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

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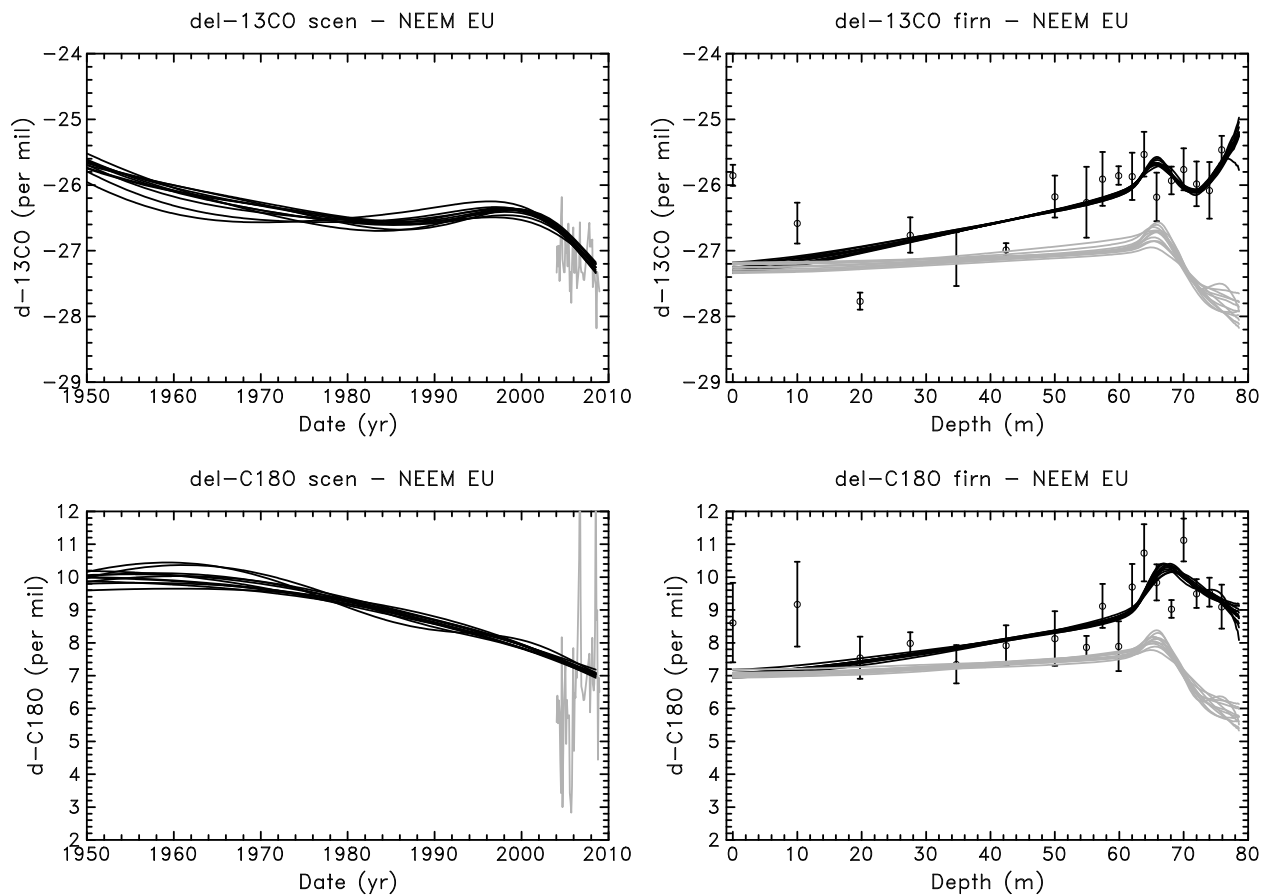This document serves as a supplement to 'The isotopic record of Northern Hemisphere atmospheric carbon monoxide since 1950, implications for the CO budget'. It consists of three figures, one table, and some text, which provides additional modeling results that were omitted in the main article in order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

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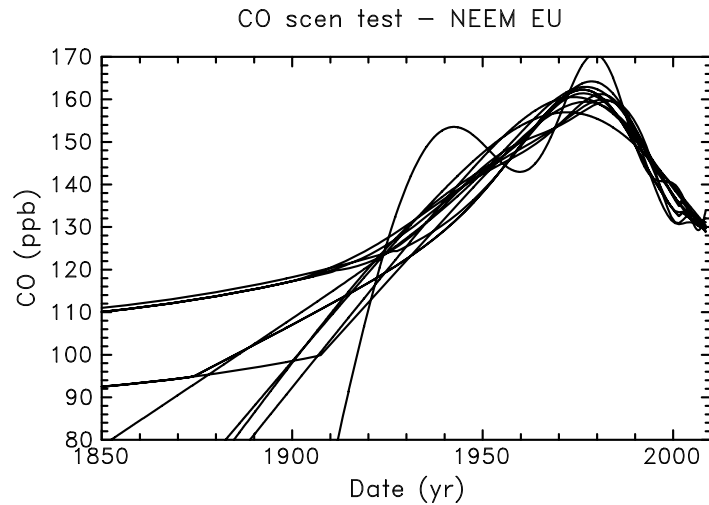
Fig. S1. Estimation of the effect of the CO trend uncertainty on CO isotopes trend
reconstructions. Upper panel: CO scenarios used for the uncertainty test. Medium panel:
reconstructed $\delta^{13}C$ trends (left) and their matching of firn data in black (right); the grey curves
show the effect of CO trends with a constant atmospheric $\delta^{13}C$. Lower panel: same as medium
panel for $\delta^{18}O$.

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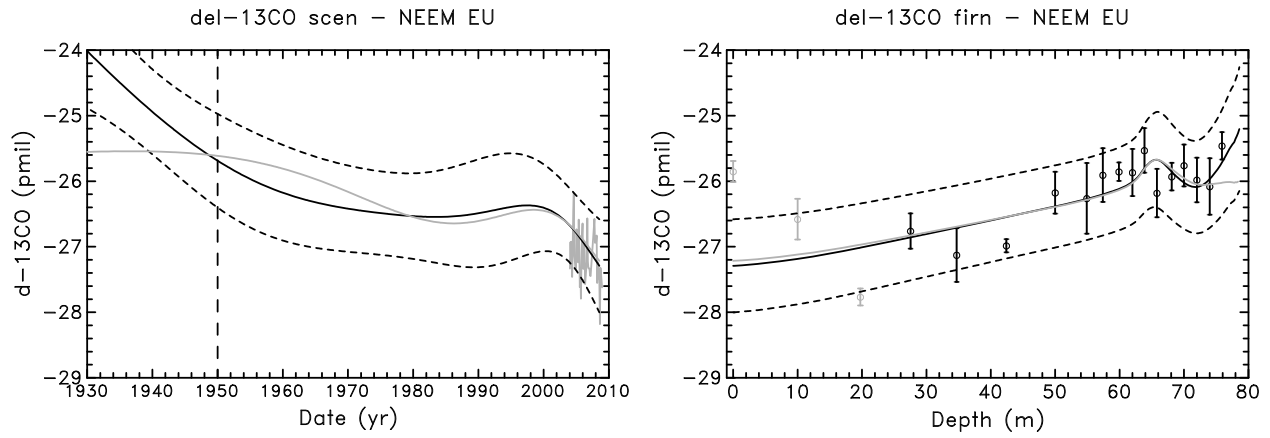
Fig. S2. Influence of removing the deepest measurement of $\delta^{13}C$ from the dataset used for atmospheric trend reconstruction. The black lines show the best estimates. The grey lines show the result of a simulation which does not use the deepest $\delta^{13}C$ measurement as a constraint. Results are shown prior to 1950 in order to visualize the effect of this test on the un-constrained part of the scenario.

Discussion on atmospheric trend of δ^{13}C

Figure S2 shows a ~1.4‰ decrease in δ^{13}C between 1950 and 2008. Based on the mean values of

[CO] (Fig 4), [CO] source contributions (Fig 6 and 7) and δ^{13}C isotopic signature at Iceland

(Emmon et al., in preparation and 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 δ^{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 δ^{18}O based mass balance model (Fig. 6 and 7) and $[CO]$ is the atmospheric

CO concentration derived from Greenland firn air measurements and diffusion model

simulations (Petrenko et al., 2011). $\delta^{13}C_i$ is the δ^{13}C source signature at high northern latitude

(Table S1). The results of calculated δ^{13}C in 1950-2008 are shown in Fig. S3. We use mean

values of [CO], δ^{13}C, and [CO] contribution from each source (Fig 4, 6, and 7) and perform tests

related to specific sources of uncertainty. There are two major sources of uncertainties in the

δ^{13}C mass balance calculation.

First the results after 2000 could have large errors due to the method used in the calculation such

as the scaling method and the assumptions of constant biofuel emissions in 2005-2008. The

biomass burning CO contribution in 2000-2004 is based on the MOZART-4 simulation (Park,

2010) and that in 2005-2008 is scaled with the annual biomass burning CO emissions from

GFED-v3 (Wiedinmyer et al., 2011), which roughly reflects the real annual biomass burning

emissions. The biofuel burning CO contribution in 2000-2004 is based on the MOZART-4

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64   simulation (Park, 2010) and that in 2005-2008 is set as the averaged value during 1997 and 2004

65   (Table 1). A possible acceleration of the decrease on calculated δ^{13}C occurred after 2000 (Fig.

66   S3). The big jump of δ^{13}C in 2002-2003 reflects the big wildfires occurring those years. In the

67   mass balance calculation of the main text, we assign constant annual biomass/biofuel burning

68   CO contribution in 2000-2008, which is 8-year average in 1997-2004 from MOZART-4

69   simulation at Iceland (Table 1) (Park, 2010). For comparison, the calculated δ^{13}C based on the

70   assigned constant is also shown in Fig 3S. The decrease in calculated δ^{13}C in 2000-2008 by

71   varying annual biomass burning CO contribution is larger than that by fixing annual biomass

72   burning CO contribution.

73   Second, as mentioned in the main text, some of the δ^{13}C source signatures are poorly known. The

74   effect of using the estimated maximum and minimum source signatures provided in Table S1 for

75   NMHC oxidation and biomass burning is illustrated by scenarios 1 to 4 on Figure S3. It results in

76   δ^{13}C variations by about $\pm$0.5‰. As source signatures may have changed with time, these

77   uncertainties may also modify the shape of the δ^{13}C time trend within the range of results from

78   the four scenarios.

79   We estimate that the increase of methane oxidation (a ^{13}C depleted source) induces a depletion of

80   ~4.2‰ in the δ^{13}C of CO between 1950 and 2008. On the contrary, the fossil fuel combustion

81   results in an enrichment of about 3.9‰ during the same period. The decrease of δ^{13}C caused by

82   all other CO sources except for the above two ranges between 1.3‰ and 1.6‰. Therefore, the

83   decrease of δ^{13}C is around 1.6-1.9‰ between 1950 and 2008, and the results from this mass

84   balance calculation are consistent with the δ^{13}C atmospheric trend inferred from NEEM firn air

85   data within uncertainties on both calculations. Moreover, it has to been pointed out that the small

86   trend in calculated $\delta^{13}C$ trend is the resultant of compensating effect between larger variations

87   due to individual sources.

88   Overall, the decrease of calculated $\delta^{13}C$ between 1950 and 2008 is consistent with our derived

89   CO source partitioning and $\delta^{18}O$ based assumption of a reduced CO production from fossil fuel

90   burning. Our results of CO source partitioning are thus basically validated.

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92   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]	-18 to -12
Biofuel[c]	-21
Biomass burning[d]	-11 to -17
Biogenic[c]	-26
Ocean	-23

93   [a]: Data in the table is based on Emmons et al., in preparation and references therein. [b]: An
94   arbitrary large range is given to show the possible large uncertainty. [c]: assume constant C3/C4
95   ratio in 1950-2008. [d]: assume C3/C4 ratio is between 3:7 and 7:3 and set it constant in 1950-
96   2008.
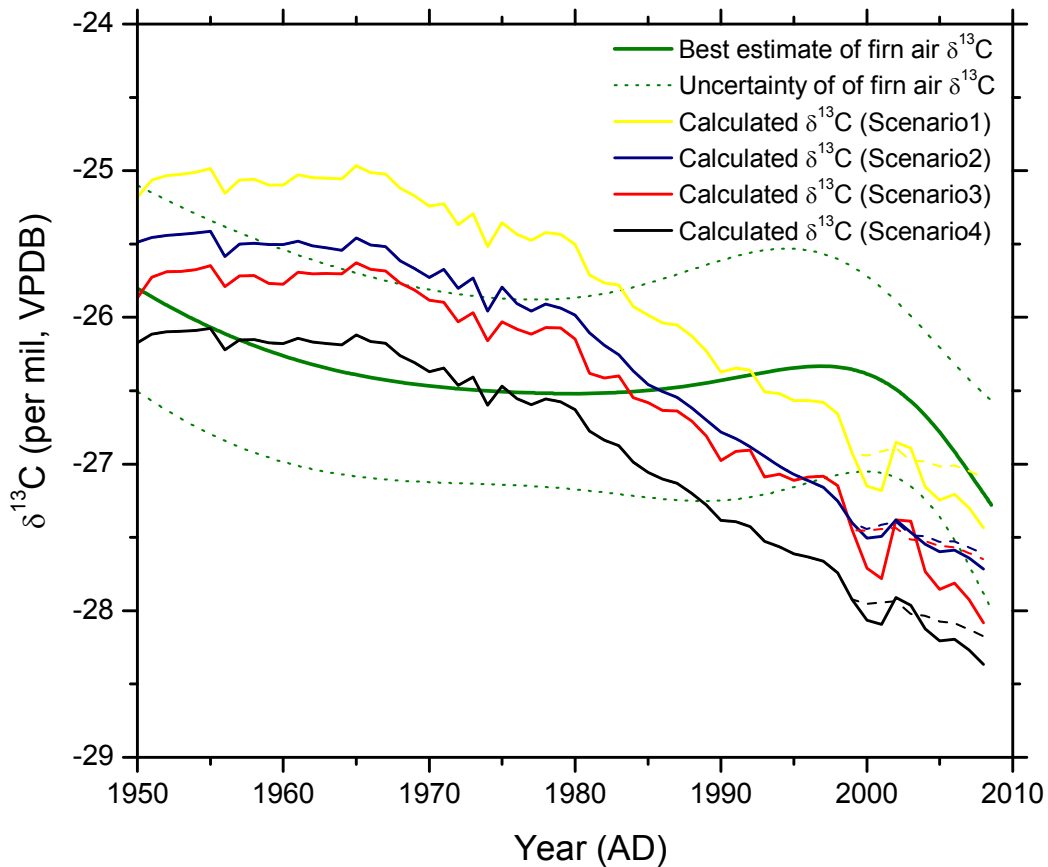
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99   Fig. S3. Comparison of calculated $\delta^{13}C$ from mass balance calculation and the estimated $\delta^{13}C$ in

100   NEEM firn air by LGGE-GIPSA models. Green solid line and dotted lines are the same as those

101   in Fig. 4. The yellow (Scenario1), blue (Scenario2), red (Scenario3), and black (Scenario4) solid

102   lines the calculated $\delta^{13}C$ range based on the different isotopic ratios used (Table S1). Scenario1:

103   $\delta^{13}C$ is -11‰ and -12‰ for biomass burning and NMHC oxidation, respectively; Scenario2:

104   $\delta^{13}C$ is -17‰ and -12‰ for biomass burning and NMHC oxidation, respectively;

105   Scenario3: $\delta^{13}C$ is -11‰ and -18‰ for biomass burning and NMHC oxidation, respectively;

106   Scenario4: $\delta^{13}C$ is -17‰ and -18‰ for biomass burning and NMHC oxidation, respectively.

107   Dashed lines between 2000 and 2008 are results based on an assigned constant annual

108   biomass/biofuel burning CO contribution, which is 8-year average in 1997-2004 (Park, 2010).

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Acknowledgements

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