**Atmospheric
Chemistry
and Physics**
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Discussions

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

Anonymous Referee #2

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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

C3617

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.

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)

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?

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)?

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.

- 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?

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.

7) Wording/typos

P93 L10: remove "from air samples"

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

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

P96 L1: "five additional NMHC"

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

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

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

P01 L3: non-sinosoidal. Please elaborate

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

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?

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

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

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

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?

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

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

P15 L24: "seeen" should be "seen"

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

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?