Interactive comment on "Reconstruction of Northern Hemisphere 1950–2010 atmospheric non-methane hydrocarbons" by D. Helmig et al.

We thank all reviewers for their careful reading of our manuscript and their constructive feedback which has been of great help for improving our publication. Below are our responses to their comments and changes that were implemented in the manuscript.

Anonymous Referee #1
Received and published: 12 June 2013

Helmig et al reconstructs non-methane hydrocarbons from NEEM firn air, and presents flask measurements from five Arctic sites. I believe this study will make a useful contribution, and is generally well written. I have some minor comments that I believe will improve the paper.

1. I suggest adding a table to the Introduction section of the paper with the name and chemical formula for each NMHC considered, plus lifetime and relative diffusion coefficient in firn and perhaps mass. The names and formulas are not related/defined as far as I can see, but are used interchangeably throughout the paper, so a table would help people unfamiliar with NMHCs. The diffusion coefficient is already given in Table 1 of the supplement, but I think it should appear in the main paper (but not necessarily the other information from the Supplement table, apart from mass).

The following table was added as new Table 1 to the paper:

Table 1.
NMHC included in this study with pertinent physical variables.

Compound Name	Molecular Formula	Molecular Mass $(g\ mol^{-1})$	Approximate Atmospheric Lifetime at 24-hour [OH] = 6.5×10^5 molecules cm^{-3} (days)	Relative Diffusion Coefficient D/D_{CO2}
Ethane	C_2H_6	30.1	66	0.905
Propane	C_3H_8	44.1	15	0.702
i-Butane	C_4H_{10}	58.1	7.6	0.583
n-Butane	C_4H_{10}	58.1	7.0	0.584
i-Pentane	C_5H_{12}	72.2	4.6	0.511
n-Pentane	C_5H_{12}	72.2	4.5	0.544

2. Page 13001, line 3 - what is a non-sinusoidal cycle?

Text was changed to: "The NOAA-INSTAAR network data were subjected to data curve fitting protocols, filtered for outliers, and fit to a function comprised by a harmonic component and polynomial term as described by (Thoning et al., 1989) and (Masarie and Tans, 1995)."

3. page 13002, line 12 - "a robustness-oriented definition of the optimal solution that uses the ..." - awkward and not very informative. It is unfortunate that the reference for the inverse model is an extended conference abstract - can some of the main details of the inverse model be included here (in language that is not too technical)?

Please note that Witrant and Martinerie (2013) is not an extended abstract but a six pages article published in a conference proceedings series that went through an international review process. As this proceedings series is not easily accessible to the environmental science community, a pre-print has been posted at http://www.gipsa-lab.grenoble-inp.fr/~e.witrant/papers/13_ifac_firn.pdf. This article describes the application of the mathematical method from Lukas (2008) to firn air data for atmospheric trend reconstruction. This reference will be cited in our revised manuscript, but we believe that further description of the method would be beyond the scope of the manuscript. We will further mention that this method has been described and applied in Sapart et al. (2013) and Petrenko et al. (2013). The manuscript text was revised to:

"The inverse model described in (Witrant and Martinerie, 2013) was used for the atmospheric history reconstructions. This is the most recent version of the LGGE-GIPSA atmospheric trend reconstruction model, based on (Rommelaere et al., 1997) and Lukas (2008) and has been been detailed in more depth in Sapart et al. (2013) and Petrenko et al. (2013). The inverse model cannot reconstruct seasonal variations, as discussed in (Wang et al., 2012). The effect of seasonality on NMHC depth profiles in firn is evaluated and discussed in Section 3.2."

4. page 13002, lines 18-20 - repetitive, you have already referred to the depth profiles in Fig 2, suggest rewording to "There are some subtle differences in the four datasets of NMHCs shown in Fig 2, however ..."

Sentence was corrected as suggested.

5. page 13005, line 6 - 'low' rather than 'declining'

It is more precise to say "declining" as we did, because the mixing ratios really do decline with decreasing depth. Sentence was changed to "The declining NMHC mole fractions with decreasing depth to the snow surface in the upper 40 m .... "

6. Page 13006, line 24 - could change to "Considering both the mean level and seasonality, none of these monitoring sites yielded ..."

Wording was changed as suggested.

7. Page 13007, 1st paragraph - put the reference to Fig 7 earlier in the paragraph.

Corrected as suggested.

8. Page 13007 (meant is 13008), line 2 - the decline for all except ethane is relative to the maximum around 1980? Be clear.

Wording was changed to: "The year 2010 NMHC mole fraction in comparison to its maximum in 1970 has declined to ~68% for ethane, and in comparison to the maxima around ~1980 to 65% for propane, to 63% for i-butane, to 51% for n-butane, 42% for i-pentane, and 50% for n-pentane."

9. page 13007 (meant is 13008), line 4 - is it just "Interesting to note" or is it the explanation for the rate of decline?

We think it is unlikely that the differences in lifetimes are the explanation for the difference in how much each gas has declined since its peak, as this would argue for 1. a change in the atmospheric oxidant concentration over time (OH), which would not agree with current understanding of OH trends or 2. for a change of the average transport time from the primary emission regions to Greenland. In a simplistic box-model, if the lifetime of each gas stays the same, and the source for each gas declines by 50%, then the mixing ratio of each gas would also decline by 50%.

We added the sentence: "This points towards relatively higher emission reductions for the heavier, gasoline-type NMHC species in comparison to the natural gas NMHC."

10. Page 13008, line 21 - What do you mean by the "model chooses different slopes"? The top 40m of measurements have been excluded due to the influence of seasonality, how far back in time does this affect the solution? Similarly Page 13010, line 10 – how far back do you go until you can trust the trend?

The flattening of the slope, respectively reversal in recent years is only obtained for C_3H_8 and i-C_4H_{10}. Our main aim in commenting this feature is to explain that we do not consider it as significant. We propose to simplify that explanation by replacing the last two sentences of Section 3.4 with:

"The flattening of the slope, respectively reverse-modeled trends in the last few simulated years obtained for C_3H_8 and i-C_4H_{10} are not significant in comparison with the uncertainty envelopes in Fig. 7a, which mostly reflect the differences between model results and firn data."

Trace gas concentrations in firn air are performed in air collected in the open porosity of the snowpack. They provide information about past atmospheric trends for a limited period of time, because air becomes trapped into closed bubbles in the deep firn. The simplest definition of the 'significant length' of a reconstructed scenario could be the mean age at the measurement depth where most of the air is in closed bubbles rather than the open porosity. Definitions of the significant length of a reconstructed scenario have been provided in the past (e.g. Sowers et al., 2005; Bernard et al., 2006), based on the proportion of air of a given age present in the open versus closed porosity of the firn. Here we define the significant length of the scenario as the mean age at either the depth for which the open/total porosity ratio is 0.5 (~76 m depth), or the depth where the open/total porosity ratio at that depth is higher than 0.5 (this is the case for NEEM 2009, leading to a shorter significant length). This significant length is gas dependent due to the different diffusion coefficients used for different gases (increasing lengths for decreasing diffusion coefficients). Significant lengths of the scenarios calculated for hydrocarbons at the three NEEM drill sites, and the definition of this term are provided in Table S1.

11. Page 13009, line 28 - Do you really mean "not statistically significant" here, or is it more about not being reliably reconstructed?

Sentence was changed to:

The flattening of the slope, respectively reverse-modeled trends in the last few simulated years obtained for C_3H_8 and i-C_4H_{10} are not significant in comparison with the uncertainty envelopes in Fig. 7a, which mostly reflect the differences between model results and firn data.

12. page 13010, line 19-23 - this refers to the possibility that a sink change is the explanation? Say that.

Yes, the reviewer is right. We state that in the preceding sentence. We modified that sentence slightly to further emphasize this point:

... These include changes in emission types and emission ratios in the source regions of these compounds, possibly a change in air transport patterns, with air from different regions representing different emission types/ratios being brought to NEEM. Another explanation might be a change in the chemical sinks, for instance changes in the relative contribution of atmospheric chemical oxidation pathways (such as a shift in the relative contribution of OH versus other oxidants (e.g., Cl, NO_3).

13. page 13011, line 18 - "have also have"

Corrected to: "Natural oceanic emissions have also been shown to have greater fluxes of n-pentane relative to i-pentane."

14. page 13013 - could changes in the atmospheric lifetime be relevant to this comparison?

The current belief is that mean atmospheric concentrations of the OH radical have remained relatively constant over the past few decades (Prinn et al., 2005; Montzka et al., 2011). Given that these NMHC are primarily oxidized by OH, consequently there is no indication that their atmospheric lifetimes may have changed to a notable degree.

15. page 13014, line 5 - 'lower' rather than 'slower'

Corrected as suggested.

16. page 13014, line 15 - also using different reconstruction methods

Sentence was changed to "....NMHC quantifications from different laboratories, and two different models of gas transport in firn and reconstruction methods".

17. Page 13014, line 17 onwards - although the difference in the maximum of the reconstructed ethane peaks is 7-10 years, these peaks are really quite flat at the top. We know from the network data that there is significant interannual variability so the actual atmospheric changes would not have been as smooth as the reconstructed changes, so I wouldn't make too much of this difference. Neither this study nor Worton et al closely fit the measured peak in ethane in the NGRIP firn (i.e. below 70m) - the reason for this may be unknown, but would lead to caution about interpreting the date for the peak based on NGRIP data. So I agree that the estimate from NEEM is probably more reliable, but still don't think the difference is that important.

Our model results showed that for all scenarios constrained from individual NEEM boreholes ethane peaks before 1980 (Figure 1). We took this exercise a bit further by investigating what peak dates we would get for scenarios constrained from the North GRIP and Summit firn data. The simulation results

of the NEEM and these two further data sets were also included in Figure 1. For the Summit data we obtain a somewhat earlier peak date, i.e. 1975, than the peak date reported by Aydin et al. This small difference can be due to a number of reasons, i.e. different diffusion coefficients, diffusivity profiles, firn models etc. used in our calculations. The North GRIP data trends reported by Worton et al. were not calculated using an inverse firn model aiming at a best fit of the data but using a forward firn model and a-priori assumptions which include a peak date in 1980 (see Worton et al. p594 second paragraph of left column). The data point with the highest concentration in ethane is not well matched by the fit (Fig 2a on page 595). Thus, the fact that we obtain an earlier peak date in our calculations for North GRIP is not in direct contradiction with the Worton et al. results/data.

Consequently, all of our NEEM calculations, as well as our calculations for the North GRIP and Summit data result in peak dates occur between the mid 60's and the late 70's. Although we cannot exclude a peak in 1980 due to the large uncertainties in these calculations, the most likely peak date is 1970 +- 5 years.
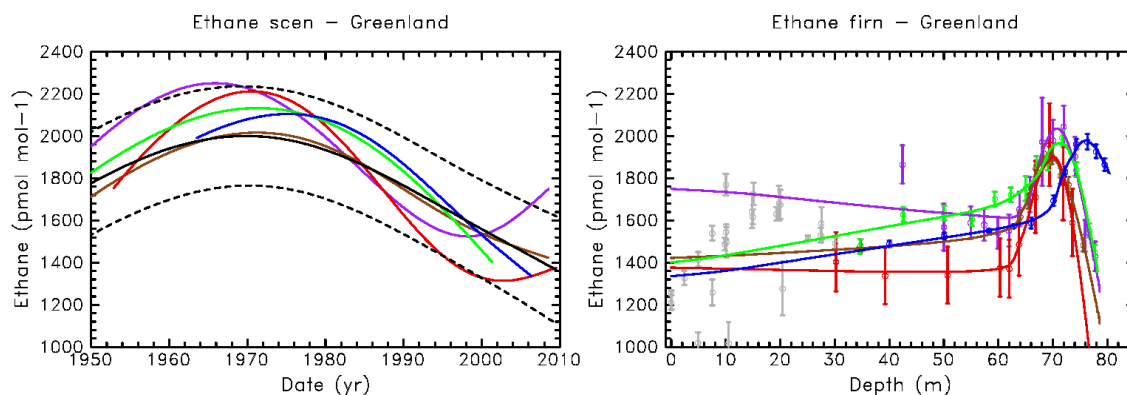
Reply Figure 1.
Ethane history reconstruction and depth profiles from the NEEM data set as well as incorporating the data from NGRIP and Summit. The colored curves are the single borehole constrained scenarios and results in firn (NEEM-EU: purple, NEEM-US: brown, NEEM-09: red, NGRIP: green, Summit: blue). The black lines in the left graph show our best guess scenario from the 3 NEEM boreholes.

While we consistently determined an earlier peak time in our modeling runs, our determined ethane peak time and the Worton et al. and Aydin et al. results overlap within the uncertainty estimates of these studies. Consequently, we agree with the reviewer that the uncertainties in the exact ethane peak dates are relatively large. We added a statement to this regard in the revised manuscript.

18. page 13014, line 28 - Apart from the greater number of species at NEEM, I would expect that having used 14CO2 for NEEM calibration (as described in Witrant et al 2012) would have been particularly helpful here because the depth profile for the NMHCs are similar to 14CO2 with a peak in the lock-in zone.

This is an interesting point. There are two species showing a sharp peak in the deep firn that can be used for tuning of NEEM-EU diffusivity: CH_3CCl_3, peaking at ~ 65 m depth, and $^{14}CO_2$, peaking at ~ 70 m depth. NMHC peak at various depths in (or close to) this depth range. However, CH_3CCl_3 and $^{14}CO_2$ were not

measured in air extracted from the NEEM-US and NEEM-09 boreholes, and their diffusivities are constrained by fewer gases than for NGRIP (Witrant et al., 2012 and Zuiderweg et al., 2013). On the other hand, the overall consistency between the NMHC scenarios reconstructed from the three individual NEEM boreholes suggests that the diffusivity tuning is not a critical parameter for NMHC (much less critical than for $^{13}CO_2$ or $^{13}CH_4$, Buizert et al. (2012), Sapart et al. (2013)).

19. page 13015, line 23 - do you mean "reflect a *recent* slowing down in the ethane decline rate"?

We replaced the sentence with:

"Notably, the peak ethane firn values in the Worton et al. and in our study are similar. Consequently, this difference in ethane decline rate possibly arises from the differences in the modeling methods used in the reconstructions, or the fact that our observations include 7-8 years of more recent data, which the data from those years potentially pushing the overall record towards a slower rate of decline. "

20. page 13015, line 24 - "seeen"

Corrected.

21. page 13015, line 24 - the network flask record is so short and has significant interannual variability, and the firn records lose the top 40m of measurements due to seasonality - can you really conclude much from the comparison?

Figure S3-a (scenario reconstruction from NEEM + NGRIP) suggests no significant discrepancies between individual records in the upper firn and a nearly constant trend after ~1990 within the margins of uncertainty of this determination. The network data provide two comparisons. 1. Mean annual atmospheric mole fractions in the atmosphere are compared with the results of the firn air retrievals, and 2. Trends from the firn air modeling are compared with trends derived in the network data. We agree that the network data record is somewhat short for a comprehensive trend comparison, but these data are the best we have at our hands, and we find the general lack of disagreement between the two data sets of high interest and added value for this discussion.

22. page 13015, line 27 - Simpson et al show a trend in their fig 2b for 48.6-90 deg N, and it is plotted at the high northern latitudes and appears to match the trend in the data there (as far as it is possible to tell from their figure). Could you use this rather than 30-90N, or is it possible to find the trend from the Simpson et al data for the high latitudes (the first author on this paper is a coauthor on Simpson et al)? Any of these estimates are probably significantly lower than the other trend estimates, and the discussion on page 13016 (particularly lines 3-10) seems unnecessarily complicated, and would benefit from being simplified.

The trend for the UCI data, for 48.6-90°N, reflecting the black line in Figure 2b of Simpson et al., 2002 is -12.2 ± 1.4 pptv y^{-1} (1 sigma), very similar to the -12.4 ± 1.3 pptv y^{-1} that we cited in the paper for 30-90N.

The discussion on page 13016 was reworded to:

The ethane declines seen in the NEEM, North GRIP, Summit, and in the ambient monitoring network data are all larger, by a factor of ~2-3. NMHC atmospheric mole fractions show a strong latitudinal

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gradient (Helmig et al., 2009; Simpson et al., 2012) and with highest mole fractions observed at high latitudes. Consequently, the three firn air sites and arctic network ambient monitoring sites, all located > 67_ N, are where global atmospheric NMHC mole fractions are the highest. These areas, showing the overall highest atmospheric levels are expected to show overall higher absolute rates of decline and consequently be sensitive regions for observing changes in atmospheric NMHC. The latitudinal gradient of ethane is ~30% between 30–70° N (Helmig et al., 2009; Simpson et al., 2012). This gradient is smaller than the differences seen in the ethane decline rate seen in the Arctic and the Simpson et al. (2012) results. Consequently, the smaller decline rate seen by Simpson et al. probably again reflects the different air mass and source region representation of these data sets, i.e. the stronger influence of Asian emission trends on the Pacific Transect data versus a stronger North American and European signature in the Greenland data.

23. page 13015, line 29 - is it appropriate to translate the trend to an earlier period when we know that the trend goes to zero and changes sign as you go back in time before 1984?

Yes, we agree, there is uncertainty in this statement. This sentence was deleted.

24. page 13016, line 3 - be clear here, 200% larger sounds like it could be 3 times the size. Could say "The ethane trends at ... are all on the order of 2-4 times the size of the trend seen by Simpson et al."

Sentence was changed to:

"The ethane trends seen in the NEEM, North GRIP, Summit, and in the ambient monitoring network data are all on the order of 2-3 times the size of the trend seen by Simpson et al."

25. page 13016, line 24 - this is a bit confusing, when does the <1 refer to?

Sentence was changed to:

"Aydin et al. (2011) concluded that global ethane emissions from fossil fuel sources have dropped from its peak value of 14-16 Tg yr^{-1} to 8-10 Tg yr^{-1} and that these changes were accompanied by an increase of biomass burning emissions of < 1 Tg yr^{-1} in 1950 to ~3 Tg yr^{-1} by 2000, and then declining to 2 Tg yr^{-1}. "

26. page 13027, line 3 - Simpson et al 2012 is in Nature not Nature Geoscience.

Corrected.

27. Page 13030, Table 2 caption - "Average last three columns list data reconstruction averaged over years ..." doesn't make sense to me.

Yes, somehow the Table caption got messed up during the print setting. The corrected table caption will read:

Table 2. NMHC concentration trends averaged over the years 1985-2000 from the firn air analyses and trends derived from the 2006–2011 arctic site flask network data (mean of individual slopes determined for five sites ±1-☐ standard deviation of the mean) in comparison with results from three other recent NMHC trend determinations.

28. Page 13030, Table 2 - put all superscripts on the references, instead of some on the data.

Corrections will be made as suggested.

29. Fig 7 - put a) and b) into captions, or better still, could 7a and 7b be combined into one figure? Same for Figs S-1 and S-3 in the supplement?

We prefer keeping these figures as they are as we fear that combining them would make the figures too cluttered, and individual panels too small and difficult to view.

30. Fig 9 - It would be easier to compare the panels if i-Butane also started from 1940. In the caption, should refer to Fig 3 not Fig 2.

Corrections were made as suggested.

31. Fig 11b - blue and black are a bit too similar, could you make the blue slightly lighter?

Figure 11 was improved according to this recommendation.

32. Fig S-1 - make the solid lines thicker and the dashed lines thinner. 'Dashed' rather than 'staggered' in caption?

"Staggered' was changed to 'dashed'. We experimented with different line styles but found that the current layout did the best job in depicting the features that we intend to show.

33. Witrant et al 2012 missing from reference list

This missing reference was added:

Witrant, E., Martinerie, P., Hogan, C., Laube, J.C., Kawamura, K., Capron, E., Montzka, S.A., Dlugokencky, E.J., Etheridge, D., Blunier, T., and Sturges W.T.: A new multi-gas constrained model of trace gas non-homogeneous transport in firn: evaluation and behaviour at eleven polar sites, Atmos. Chem. Phys., 12, 11465-11483, 2012.

34. The NMHCs are sometimes referred to using their names in figures (eg fig 9), other times using their formulas (eg Fig 7), this should be made consistent.

All figures were corrected and now all use the compound name.

Interactive comment on "Reconstruction of Northern Hemisphere 1950–2010 atmospheric non-methane hydrocarbons" by D. Helmig et al.

Anonymous Referee #2
Received and published: 14 June 2013

The work under review by Helmig et al. presents a reconstruction of non-methane hydrocarbons (C2-C5) from NEEM firn air and direct atmospheric sampling. Their reconstructions for the last 60 years show clear atmospheric trends for all species, with NMHC mole fractions peaking in the 1970s to early 80s. Both the analytical work and firn air transport modeling are of good quality, giving confidence in the reconstructed atmospheric histories. Although well structured, the interpretation/discussion of the data can still be improved in terms of focus, length and clarity. I think the work should be published in ACP after only some minor revisions, as listed below. I list only last two digits of all page numbers.

Comments

1) In section 3.2 the seasonality is evaluated by repetition of the mean seasonal cycle. Fig 3 makes it clear that not all years are created equal. So why not just feed the raw timeseries into the model (perhaps with averaged cycles placed in front)? This might explain (part) of why the 2009 data look so much different from the 2008 data.

We are not overly optimistic about how much this would improve the results because the firn and atmospheric data sets are not from the same site. Besides the geographic difference the non-continuous nature of the flask sampling introduces another uncertainty as these cannot capture the fine scale temporal variability, which could be constrained only by "continuous" measurements at the firn drilling site.

2) Throughout the text references are made to the lifetime of the species. Could they be listed in a table? (E.g. add to table 1, or make a new one).

NMHC lifetimes were included in the new Table 1.

3) Most of the NMHC have summer concentrations that are only 10% of the winter concentrations. So that means that roughly 90% of the NMHC molecules found in the deep firn entered the snowpack during the winter months. This makes your reconstruction strongly biased towards winter. Would such a winter bias have any consequences for the (interpretation of) NMHC ratios that you present?

We have explored the possibility of a small (meteorological) winter bias for CO (Petrenko et al., 2013) and have done that test of comparing the results of the forward firn model constrained with a monthly or annual mean atmospheric trend for all NMHC (as well as CO and its stable isotopes) and never saw significant differences below ~40 m depth.

4) In Fig 10, could you add uncertainty estimates for the ratios, like in figs 7+8? This can be done easily by dividing the high n-butane by the low i-butane envelope, and vice versa. Also, on pages P09 and P10 you make claims about features in the curves being not statistically significant. Could this be indicated by making those unreliable segments of the ratio curves dashed instead of solid (or grey instead of black)?

2-σ uncertainty margins were added to all three shown variables and the figure caption was changed accordingly. This is the revised figure:
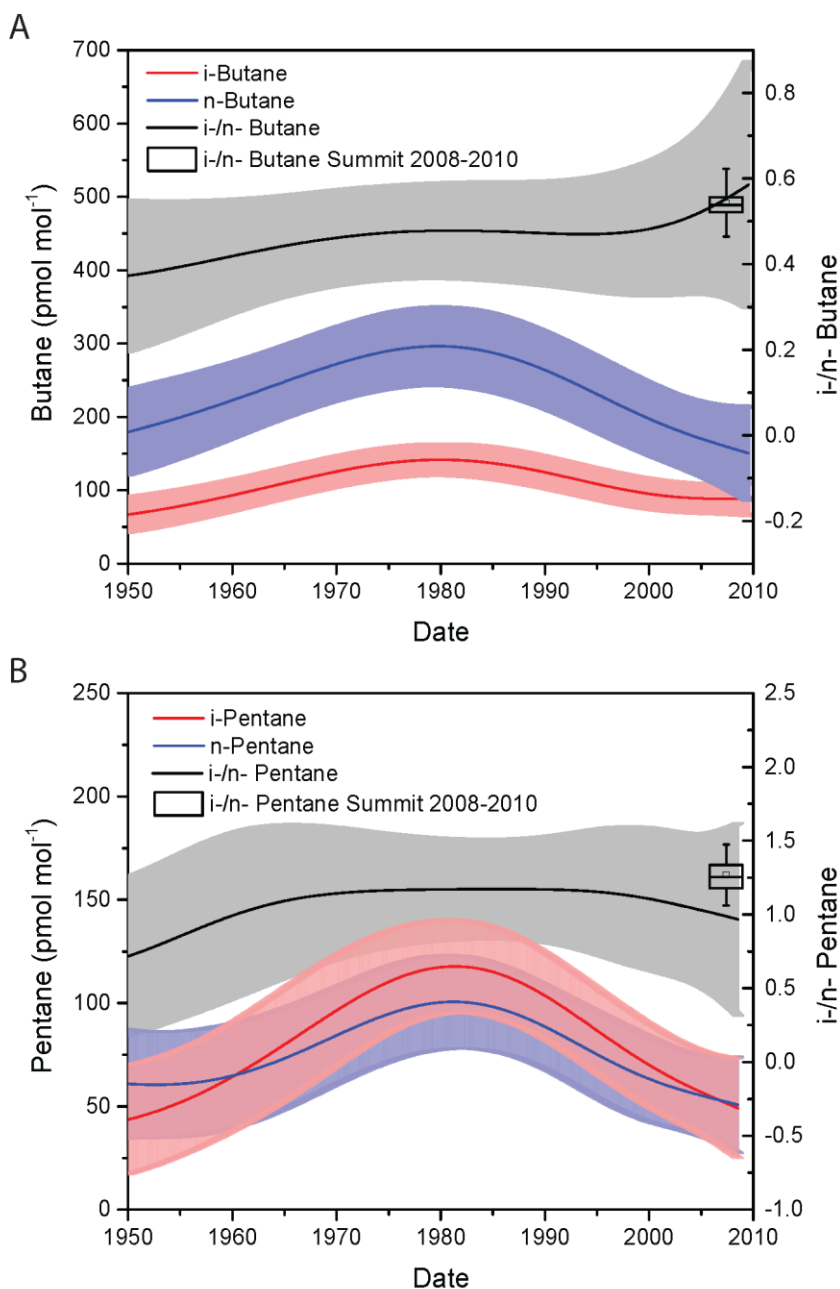
Manuscript Figure 10.
Reconstructed NMHC histories based on the NEEM firn air data for the isomeric butane (A) and pentane pairs (B) with shaded area indicating the 2-σ uncertainty envelopes. Also included in this graph are whisker plots showing the statistical distribution of the isomer ratios (from ~2600 individual measurements) determined for butane and pentane from the in-situ NMHC measurements conducted at Summit during 2008-2010.

5) Overall the discussion section touches on many topics, without reaching firm conclusions (other than the conclusion that proximate sources dominate, which is rather obvious for such short lived species). I

understand there are many uncertainties and complications related to atmospheric chemistry and transport, but still I think the data can be interpreted more clearly without using a full atmospheric chemistry model. Although I don't think a more focused analysis is a necessary requirement for publication, it would make the paper stronger. Points below are merely suggestions: - As the authors state themselves, the NMHC ratios are a very powerful tool in analyzing changes in sources and sinks. The propane/butane propane/pentane etc ratios show an amazing variability with time (Fig 8), yet they are not analyzed. On P17 the authors note that the NMHC are oxidized at different rates, rendering this analysis useless. Each sink mechanism must fractionate the ratios in a predictable way. An increase in an NMHC ratio at NEEM must mean that either the emission ratio increased, or that the oxidation rates changed... Isn't that exactly the type of thing you're trying to tease out? And aren't the i/n ratios affected by a difference in oxidation rate as well?

- Is it possible to visualize the effect of different source/sink mechanisms on the NMHC ratios? E.g a plot with i-butane/n-butane ratio on one axis and i-pentane/n-pentane ratio on the other. Each source has a unique signature, and presumably so does each sink. By plotting the atmospheric ratios, one can visualize what is going on. Alternatively total butane concentration could be plotted vs. i-butane/n-butane, again with the sources and sinks indicated. A similar analysis could be done e.g with butane/ethane ratios vs pentane/ethane, etc.

Motivated by this reviewer comment we conducted a series of further correlation analyses between the determined NMHC trends. Reply Figure 2 shows for an example the ratio of ln([propane]/[ethane]) plotted versus [ethane]. ln([propane]/[ethane]) has been used extensively in studies on photochemical processing and atmospheric transport analyses. The added color coding of the data, indicating the time of measurement, illustrates that the ln([propane]/[ethane]) versus ethane relationship has changed from the 1950s to 2000s as ethane has gone through a rise, plateau, and subsequent decline. Contrary to studies on seasonal oxidation and transport studies (e.g. Honrath et al., 2008; Helmig et al., 2008) in this case this behavior can not be interpreted as a change in oxidation chemistry, as for these data the underlying driver is the change in the relative emissions of these compounds. Similar findings were obtained for other NMHC pairs. A more comprehensive study of this question would require an in-depth review of historical trends of source region emission ratio data for these compounds, which was beyond the scope of our manuscript.
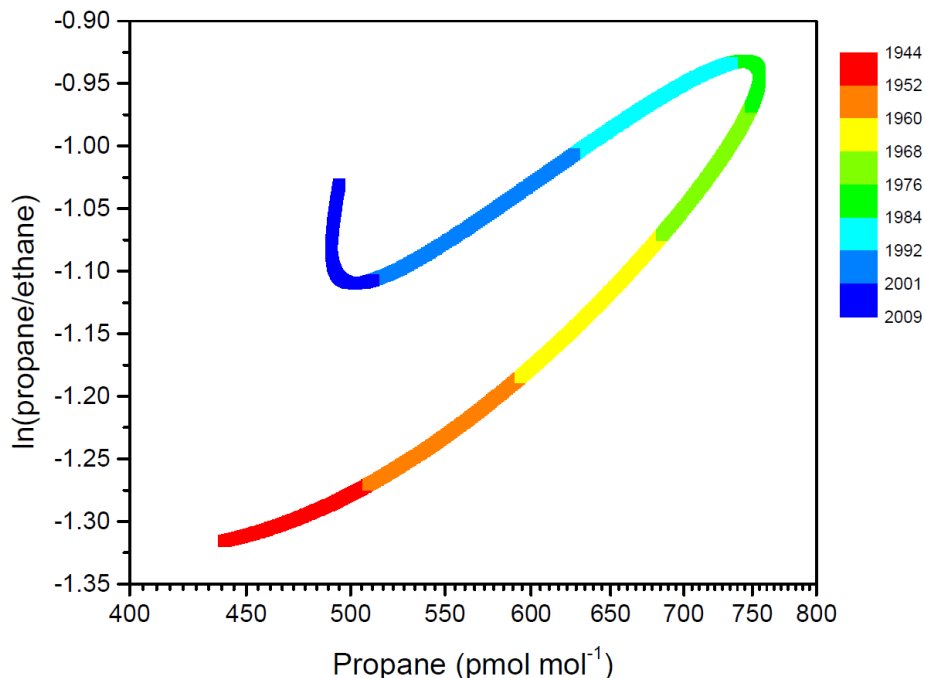
Reply Figure 2.
Evolution of the ln([propane]/[ethane]) versus propane relationship from the reconstructed NEEM NMHC histories color coded by time.

- The authors claim that WE and NA emission estimates (Fig 9) give a (qualitatively) good fit to the NEEM reconstruction. Using published NMHC ratios for BB and anthropogenic emissions, can the emission estimates be turned into NMHC ratios, for comparison?

This is an interesting idea. This work would require an extensive review with compiling speciated source region NMHC data and transport modeling. While we agree that this would be worth pursuing this work goes beyond the intentions and the resources we have for this current manuscript.

6) Overall the paper is rather long. The readership would probably appreciate more concise writing throughout. E.g., much of sections 3.1 and 3.2 (with fig 4+6) could be moved to the supplement.

This research covers quite a number of measurements and comparisons, which dictates the length of the article. This comment is somewhat contrary to statements from the two other reviewers, i.e. reviewer one states: "I believe this study will make a useful contribution, and is generally well written", and reviewer 3 ads: "Although this article is quite long, it is well written." We prefer keeping these sections in the main article.

7) Wording/typos

P93 L10: remove "from air samples"

Corrected as suggested.

P94 L2-3: "extraction of petroleum from geological reservoirs"

Corrected as suggested.

P95 L14-15: "Further evidence linking..."

Corrected as suggested.

P96 L1: "five additional NMHC"

Sentence was changed as suggested.

P96 L26: Note here that filling the flasks through the sampling line does not mimic possible leaking and outgassing from the bladder itself.

Sentence was changed to: "Flask flushing and filling procedure for these tests mimicked normal sample collection, except consideration of possible leaking and outgassing from the bladder."

P97 L8: Don't the samples have a -30 dewpoint already? (they were pumped from -30C firn!).

Yes, the reviewer is right. Even more so, not only were they pumped from a -29°C firn, but the air was also passed through a magnesium perchlorate drying trap at the time of sampling. The sample drying to a -30°C dewpoint is a standard procedure of the analytical system that all samples, standards, and blanks are subjected to in the same manner.

P98 L12-27: Define acronyms UEA, STP, BHT, WCOT, DH, CARIBIC

Acronyms are now spelled out when first used where applicable.

P01 L3: non-sinosoidal. Please elaborate

Text was changed to: "The NOAA-INSTAAR network data were subjected to data curve fitting protocols, filtered for outliers, and fit to a function comprised by a harmonic component and polynomial term as described by (Thoning et al., 1989) and (Masarie and Tans, 1995)."

P02 L12-14 "includes a ... technique" Not sure what this means. This statement can easily be left out, or should be elaborated upon.

The section was rewritten as detailed in the response to reviewer #1.

P03 L28-29: "expected to be a cleaner site with respect to the deposition of trace impurities". Not sure this is necessarily true, depends on e.g. accumulation rate and atmospheric transport patterns. Do you have a reference for this?

Sentence was changed to: ".... and for these reasons is expected to be a cleaner site with respect to the deposition of trace organic impurities that could potentially result in some in-situ production of hydrocarbons. However, we are not aware of any studies that directly compare trace organic content between NEEM and NGRIP firn."

P05 L20: Contrary to your claim, in Fig. 5 the amplitude of the seasonal cycle appears to be smaller for pentane than for butane

The data shown in the graph indeed suggest that the pentane isomers do not drop as low during the late spring to early summer as the butanes. This is quite unexpected. We spent a considerable amount of time further investigating this feature. At the low spring-summer mole fractions there is a larger risk of a contributing error in these GC measurements from co-eluting compounds present at low mixing ratios or with low FID response, such as from halogenated trace gases. However, this effect would not explain why the pentanes, in particular, i-pentane, show a pronounced mid-summer increase, as other than the light alkenes ethene and propene (Helmig et al., 2013) atmospheric mole fractions of organic trace gases are lowest during the spring-summer (VOC), respectively constant throughout the year (long-lived halogenated gases). In the figure below (Reply Figure 3) we compare newer Summit data from in-situ GC measurements and the flask sampling program, again normalized to the seasonal maximum. These two completely independent measurements show a very similar feature in late-spring increases of the pentane isomers. Secondly, this behavior resembles what we show in the manuscript, based on the earlier 6-year flask observations. We do not have a plausible explanation for this behavior at this time but intend to investigate this question further in the future. A comment about this topic was added in the manuscript.
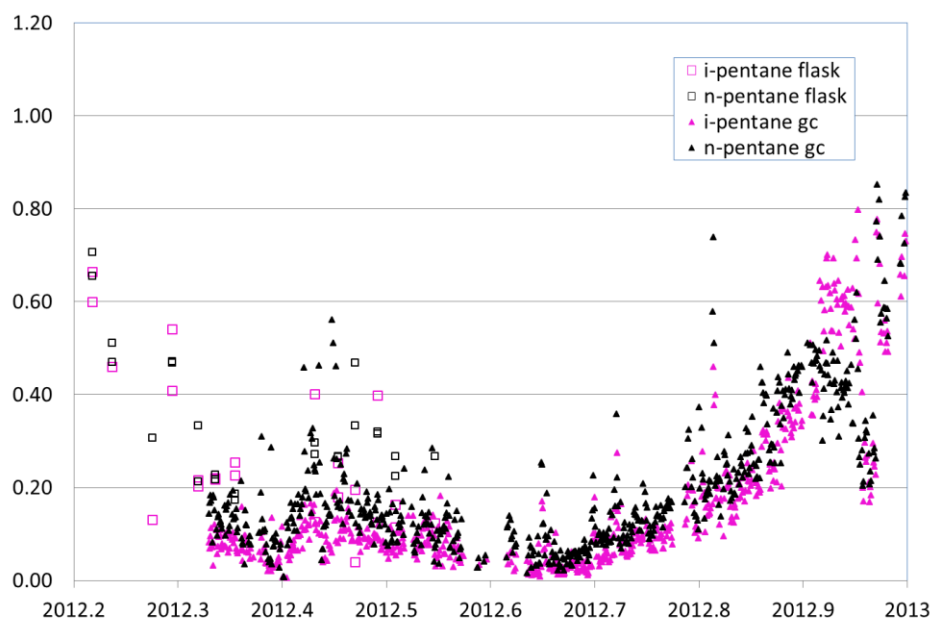
Reply Figure 3:
Seasonal behavior of i- and n-pentane at Summit from in-situ GC measurements and network flask sampling at Summit.

P09 L28: "... this increase in the firn air results is not..."

Text was reworded to: "...in the firn air model results...“

P10 L8: "The decline seen in the firn air results during…"

Text was reworded to: "The decline seen in the firn air model results…"

P11 L24: "The ratio of the butanes … contributions". If the ratio is similar for all sources, then how can the atmospheric ratio change?? Does this imply changes in sink?

What's meant with this statement is that the emission ratio of the two isomeric butanes is relatively uniform between these sources in the data from the most recent 10-20 years. However, this does not imply that the isomeric ratio in butane emissions has been constant during the ~50 year time span covered by the firn data. Unfortunately, earlier ambient measurements of these NMHC species are too scarce to substantiate this hypothesis.

P12 L13: "That study provides …" (THIS study can be interpreted to mean Helmig et al. 2013)

Text was corrected as suggested.

P12 L19: "deemed to be only representative of…"

This statement applies mostly for short-lived compounds. We clarified this by revising this sentence to: "…As the NEEM observations are deemed to be mostly representative of Northern Hemisphere (NH) NMHC emissions and atmospheric composition, …."

P15 L24: "seeen" should be "seen"

This error was corrected.

P20 L21: "These findings suggest that for short-lived species such as NMHC, emissions from …"

Wording was corrected as suggested.

P33 caption Fig3: What is meant by "6yr trend in the data"? Does this mean a running mean with 6 yr window? The entire dataset only spans 6yrs, so the 6 yr mean would be a single number?

The purple trace shows the trend for the period of available data. The figure caption was corrected to clarify this.

Interactive comment on "Reconstruction of Northern Hemisphere 1950–2010 atmospheric non-methane hydrocarbons" by D. Helmig et al.

Anonymous Referee #3
Received and published: 8 July 2013

The work performed by Helmig et al. presents a clear atmospheric history of NMHC (C2-C5) of the Northern Hemisphere reconstructed from HEEM firn air. The reconstructed atmospheric history of

NMHC in this study is compared with direct atmospheric measurements and seems in good agreement. Even the seasonality of the studied NMHCs are reconstructed and seems in good agreement with direct atmospheric measurements. Although this article is quite long, it is well written. I think it should be published in ACP, since it will be a nice contribution to the study of NMHC . I still have some minor comments as listed below.

1. Page 12997 line 8: dewpoint of -30 _C seems rather high to me, please verify.

The INSTAAR preconcentration system dries air samples to a dew point of -30°C, which is a pretty common procedure for NMHC sample preparation for gas chromatographic separation.

2. Page 12998 line 2: The auteur has used an isotopic ratio mass spectrometer for the analyses of 14C. Unfortunately these data are not presented in this work. Furthermore, could 13C also be measured with this instrument? If so, this might be a welcome contribution to source (anthropogenic) identification.

The determined isotopic ratios are not reported in this manuscript; therefore we deleted the second part of this sentence.

3. Page 13000 line 19 to 21: "Further, several points were rejected because mole fractions results deviated from the seasonal cycle behaviour…". Is this a valid reason?

Yes, we consider this to be a valid reason. The seasonal signals for the NMHC (as recorded in the shallowest firn) are quite large and well-enough simulated by our model (see Figure 6) to help in identification of spurious data. The most obvious example of data points rejected using this criterion are MPI-UEA measurements of i-pentane and n-pentane from the 2.5 m depth level (see Figure 2). These were the only data points for these species for this depth level; thus examination of the data points by comparison to data from the same depth from other labs is not possible. However, these data show a trend in the firn that is opposite from the well-understood seasonal signal."

4. Page 13001 line 3: "non-sinusoidal cycle". What do the authors mean by this term and is a sinusoidal cycle not expected for a seasonal cycle?

Text was changed to: "The NOAA-INSTAAR network data were subjected to data curve fitting protocols, filtered for outliers, and fit to a function comprised by a harmonic component and polynomial term as described by (Thoning et al., 1989) and (Masarie and Tans, 1995)."

5. Page 13003 line 8 : "these 6 NMHC suggests similar histories and likely common emission sources of these gases", page 13007 line 9 "ethane peaking significantly earlier" and page 13020 lines 3 to 8 "Ethane emissions are to a lager degree associated with natural gas..". The sources of the various NMHCs described in this study are already known in literature and I find the line of reasoning in this study therefore unnecessary.

The sentence was deleted from the Summary and Conclusion section to avoid this redundancy.

6. Page 13008 line 24: "not statistically significant" . What kind of statistical method has been used here?

Sentence was changed to: "However, the difference in slopes is small in comparison with the uncertainties on the data."

7. Page 1305 line 24 : "seeen" should be seen

Corrected.

8. Page 13019 line 26 to page 13020 line 3: "There is a correlation seen..." I find this part confusing while the authors have only compared ethane to CO and not the other NMHC directly to CO.

We added a reference to Petrenko et al., 2013, who discuss the CO - NMHC correlation in more detail in that paper (Section 5.3).

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