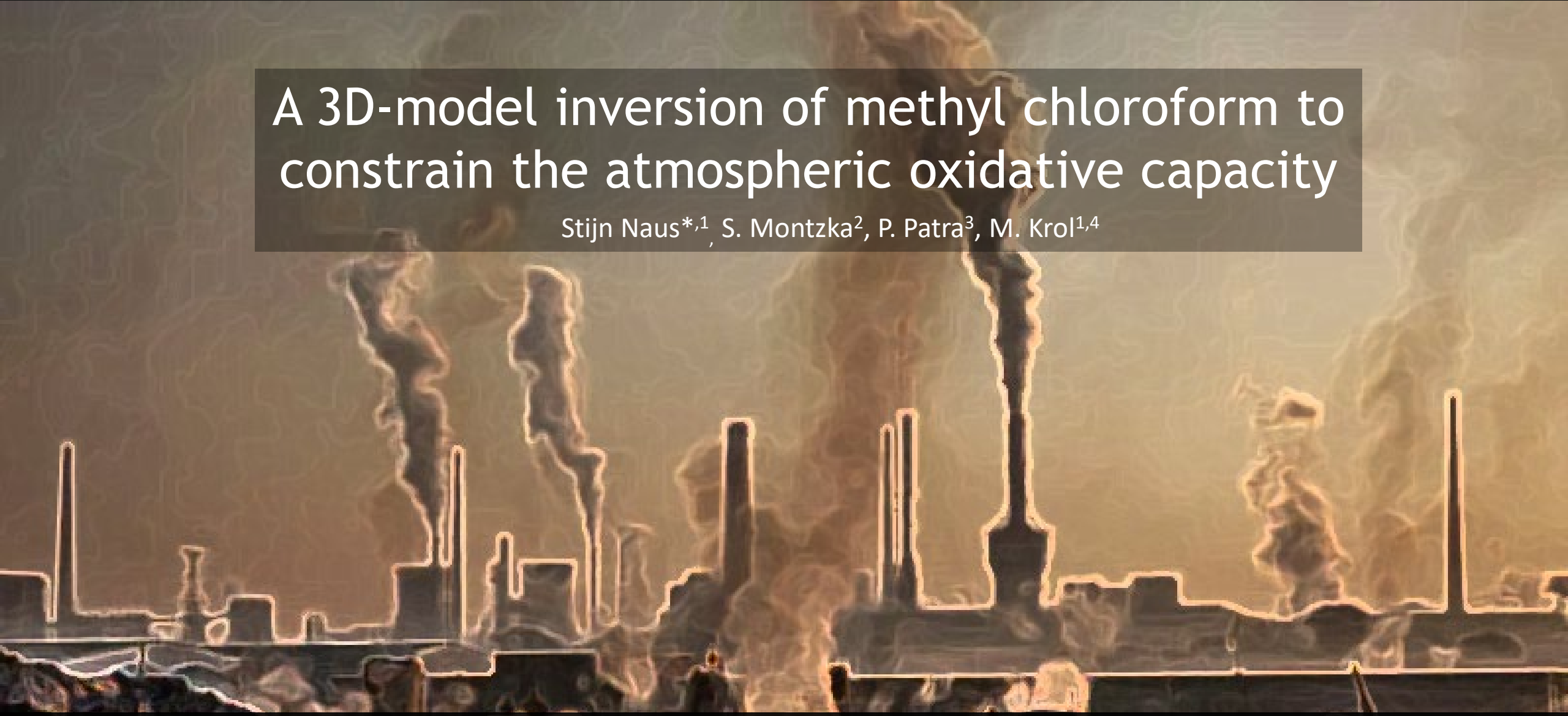
A 3D-model inversion of methyl chloroform to constrain the atmospheric oxidative capacity

Stijn Naus*[,1], S. Montzka[2], P. Patra[3], M. Krol[1,4]



* Corresponding author: stijn.naus@wur.nl

1. Meteorology and Air Quality, Wageningen University & Research, The Netherlands
2. NOAA Earth System Research Laboratory, Global Monitoring Laboratory, Boulder, CO, USA
3. Research Institute for Global Change, JAMSTEC, Yokohama, Japan
4. Institute for Marine and Atmospheric Research, Utrecht University, the Netherlands

100-word summary

OH is a gas central to atmospheric chemistry, involved in the removal of many pollutants. We used methyl chloroform observations to constrain large-scale, long-term OH variability in a global 3D model inversion from 1998 to 2018. We find that:

1. We only need small interannual variability in OH and no trend to reproduce most MCF observations.

2. Interannual variability in OH correlates well with the El Niño Southern Oscillation.

3. However, we underestimate MCF gradients between the tropics and the poles in both hemispheres. This could indicate a partial reversal of the oceanic MCF sink, as hypothesized in Wennberg et al. (2004)*.

* *Wennberg, Paul O., et al. "Recent changes in the air-sea gas exchange of methyl chloroform." Geophysical research letters 31.16 (2004).*

Table of contents

1. Background

Background

- OH is the main atmospheric oxidant
- OH is involved in the removal of a wide variety of pollutants
- As an example, the contribution of OH variations to growth rate variations of the greenhouse gas CH_4 is very uncertain, which greatly complicates interpretation of the CH_4 budget.

Methods for constraining OH

1. Direct OH measurements

   -> Difficult to make, because of low OH abundance and difficult to extrapolate to meaningful scales because of the short atmospheric lifetime of OH (seconds)

2. Bottom-up modelling of chemistry

   -> All atmospheric constituents related to OH can be modeled, but the integrated effect on the global OH abundance hinges on uncertain emission inventories and imperfect understanding of chemistry.

3. Indirect estimates from tracers: Inverse modelling

   -> Variations in OH are derived indirectly from growth rate variations of a proxy tracer

Methods for constraining OH

1. Direct OH measurements

   -> Difficult to make, because of low OH abundance and difficult to extrapolate to meaningful scales because of the short atmospheric lifetime of OH (seconds)

2. Bottom-up modelling of chemistry

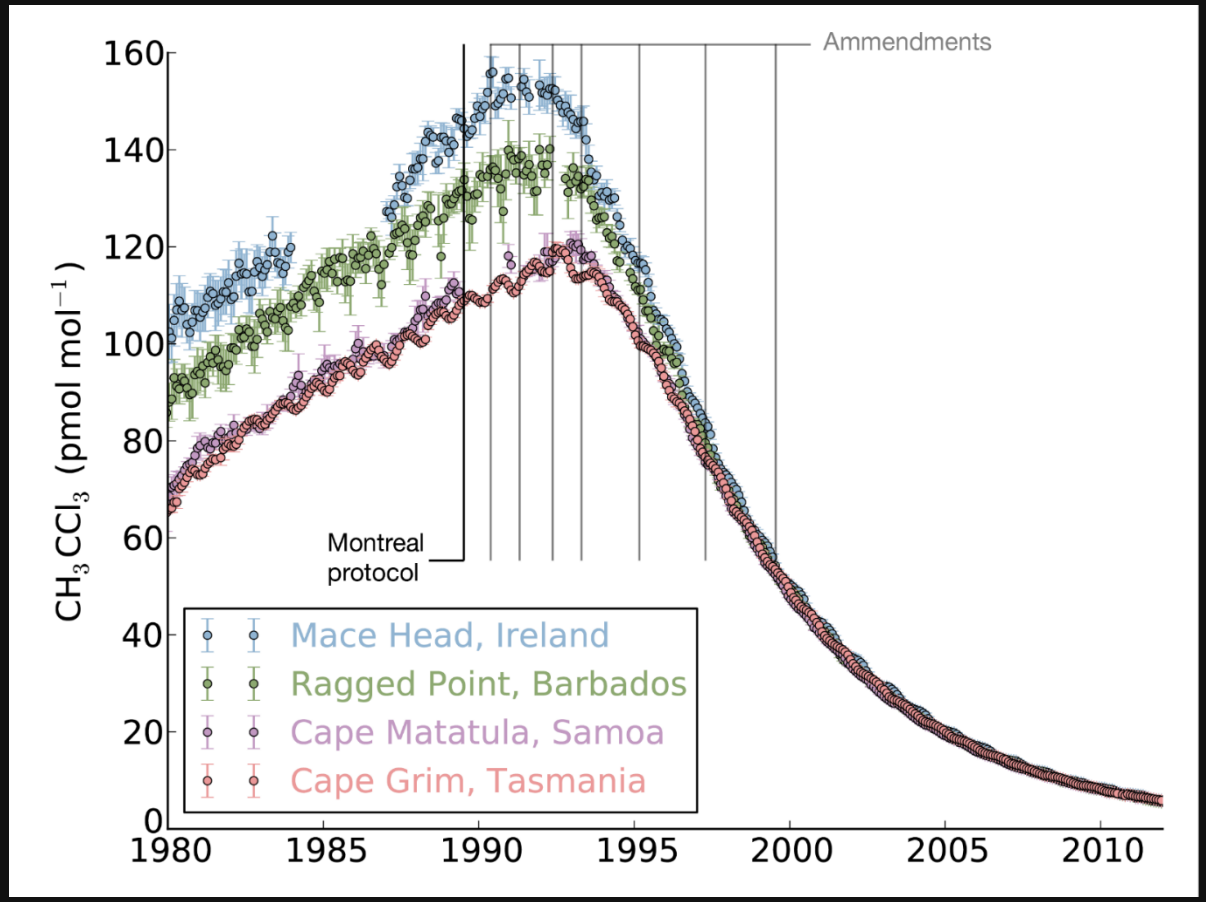
   -> All atmospheric constituents related to OH can be modeled, but the integrated effect on the global OH abundance hinges on uncertain emission inventories and imperfect understanding of chemistry.

3. Indirect estimates from tracers: Inverse modelling

   -> Variations in OH are derived indirectly from growth rate variations of a proxy tracer

   -> This is the method discussed here

Methyl chloroform (CH_3CCl_3 or MCF)



MCF is the tracer most widely used to constrain large-scale OH variations. It's production was banned in the early 90's. Consequently, it's atmospheric budget became dominated by loss processes, mainly oxidation by OH.

In this study, we focus on the 1998-2018 period, where the atmospheric decline of MCF has been relatively constant at ~20%/year, variations in which are (hopefully) closely linked to OH variations.

2. Methods

Set-up of the 3D model inversion

Model configuration

- Transport Model 5 (TM5)
- 6 x 4 degrees horizontal resolution, 25 vertical layers
- Study period 1998 – 2018

Observations

- MCF observations from 12 NOAA surface sites (click here for a map)
- HIPPO and ATom aircraft campaigns for independent validation (i.e. not assimilated)

Inverse system

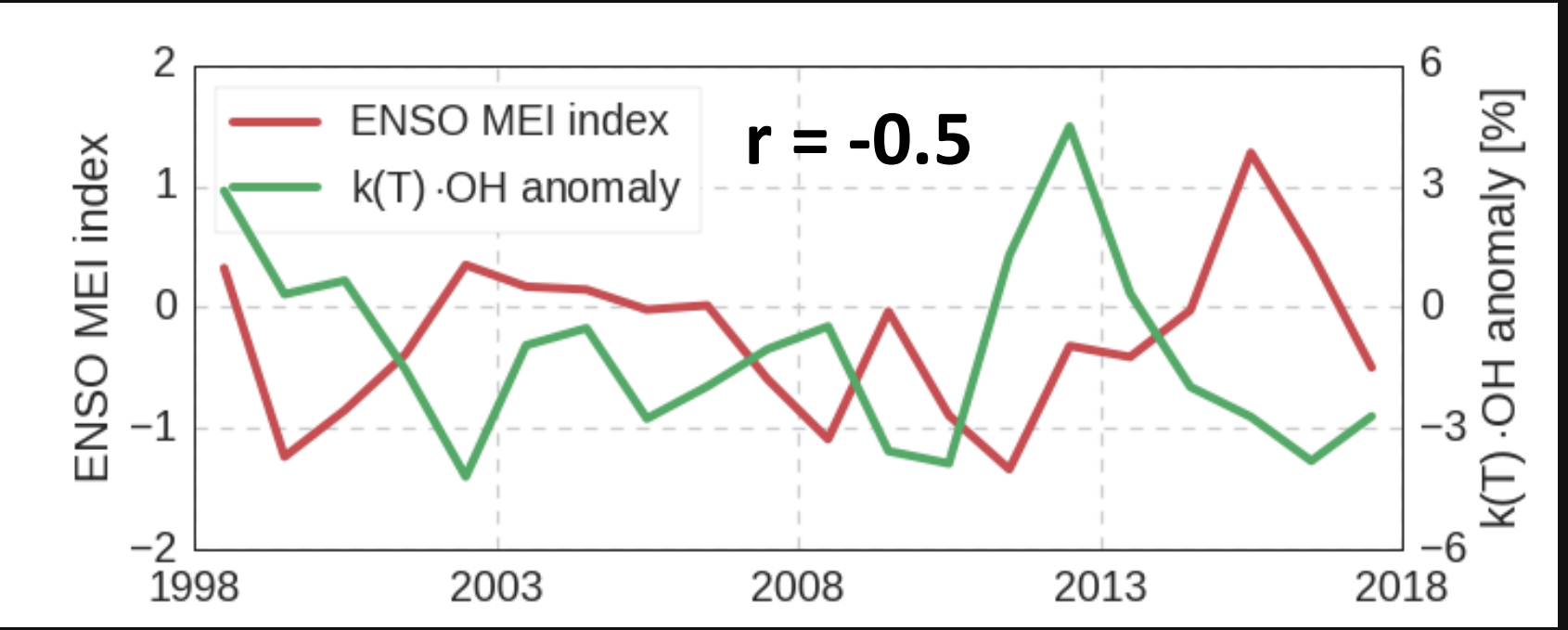
- TM5-4DVAR
- Prior OH field : Spivakovsky et al. (2000) (= annually repeating)
- Prior emissions: TransCom emissions fitted to reproduce global mean MCF
- Both OH and emissions are optimized with long spatio-temporal correlations

3. Results

Variations in global total oxidation

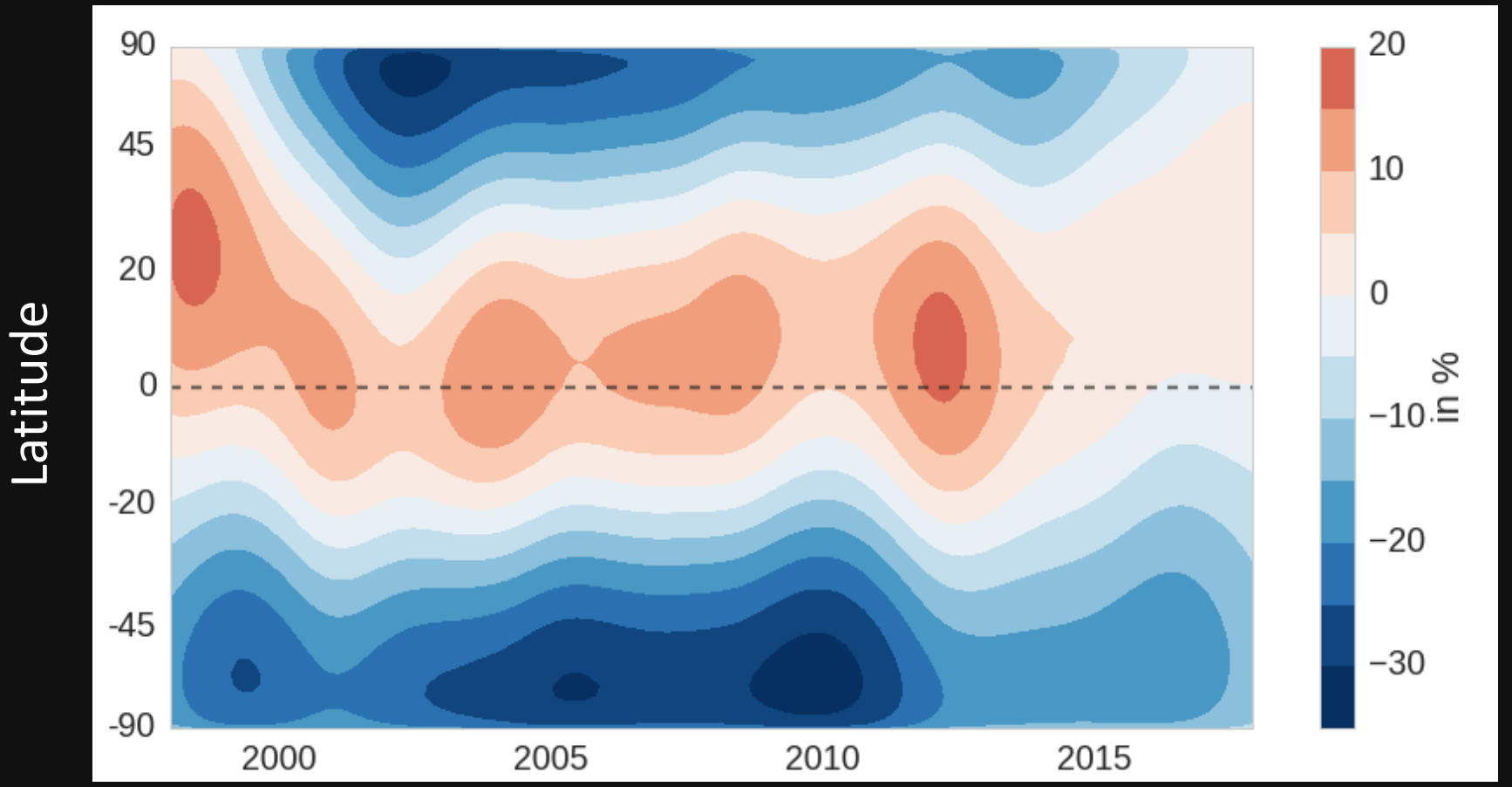
Note: We show variations in k(T) x OH, i.e. effective oxidation of MCF, not variations in OH.

Physical drivers of interannual OH variations



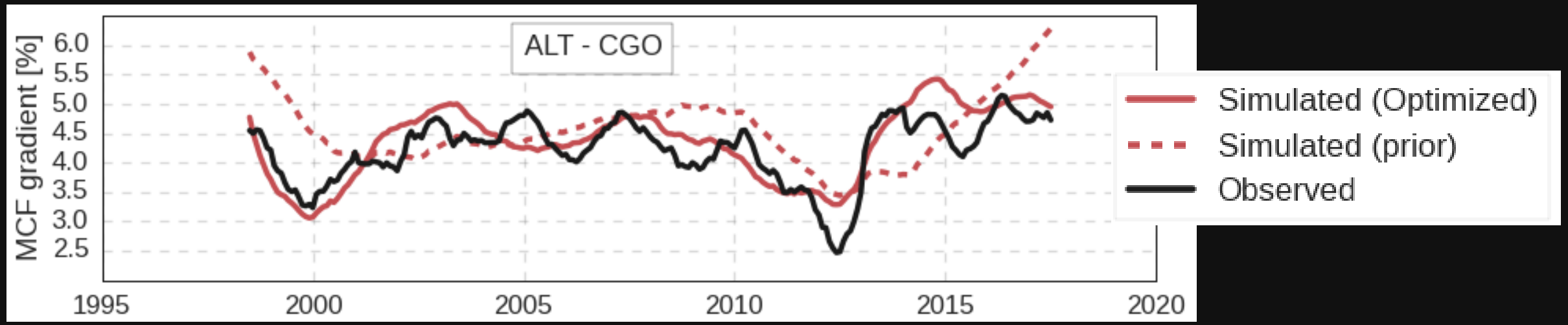
- We find a significant (negative) link between the El Niño Southern Oscillation and derived OH variations. There are various hypothetical drivers for this link, for example:
  - a) More emissions from wildfires during an El Niño event can suppress OH abundance. (Banda et al., 2018)
  - b) Increased NO_x production from lighting during La Niña events can enhance OH recycling. (Turner et al., 2018)
- This correlation is not found, or much weaker, in previous box model studies that miss most transport effects

Hovmöller plot of latitudinal adjustments in OH



- We find strong (up to 30%) adjustments in the latitudinal distribution of OH, with an increase in tropical OH and a decrease in extra-tropical OH. Linked to this result?

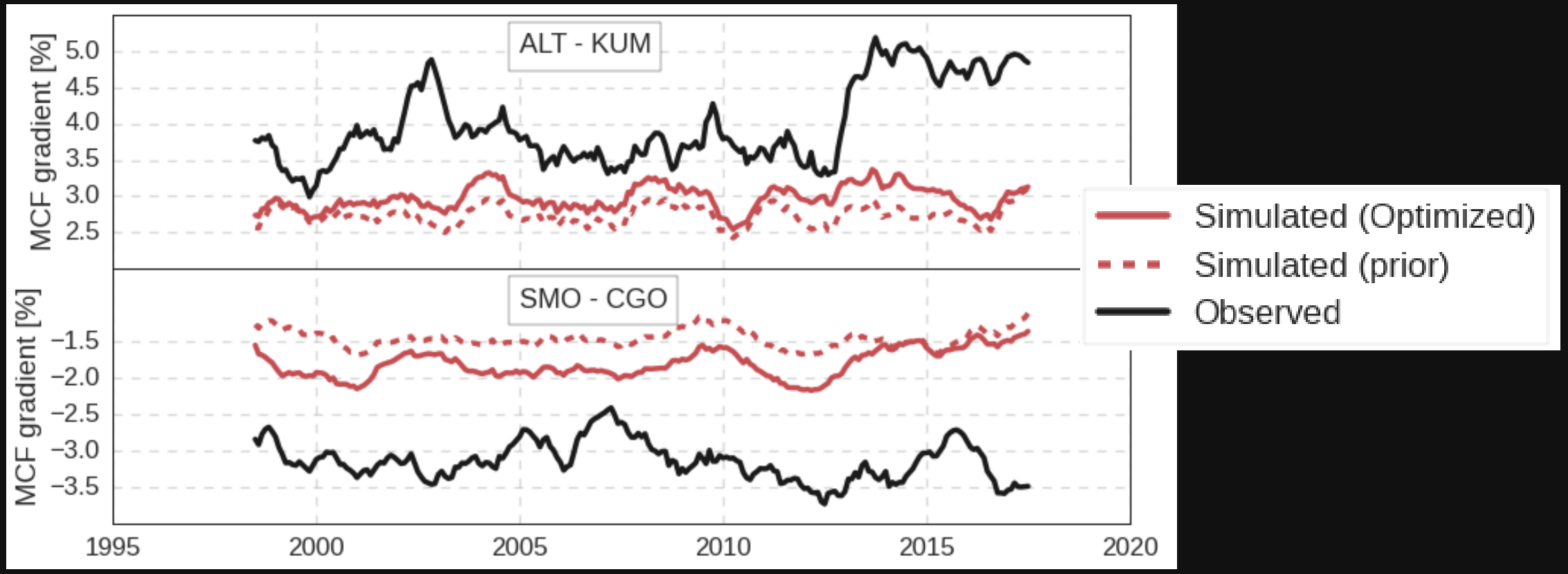
Observations: Gradients between NOAA surface sites



1. Gradients between hemispheres are reproduced well.

Note: Click here for a map of the NOAA surface sites

Observations: Gradients between NOAA surface sites



2. Gradients within hemispheres are underestimated. The inverse system is only partly able to correct with large adjustments in the latitudinal distribution of OH.

Note: Click here for a map of the NOAA surface sites

4. Discussion

Underestimation of intrahemispheric gradients

- The inverse system derives **unphysically large latitudinal adjustments in OH** to correct for the underestimate in intrahemispheric gradients. Even with these adjustments, a residual underestimate remains.

- Alternative (or complimentary) explanations:
  1. **TM5 has too-fast intrahemispheric mixing.**
     -> But we can reproduce intrahemispheric gradients of other trace gases (SF_6, HFC-152a) well.
  2. **A site-dependent measurement bias.**
     -> Measurements for all sampling systems are performed on one central sampling system, so unlikely.
  3. **Changes in the air-sea exchange of MCF.**
     -> Hypothesized in Wennberg et al. (2004), and it fits all the evidence.

Changes in air-sea exchange

- Effective oceanic uptake of MCF, combined with low hydrolysis rates in cold, high-latitude oceans may have resulted in a buffering of MCF that was (/is) gradually released. (Wennberg et al., 2004)

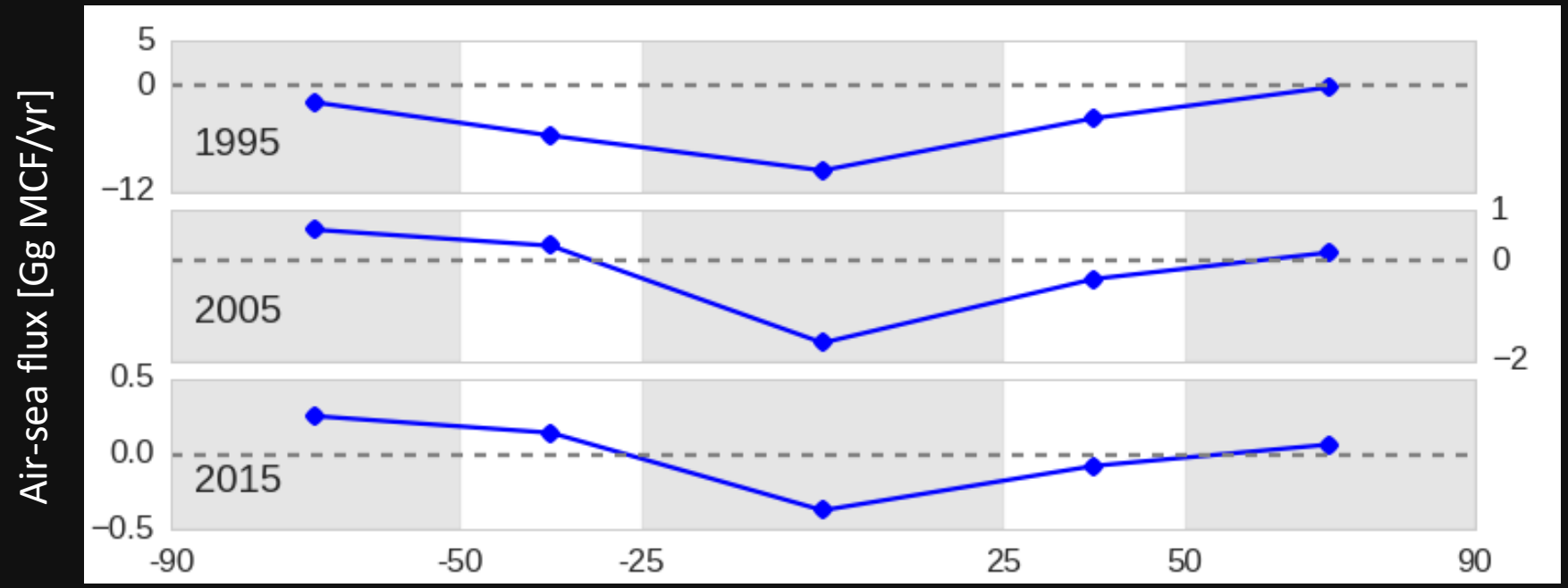


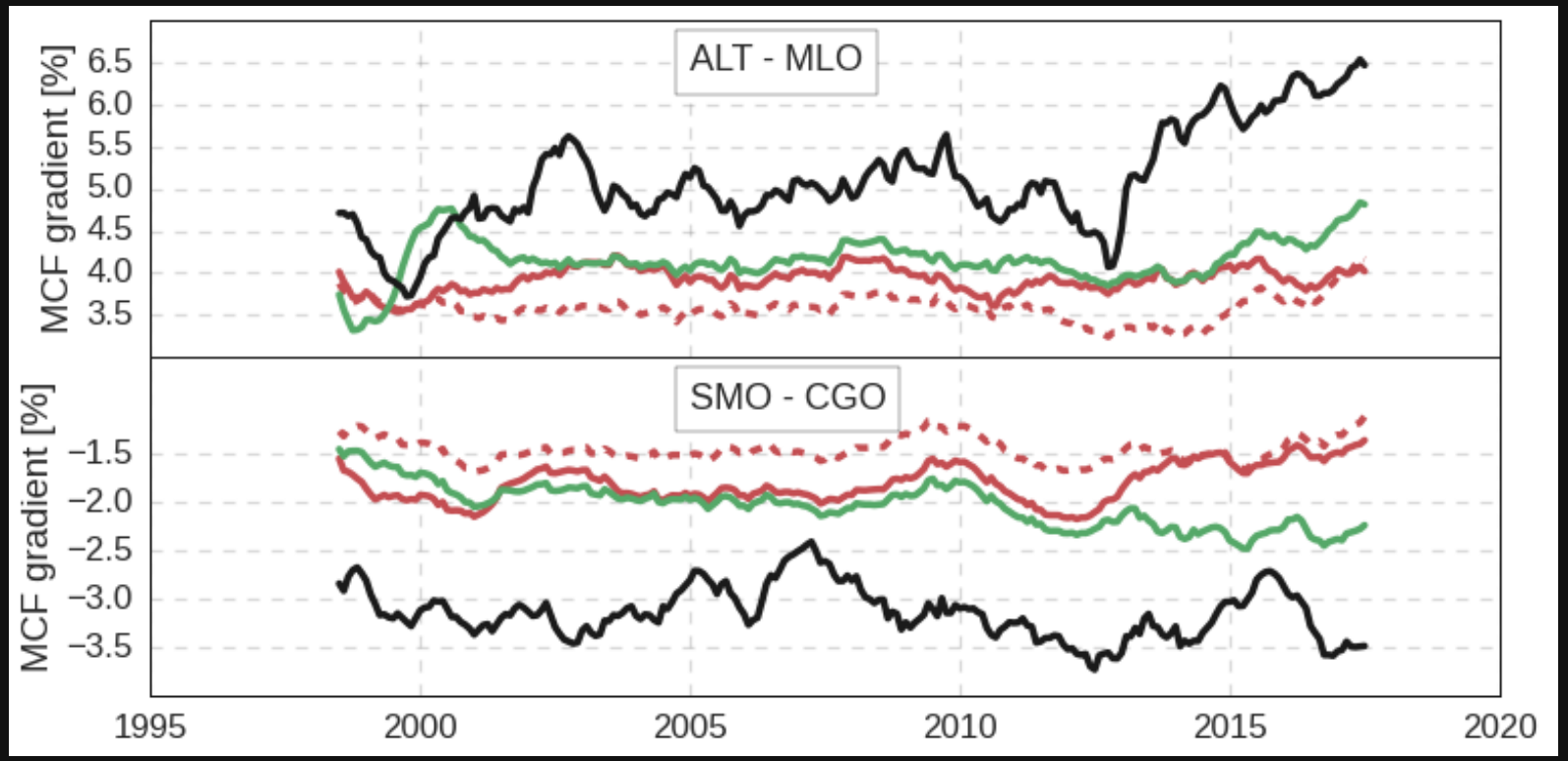
Figure of the air-sea exchange of MCF: Positive is release of MCF, negative is uptake.

Uptake at all latitudes becomes uptake of MCF in the tropics, and release of MCF at high latitudes.

(Data from Wennberg et al. (2004))

Effect of a different ocean flux on intrahemispheric gradients

We performed a forward simulation with the Wennberg ocean flux implemented.
We find that **the intrahemispheric gradients are highly sensitive to the oceanic sink.**
Changing from a first-order ocean sink to the Wennberg flux already reduces the intrahemispheric bias by more than the very large latitudinal (>30%) adjustments in OH.



Note: Since the atmospheric distribution of MCF has a tropical minimum due to OH loss, oceanic release of MCF at high latitudes will deepen the intrahemispheric gradients.

Changes in air-sea exchange: Implications for OH

- Makes it much **more difficult to derive trends** in OH from MCF, since long-term variations in the oceanic flux remain uncertain.

- But the **most likely driver of interannual variations of MCF are still OH variations**. These, we therefore deem a robust property of the inversion.

- Negatively, this finding complicates the use of MCF as a tracer for OH. Positively, it emphasizes the resolving power of a sparse network of internally-consistent, low-frequency observations.

5. Key Findings

Key Findings

1. We have derived a 1998-2018 timeseries of interannual variations of OH that are most consistent with the MCF observational record, in a 3D transport model.
2. Relatively small (~2-3%) interannual variations of OH, with no clear trend, allow for a good fit with most observational sites.
3. The OH variations correlate well with the El Niño Southern Oscillation.
4. A residual underestimate of intrahemispheric MCF gradients seems to be unresolvable with only OH and MCF emission adjustments. We suggest a role for oceanic release of MCF at high latitudes, based on a set of forward simulations.

References

1. Spivakovsky, C. M., et al. "Three-dimensional climatological distribution of tropospheric OH: Update and evaluation." *Journal of Geophysical Research: Atmospheres* 105.D7 (2000): 8931-8980.

2. Nechita-Banda, Narcisa, et al. "Monitoring emissions from the 2015 Indonesian fires using CO satellite data." *Philosophical Transactions of the Royal Society B: Biological Sciences* 373.1760 (2018): 20170307.

3. Turner, Alexander J., et al. "Modulation of hydroxyl variability by ENSO in the absence of external forcing." *Proceedings of the National Academy of Sciences* 115.36 (2018): 8931-8936.

4. Wennberg, Paul O., et al. "Recent changes in the air-sea gas exchange of methyl chloroform." *Geophysical research letters* 31.16 (2004).

6. Supplementary slides

Map of NOAA surface sites that sample MCF