The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950; implications for the CO budget – Supplementary Material

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This document serves as a supplement to 'The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950; implications for the CO budget'. It consists of four figures, one table, and some text**,** which provide additional modeling results that were omitted in the main article in order to improve its readability.

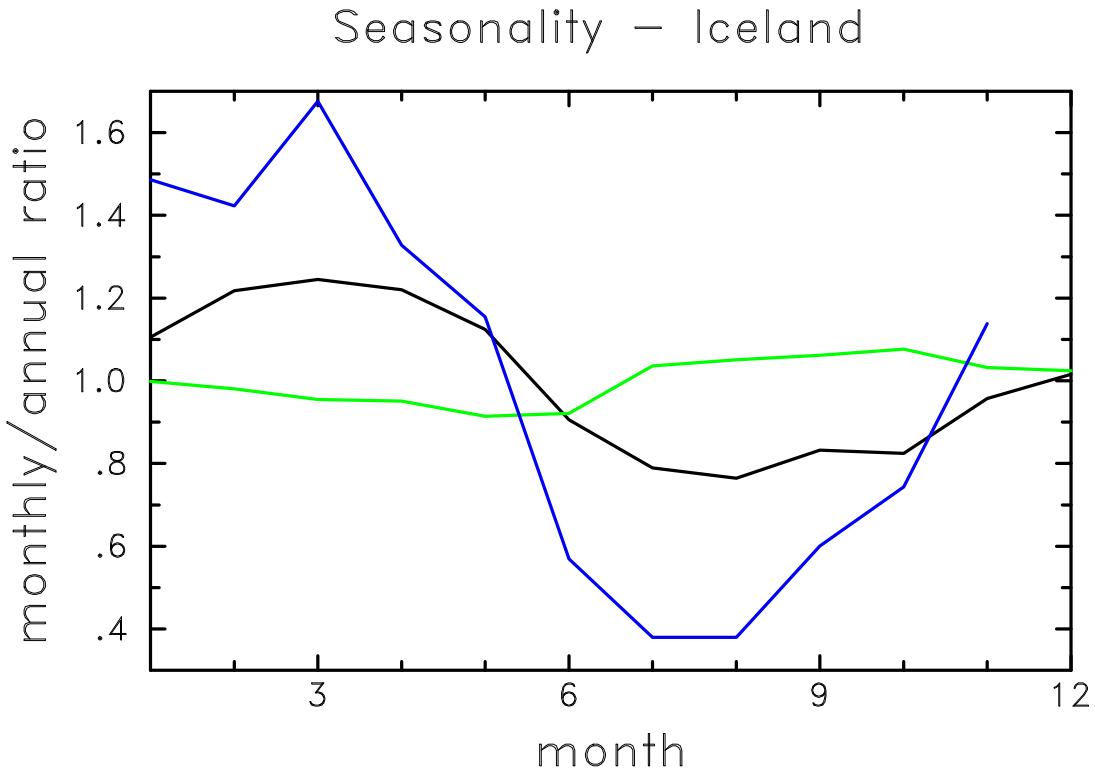

Fig. S1. Mean seasonality of CO (in black), $\delta^{13}C$ (in green) and $\delta^{18}O$ (in blue) of CO in Iceland expressed a relative values: monthly mean value divided by annual mean value (Wang et al., 2012).

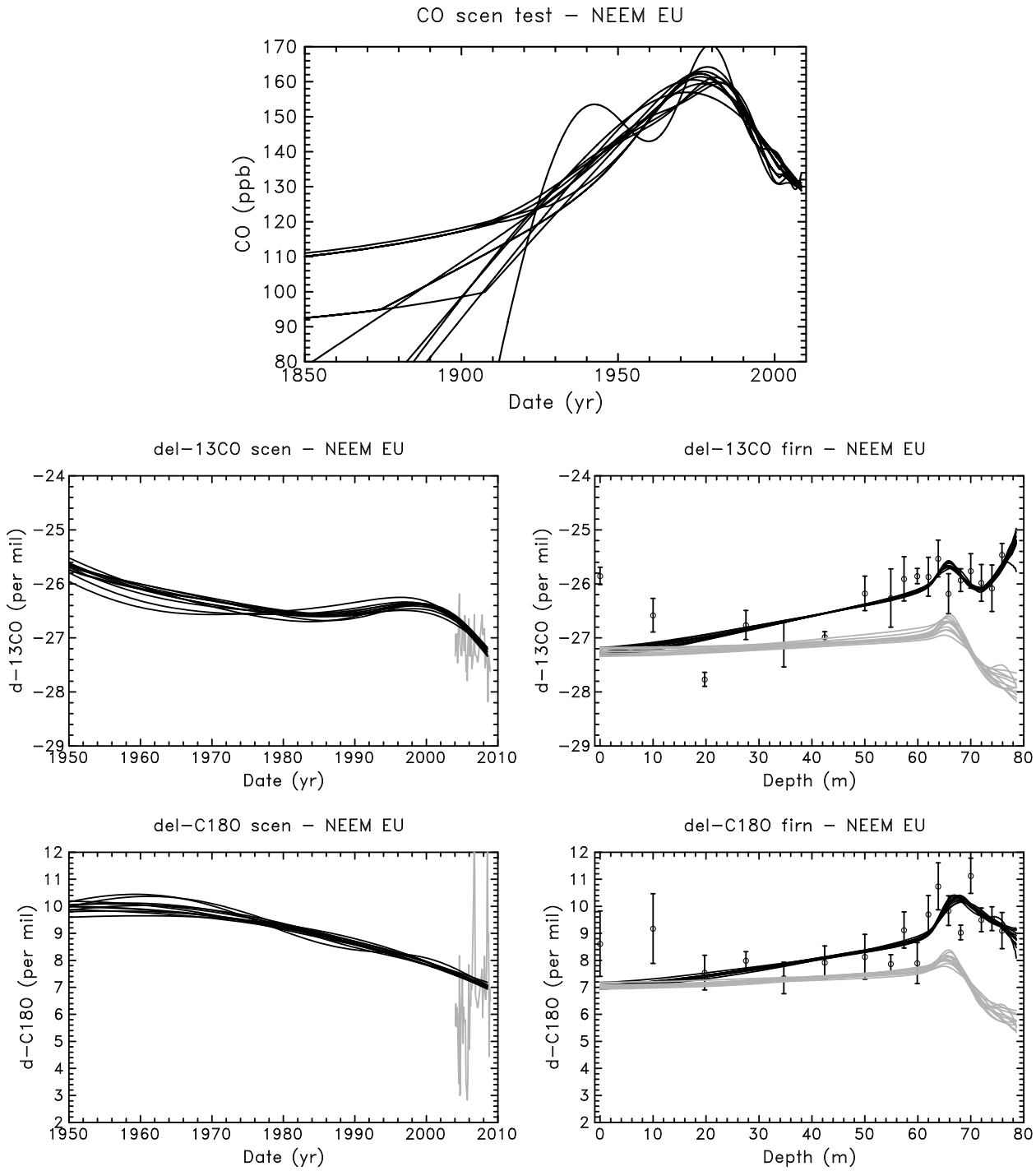

Fig. S2. Estimation of the effect of the CO trend uncertainty on CO isotopes trend reconstructions. Upper panel: CO scenarios used for the uncertainty test. Medium panel: reconstructed $\delta^{13}C$ trends (left) and their matching of firn data in black (right); the grey curves in left panel show the recent de-seasonalized isotopic trend in Iceland ; the grey curves in right

panel show the effect of CO trends with a constant atmospheric $\delta^{13}C$. Lower panel: same as medium panel for $\delta^{18}O$.

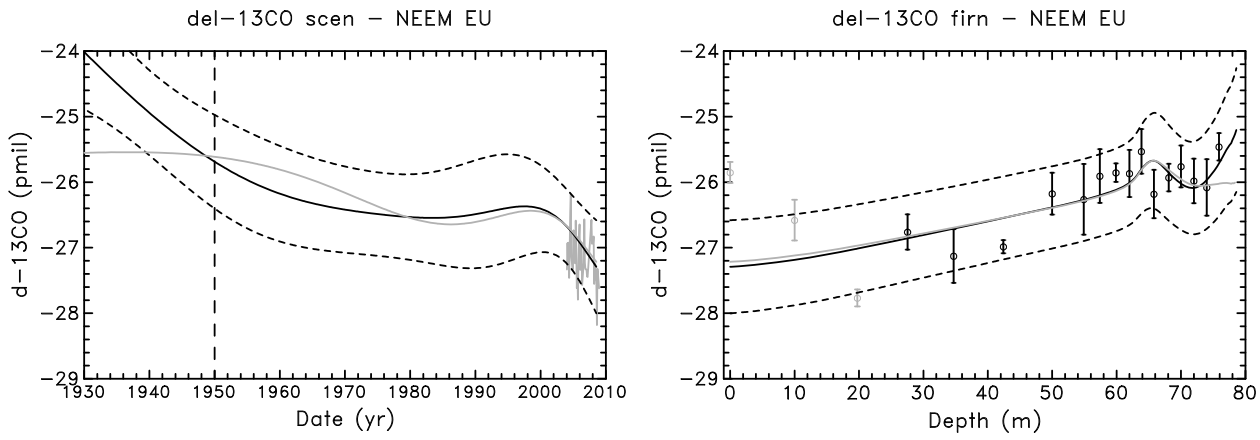

Fig. S3. Influence of removing the deepest measurement of $\delta^{13}C$ from the dataset used for the atmospheric trend reconstruction. The black lines show the best estimates. The grey lines show the result of a simulation that does not use the deepest $\delta^{13}C$ measurement as a constraint. Results are shown prior to 1950 in order to visualize the effect of this test on the un-constrained part of the scenario (see section 4.5).

Discussion on atmospheric trend of $\delta^{13}C$

Figure S2 shows a ~1.4‰ decrease in $\delta^{13}C$ between 1950 and 2008. Based on the mean values of [CO] (Fig. 3), [CO] source contributions (Fig. 5 and 6) and the $\delta^{13}C$ isotopic signature at Iceland (Table S1), the mass balance calculation can be performed with the following equation:

$$\delta^{13}C = \sum_{i=1}^{7} [CO_i]/[CO] \times \delta^{13}C_i \quad (1)$$

where $\delta^{13}C$ is the calculated $\delta^{13}C$ and *i* denotes an individual CO source: fossil fuel combustion, methane oxidation, NMHC oxidation, biofuel burning, biomass burning, direct biogenic, and oceanic emission. $[CO_i]$ stands for CO concentration from each source calculated from [CO] and the $\delta^{18}O$ based mass balance model (Fig. 5 and 6) and $[CO]$ is the atmospheric CO concentration derived from Greenland firn air measurements and firn model simulations (Petrenko et al., 2012). $\delta^{13}C_i$ is the $\delta^{13}C$ source signature at high northern latitudes (Table S1). The results of calculated $\delta^{13}C$ in 1950-2008 are shown in Fig. S4. The $\delta^{13}C$ source signatures used here are listed in Table S1. We perform tests with mean CO source contributions and with corresponding uncertainties of CO source contributions. The upper limit and lower limit of calculated $\delta^{13}C$ is shown in Fig. S4.

The uncertainties of CO source contributions from our mass balance model and $\delta^{13}C$ source signature contribute to the uncertainties of calculated $\delta^{13}C$ values. Even though large uncertainties of calculated $\delta^{13}C$ values are obtained, the observation based firn air $\delta^{13}C$ (green lines) roughly falls within the range of the calculated $\delta^{13}C$ (pink lines) (Fig. S4). We do not expect that the calculated $\delta^{13}C$ trend perfectly reproduces the firn air $\delta^{13}C$ trend. We do this comparison in order to see if the calculated $\delta^{13}C$ trend between 1950 and 2008 is significantly different from the observation based firn $\delta^{13}C$ trend. It has to be pointed out that we have more

confidence on the observation based firn air $\delta^{13}C$ trend than on the calculated $\delta^{13}C$ since our mass balance calculation involve important assumptions (e.g. steady state assumption and constant OH). We present here the most-likely scenarios of calculated $\delta^{13}C$ trend based on the data, which are still very valuable.

77 Table S1. MOZART-4 simulations on atmospheric CO at Iceland in 1997-2004[(a)]

Sources	Estimated $\delta^{13}C$ at Iceland (‰)[(b)]
Fossil fuel	-24
Methane oxidation	-49
NMHC oxidation[(b)]	-15
Biofuel[(c)]	-21
Biomass burning[(d)]	-8 to -20
Biogenic	-26
Ocean	-23

78 [(a)]: Data in the table is based on MOZART-4 simulation and original $\delta^{13}C$ source signatures
79 (Manning et al., 1997 and references therein). (b): assume a constant source signature for the
80 period 1950-2008. (d): assume C3/C4 plant ratio of burned biomass is between 1:9 and 9:1.

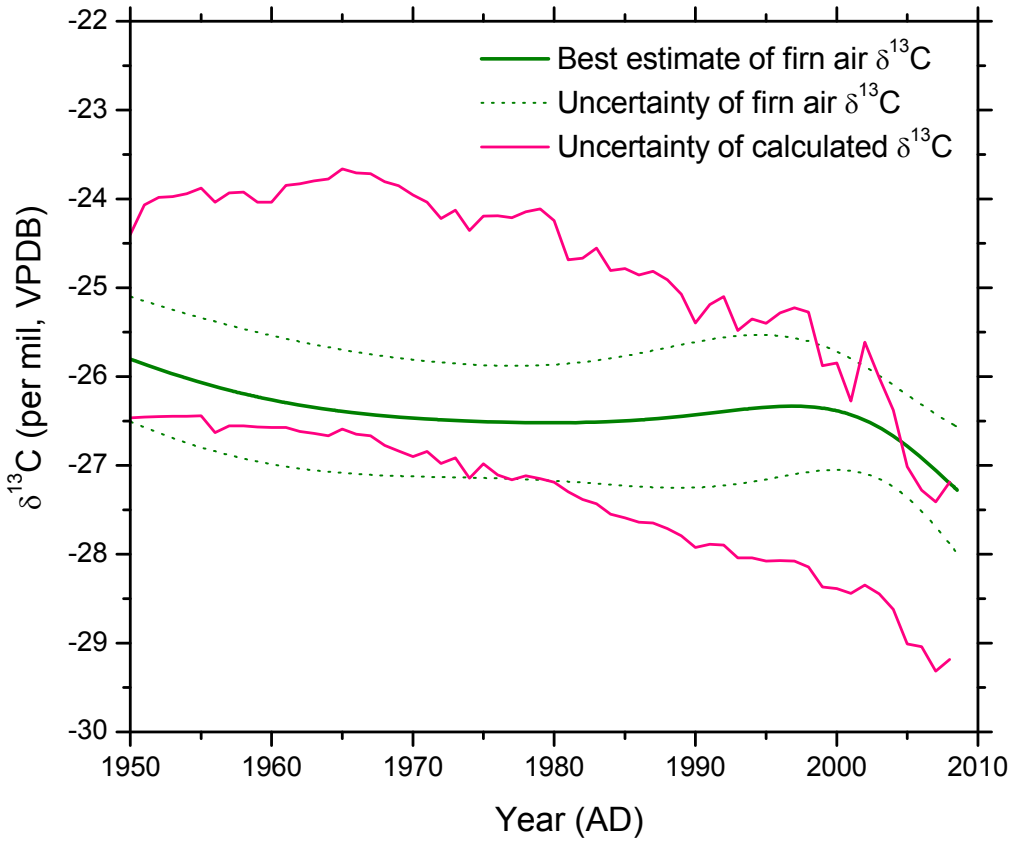

Fig. S4. Comparison of calculated $\delta^{13}C$ from mass balance calculation and the estimated $\delta^{13}C$ in NEEM firn air by LGGE-GIPSA models. Green solid line and dotted lines are the same as those in Fig. 4. Pink lines are uncertainties of calculated $\delta^{13}C$ derived from all the uncertainties (see text).

References

Manning, M. R., Brenninkmeijer, C. A. M., and Allan, W.: Atmospheric carbon monoxide budget of the southern hemisphere: Implications of $^{13}C/^{12}C$ measurements, Journal of Geophysical Research-Atmospheres, 102, 10673-10682, 1997.

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