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Comment on acp-2021-736

Anonymous Referee #1

Referee comment on "Towards reconstructing the Arctic atmospheric methane history over the 20th century: measurement and modelling results for the North Greenland Ice Core Project firn" by Taku Umezawa et al., Atmos. Chem. Phys. Discuss.,
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General comments:

This paper uses firn air measurements from two Greenland sites (NEEM and NGRIP) to investigate the Arctic atmospheric methane history over the 20th century. A firn model is applied first to NEEM to demonstrate model performance, then to NGRIP to try to infer the Arctic methane atmospheric history.

A key assumption of this study is that the Arctic CH₄ atmospheric history is uncertain but that the atmospheric histories of the other six gases (CO₂, SF₆, CFC-11, CFC-12, CFC-113 and CH₃CCl₃) are known with sufficient accuracy to constrain the firn model. More should be added to justify this assumption - I am not convinced. I do agree that it is a problem that the Arctic methane history is not known as well as has been assumed in previous firn model studies. However, the CO₂ atmospheric history from Buizert et al is created in much the same way as CH₄ (with an assumed offset from the SH ice core record), but has the added complication that CO₂ has the possibility of elevated levels in NH firn due to in situ artefacts (e.g. mentioned in Buizert et al and elsewhere in the literature) - this could affect the ability of CO₂ to constrain the firn model. The ¹⁴CO₂ atmospheric history (relevant for NEEM, but unfortunately not measured at NGRIP) is probably quite reliable when it is based on atmospheric or tree ring measurements. The halocarbon histories are based on estimates of emissions, but these also have inherent uncertainty (the emissions themselves are due to reported production/sales, assumed emission functions, and atmospheric lifetimes and therefore have uncertainties). I am not convinced that the atmospheric history of CH₄ is significantly more uncertain than these other gases, I think all are known to some extent, but not perfectly.

In addition to the question of how well atmospheric histories are known, it is also relevant to consider how well different gases can constrain firn diffusivity. Halocarbons measured in the deepest few firn samples at both NEEM and NGRIP are very close to zero, so do not provide a strong constraint on diffusivity in that region of the firn. As discussed at line

307, it is the region below about 74m at NGRIP that is used to infer the CH₄ atmospheric reconstruction before 1980. The blue, orange and red lines in Figs 5 and 6 have a large spread below 74m for CH₄ and CO₂, but there is not a very large spread for the other gases, with the spread for some of these gases dropping rapidly to zero as depth increases. This shows that the modeled mole fraction profile for the CFCs, SF₆ and CH₃CCl₃ in the deep firn is not very sensitive to the diffusivity profile, and consequently that the diffusivity profile is not as well constrained by these gases. It has been pointed out in previous studies that methane provides a strong constraint on diffusivity in the deep firn, but, as the authors note, only if the atmospheric history is well known, and unfortunately the authors are correct that it is not well known in the Arctic. CO₂ would provide a similarly strong constraint on diffusivity, but I would suggest that the Arctic CO₂ atmospheric history is also not well known and has the possibility of in situ artefacts in Arctic firn, as mentioned above. Thus, calibrating the firn model without CH₄ for NGRIP, then expecting to reconstruct atmospheric CH₄ is risky, and I believe the results show that it has not been successful (the model appears not to have been well constrained by the observations used).

The most important contribution of this paper is questioning the assumption of a known Arctic atmospheric methane history for constraining firn models for Greenland firn sites. This has consequences both for calibrating firn models and for interpreting the CH₄ north-south gradient in terms of emissions, as the authors discuss. However, as I have said, I believe the Arctic atmospheric histories for the other gases should be similarly questioned. I am not convinced that substantial conclusions have been reached in this study. The result that it is difficult to identify the atmospheric CH₄ history that consistently reproduces the depth profiles of CH₄ in NEEM and NGRIP firn is due to the fact that the firn model has not been adequately constrained by the other gases. The last 2 sentences of the abstract say that a consequence of this result is that the Arctic CH₄ history should be considered preliminary - it may be true that the methane history is not well known, however is not a consequence of that result. Rather, it is a prior assumption that has not changed as a result of the study.

While this study does highlight the deficiency that we don't know Arctic atmospheric CH₄ well, in my opinion it doesn't go any way towards solving it. This makes me question the value of the study as it is currently presented.

Specific comments:

A conclusion in the abstract and at line 374 that "We find that, given the currently available firn air data sets from Greenland, reliable reconstruction of the Arctic CH₄ mole fraction is possible only back to the mid 1970s" - atmospheric observations began around 1980, so this isn't much of a result. The title of the paper is 'Towards reconstructing the Arctic atmospheric methane history ...', but the study doesn't move very far towards that goal.

Line 61 - "The NEEM-S1 data are notably higher than the ice core data after ~1850." The NEEM-S1 data after 1850 are fairly consistent with the Blunier et al 1993 data in Fig 1.

The NEEM-S1 data are definitely higher than the Nakazawa data, but some of the Nakazawa data are lower than the SH Law Dome data which is unrealistic. Rhodes et al note that the uncertainty in absolute mole fraction of the NEEM-S1 data is about 6-9 ppb, and that that is a limitation to deducing the inter-polar gradient, but perhaps the NEEM-S1 are our best chance at the moment to reconstruct NH methane between 1850 and 1945, seemingly better than the firn reconstruction presented here. The NEEM-S1 data were mentioned once in this study but otherwise dismissed (unfairly, in my opinion).

The strategy with prior and calibrated diffusivity profiles is not clear to me. For example: Line 177 - "The diffusivity profile optimised for the CIC model was tuned for our model" - what does this mean? Was the CIC profile used as a prior then improved by comparing to observations?

Line 182 - What diffusivity profile gave the RMSD value for NEEM of 0.83? Is this the same as the case shown in Fig 2?

Line 197 - was that the initial diffusivity from equation 4 or Ishijima et al (2007)?

Lines 198-203 - This paragraph is a little hard to follow, it became clearer as you read further, but could be improved. For example, line 198 "We examined the different sets of profiles" .. which different sets? (It becomes clearer, but is confusing at this point). Line 201 - "We prepared 100 different sets" - at this point the reader wonders how they are prepared, this also becomes clearer (page 12), but if this information was given when the steps are first discussed, it would improve readability.

Line 222 - which diffusivity profile was used in Fig 3? Eqn 4, Ishijima or a tuned profile?

Why aren't the NGRIP results corresponding to the diffusivity profile giving RMSD=0.51 shown as a case (e.g. dashed black line) in Figs 4, 5, 6, 7 and 8? This would be good to see.

Fig 2 - It is difficult to see some of the observations, particularly CH₄ in the deep firn. Could the observations be shown more clearly?

line 212 - the atmospheric history is not quite monotonic, so there could be more than one time with atmospheric mole fraction matching the mole fraction at the firn depth - how is that handled? Was the atmospheric history smoothed?

Line 230 - at this point I'm already wondering what the modeled CH₄ depth profile at NGRIP looks like with the Buizert et al atmospheric scenario in the model, but I need to wait....

The colored lines (red, orange, blue) cover many different diffusivity profiles, some of which don't fit the firn data well at all, particularly the blue cases. Is it worth showing the blue cases at all? At line 293, they are described as "less likely", but many of them simply do not fit the observations. Could the red group be split into two to highlight the really good cases? Do the better diffusivity profiles tend to fit all gases well, or do some profiles fit some of the gases well and others not so well, and vice versa (for groups of gases)?

line 297 "suggesting that the CH₄ mole fraction may have been lower than the initial modeling scenario" - I am not convinced that this is a robust result. I am not convinced that the atmospheric scenarios are known more accurately for the other gases, or that they provide sufficient constraint on the model so that it can be used to infer the CH₄ history, as discussed above.

Line 309 - "The differences between the initial and corrected atmospheric CH₄ scenario from these three deepest data are up to ~ 100ppb" - because the model is not well constrained by the other gases.

Line 313 - "NGRIP firn data suggests decreased CH₄ mole fraction from the 1950s to 1970s in any case, albeit with large uncertainty" - I do not believe this is a robust result, for reasons given above.

Line 320-322 - if I understand this correctly, the CH₄ history reconstructed from NGRIP gives a larger model-data difference at NEEM than the original history, is that not indicating an inconsistency?