**

Fig2 caption – [CO] is plotted using green triangles not squares

**Answer: This has been fixed.**

Fig5 caption – Grey lines are on left panels not right.

**Answer: There are grey lines on both left and right panels. They are of different nature which is confusing. This will be modified in the revised manuscript.**

## References

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