**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "A 60-yr record of atmospheric carbon monoxide reconstructed from Greenland firn air" *by* V. V. Petrenko et al.

M. Krol (Referee)

m.c.krol@uu.nl

This article presents and analyses firn CO mixing ratios from the recent NEEM ice core site in Greenland. The most important conclusion from the paper is that the peak CO was in the 1970s or early 1980s. This finding is in conflict with bottom-up emission estimates, which predict highest emission (and hence concentrations, although this relation depends on other factors) later in the 1980s. Given the firn mixing ratios, the authors claim that and emission decline should have started already in the late 1970s. They attribute this to reduced emissions from road transportation, in line with an analysis of CO isotopic signals in firn, as outlined in an accompanying paper by Wang et al..

Besides, it is concluded that the 1950 CO concentration was already higher than the

current concentration. This latter result is surprising, since the production of CO from CH_4 oxidation is considerably larger nowadays. If is assumed that emissions of CO scale with population (use of biofuels and fossil fuels) the emissions probably also increased, due to the large increases in population. However, technology of combustion plays an important role in the CO/CO_2 emission ratio. Moreover, the shift in CO emissions from NH mid-lattitudes to more sub-tropical latitudes (India, SE Asia) plays also an important role. This factor is hardly quantified and discussed and this aspect should be improved in the final manuscript. The rest of the analysis in the paper is mostly sound and is back-upped by analysis of other gases H_2, CH_4, and VOCs. I have some comments and questions that should be addressed and are aimed at improving an already interesting paper.

1 Major Comments

As discussed above, major CO sources probably decreased in Europe and North America since the 1970s, but increases are expected in SE Asia and India, due to large industrial developments since the 2000s. Since these sources are located further south, they are prone to faster oxidation by OH and might escape NH wintertime accumulation in the OH-void high northern latitudes and thus accumulation in firn air. This important caveat in the analysis of firn is hardly quantified and discussed in the paper and therefore deserves more attention. Given a lifetime of two month for CO and transport times from low NH latitudes to Greenland, it is obvious that the latitude of emission cannot be ignored.

The most surprising conclusion of the paper is the higher 1950 high latitude CO concentration, compared to the present day concentration. Since (i) the CO production from CH_4 must have increased, (ii) CO production from natural VOCs probably did not decrease, (iii) the use of bio and fossil fuel increased (albeit with better technology, at

least at high NH latitudes), this calls for additional discussion and quantification. The interpretation of firn air remains a delicate exercise and, as recognized by the authors, in situ CO production in the firn close the the lock-in zone cannot be totally excluded.

The inverse method, described in section 4.2, states that the method used is similar, but also slightly different than Rommelaere et al. (1997). One of the differences is in the aim to match the experimental error estimate (page 19008, line 26). The authors should show, e.g. in the Appendix, how the methods differ exactly. Now they use a minimum of the sum of two error terms as is done in Rommelaere et al. (1997). So the difference between the methods is not totally clear at the moment. Furthermore, some arbitrary decisions are taken later in the manuscript. First, at page 19009, line 22, an exemption is made to the "all data points must be matched"-rule. Even if the excluded point is caused by the 1998-1999 biomass burning event, the inverted atmospheric concentration scenario should resolve this event, since the signal is recorded in the firn. Second, at page 19010 some scenarios are claimed to be visibly too irregular and are excluded from the analysis while they pass the data-model comparison test. So either the error criteria chosen wrongly and retuning of the method is required, or all the scenarios that pass the test should be included. Now, some unwanted arbitrariness is introduced, and repeatability is not guaranteed.

Another note about the inverse modeling concerns the prior information that is used. In the source inversion world, a different kind of of prior information is used. Starting from a "best-guess" scenario of the emissions, improvements are sought that better fit the available atmospheric measurements. In In the method described by Rommelaere et al. (1997), no information about the atmospheric concentrations are used. Instead, a smoothness constraint is used, that requests that the atmospheric concentration scenario is not too noisy. I would argue that, especially after 1980, good prior information is available about the atmospheric concentrations over Greenland (seasonal cycle, and special events, such as the 1998 biomass burning). In fact, this is illustrated perfectly in figure S2. The authors should argue more clearly why this information is not used in

C5442

their reconstruction, or better, present a results in which this valuable prior information is used.

A final point about the inverse method concerns the error estimate. I think it is extremely important that for the problem at hand an error estimate in the exact chronology is provided. From figure 7 it is clear that some scenarios show CO mixing ratio maxima around 1970, while in other scenarios the peak is shifted towards 1980. The timing error will depend on time and will probably increase for older air. Discussion about the time-error estimate is therefore vital for the interpretation of the data.

At the start of section 5.2, the CO record is compared to the d[CH_4]/dt record. The authors argue that CH_4 would react slowly to OH changes, but that the methane growth rate is more sensitive to OH. In box-formula form:

$$\frac{dCH4}{dt} = E - k.OH.CH_4 \tag{1}$$

Most people believe that the leveling-off towards 2000 of the methane growth-rate is due to an approach to steady state, e.g. due to stabilizing emissions.The role of OH changes is hard to quantify and the shape of the methane growth-rate curve can be explained perfectly by assuming constant OH. The correspondence between the reconstructed CO mixing ratios and the methane growth rate curve appears to me coincidental and I see no physical arguments to show both curves together. Of course, increasing OH cannot be excluded as a possible cause for both for both CO decline and decline methane growth rate, but the analysis should then include (i) a model in which the impact of the OH change is calculated on both CO and CH_4, and (ii) realistic scenarios of the methane (and CO) emission histories (see equation above).

C5443

2 Minor Comments

On page 18997 the OGI record is discussed (figure 1). This record should have peaked in 1984. However, this notion seems to be based on the wintertime values only. I suggest to plot the data (both OGI and NOAA) also as 12-month running means (NOAA provides great tools for this) to avoid the visual dominance by the wintertime maxima.

In section 2, the sampling and analytical methods are described in (too much) detail. Yet, more information is given in the appendix. I suggest to move more text to the appendix. Furthermore, the claimed agreement in figure 3 still contains the know calibration offsets between the different labs. Since these offsets are known, I do not see any reason not to apply them in figure 3 to show better the remaining discrepancies after correction. Also, the discussion about data-selection on page 19003 is rather vague and the selected procedure seems rather arbitrary. Maybe it can be shown in an Appendix what the consequences are of including the UEA and Stony Brook CO data. Now the inclusion of these data in the paper seems driven by politeness rather than by scientific considerations.

On page 19011 the OGI record is discussed. I wonder how the OGI record (corrected for offsets) would translate in the firn history (like figure S2).

In section 5.1, page 19011 at the bottom, it is said that no model is available to explore the implications of the reconstructed history. However, some kind of analysis as presented in the accompanying Wang et al. (2012) paper (Table 1) is needed in this paper also (see major comments).

In section 5.5 it is argued that an increase in OH would lead to an increase in H_2 due to an increase in production from hydrocarbons. This seems to quickly argued, since part of the H_2 is also oxidized by OH and NMVOCs quickly reach a new and lower concentration, feeding back negatively on the H_2 production.

On page 19015 and 19016 the work of Dentener et al. (2003) is wrongly interpreted.

C5444

In this work a full chemistry simulation was performed in which the methane concentrations we forced to follow the observations (mass-balance approach). The analysis of OH in this long term simulation showed a small long term positive trend. Methane variability is explored in Monzka et al. (2011), a reference that is missing (Montzka et al. (2011). Small interannual variability of global atmospheric hydroxyl. Science, 331(6013), 67–69. doi:10.1126/science.1197640).

3 Textual Comments

page 18996, line 10: replace "atmospheric chemistry" by "atmospheric composition"

page 19006, line 3: "discussed below": please state where exactly (next section?).

caption figure 9: Brown line not found.

Table S5: A more recent H_2 budget estimate is provided by Pieterse et al., Atmos. Chem. Phys., 11, 7001–7026, 2011.

Figure S2/S4/S6, caption: The blue line? I would call this purple.