

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

Anonymous Referee #2

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The manuscript presents new CO measurements in firn air from 3 different sites in Greenland and uses the fir air CO record to reconstruct atmospheric histories for the last 60 years. The manuscript also includes the first measurements of H₂ in Greenland firn air that can help interpret the CO record. The CO atmospheric histories reveal an interesting trend: CO was considerably higher in 1950 than it is today and there has been a decline during the last 20-30 years of the 20th century. One important implication of these trends is that historical CO emissions appear to be seriously underestimated in the emission inventories.

The paper is very well written, especially sections 1-4. The overall agreement between the CO data from five different groups is pretty remarkable, considering the different sampling methods and equipment used at three different firn sites, and the potential

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calibration offsets between different laboratories. One fundamental scientific question is whether the main features of the firn air CO records (specifically the long term trends) reflect real atmospheric changes. The authors take a conservative approach and put heavy emphasis on this issue. They highlight a few instances of apparent measurements discrepancies and explore the possible explanations to conclude that there may be room for in situ production of about 5 ppb in the firn. I would argue ~5ppb is well within the range of uncertainties due, for example, to the potential differences and variability in transport of polluted air to the different firn sites and the surface sites they are using in their comparisons. They also thoroughly explore the modeling uncertainties that arise from the signal smoothing in the firn. Overall, there is robust and convincing evidence that CO is well preserved in Greenland firn air and the atmospheric histories display real long-term atmospheric trends. This is a unique data set that will enhance our understanding of changes in fossil fuel use that results in CO emissions (and possibly NMHCs) and may also provide some constraints on OH variability in the NH. In contrast, the interpretation of the H₂ firn air measurements is very challenging and it is not yet possible to develop H₂ atmospheric histories with much confidence.

The manuscript fits well within the scope of ACP and warrants publication, although I do have a few reservations that I would like to see addressed before it is accepted in its final form. I found some of the discussions to be overly qualitative and somewhat out of focus on what the authors think was driving the observed CO trends. For example, I had trouble getting a clear message from sections 5.2, 5.5, and 5.6. These three sections seem to be written in a way to leave an element of doubt about the role of OH. With that, I mean doubt about what the authors think the role of OH is, otherwise, I understand that there is a lot of unknowns about past OH variability. For example, it is very difficult for the reader to follow the train of thought that gets us to the conclusion on the role of OH based on H₂ measurements: “Overall, the examined evidence does allow for a modest increase in OH during the 1980s to be part of the explanation for the [CO] trend.” (Ins. 26-27, pg. 19018)

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I also found the supplemental material to be well organized, appropriate, and helpful, except the section about H₂ in NEEM firm air (details below).

More specific comments

Introduction: Somewhere in the in the introduction there should be a justification of why Greenland is representative of high NH and a description of what is meant by high NH.

I also think there should be a little more on the CO budget: A more quantitative analysis of the best estimate CO sources in the NH, for example.

Section 5.2: The correlation in fig. 7 is very strong and intriguing. The authors report a ± 10 years age uncertainty for the $d\text{CH}_4/dt$ based on NOAA (flasks) and Law Dome (ice core). Can we not do better if we try to get an estimate of the relative uncertainty (we don't really care about the absolute uncertainty in this context) between the firm inversions alone?

I agree with the authors that Fig. 7 is suggestive of a large role for OH in driving CO and $d\text{CH}_4/dt$ trends, although I cannot readily dismiss a connection (may be environmental policy related) on the source side very easily. An immediate question is: what would be the impact of large OH changes on methane emission estimates? I cannot think of an easy way to answer this (my guess is very large and unrealistic), not without getting into modeling, which the authors don't deem within the scope of this paper. However, I still did expect a qualitative discussion. What seems logical to me is to carry out that discussion for 1950-1970 and 1980-2000 periods when things are changing a lot. Instead, the focus here is on 1970s and 1980s (lns. 26-29 on pg. 19012 and continuing onto pg. 19013). I was quite puzzled by this at first, but after reading the whole manuscript it occurred to me that may be they are trying to set up the stage for later OH arguments based on the CO-H₂ comparison? I have to say this is very confusing for the reader. Why not add a separate section about the role of OH to the very end of the discussion section (I'm assuming they feel strongly about getting a point across about a potential role for OH during 70s and 80s), after they are done with all

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the comparison sections.

The last sentence of this section is problematic because the information in parenthesis applies only to the decline period (1980s -1990s). As a side note, assuming methane steady state by ~ 2000 with constant sinks, total methane emissions must have stabilized (not just slowed their growth) some years before.

Section 5.3: It would be nice to provide at least a scaling on how much CO is directly emitted vs. how much is coming from oxidation of methane and light hydrocarbons in the present day. The arguments are very qualitative and a bit taxing on the mind.

Section 5.4: This section relies on the Wang et al. (2012) study, essentially providing a short summary of the relevant information from that paper. Given that there is no original isotope analysis in this manuscript, I think this section would be better placed as the last of their comparison sections. The purpose would be to bring in an isotope perspective from Wang et al. (2012) and discuss whether those results support or weaken their analyses of other comparisons.

Again, I cannot see any justification for the specific focus on the 1970-1990 period. I realize the CO peak is within that period but the largest changes in the CO histories are during 1950-1970 and 1980-2000. Is it not more logical to look for a signal in isotopes when things are changing the fastest?

Another issue here is the fact that Stony Brook CO data were excluded from the CO inversions. I understand and accept the reasoning in section 3.1, but it seems necessary to state (or show in a figure) how a Stony Brook only inversion compares with the ensemble results.

Section 5.5: This is probably the most problematic section in the manuscript from my perspective because I'm not sure what to make out of the H₂ data. It seems to me that the first order scientific questions about H₂ appear to be on the sampling, measurements, and modeling sides. I think the authors' interpretation of the lag between CO

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and H2 peaks as being supportive of “the sink hypothesis” is overly simplistic. First, they have to carefully frame it in time when OH could be rising to decrease CO and increase H2. This is difficult because the firn inversions are highly uncertain, and they are not even shown in the main body of the manuscript, which makes it harder for the reader to follow these arguments. Given the lack of understanding of the H2 behaviour in the firn, I recommend this section to be modified to focus more heavily on the challenges in developing H2 atmospheric histories from firn measurements. To this end, it would make sense to move all the supplemental info on H2 into the main text (removing redundant info of course). The figure (fig. S6) especially, since timing is central to the OH arguments.

One other mechanism that comes to mind is the exchange between neighboring open and close pores within the lock-in zone. This could become significant if the age difference between air in open and closed pores is large enough.

Section 5.6: The discussion on the OH literature needs some revisions. Prinn et al. (2005) published methyl chloroform based OH estimates for 1978-2004 and Montzka et al. (2011) push it out to 2008, including a synthesis of their results with results of Prinn et al. (2005) and Bousquet et al. (2005). The uncertainties are large as discussed in the text but Prinn et al. (2005) inversions show an increase during 1978-1985 (likely not significant) and a decline in OH from mid to late 1980's to late 1990's, both of which are on the order of 10% or so. I'm not sure if anyone thinks methyl chloroform inversions imply a 30% change in OH between 1979-1990.

Conclusions: Lns. 10-12: There is no way to fully reconcile the discrepancy presented in fig. 9 with OH changes that are within range of sanity. I would scrap the second half of the sentence: everything starting with “under the assumption...” Lns. 23-25: I already stated my reservations about section 5.5. What goes into conclusions about H2 may need revisiting based on what happens with 5.5.

Minor comments:

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Pg. 19000, Lns. 19-21: The sentence that starts with “NOAA [H2] overall...” needs revision

Pg. 19001, Lns. 6-9: I don't understand the implication of this sentence.

Pg. 19003, Ln. 17: I think “a best estimate combined data set” is more appropriate than “the best estimate combined data sets”. You may have to write another sentence to tell there are more than one data set because of the US and Europe holes etc.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 18993, 2012.

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