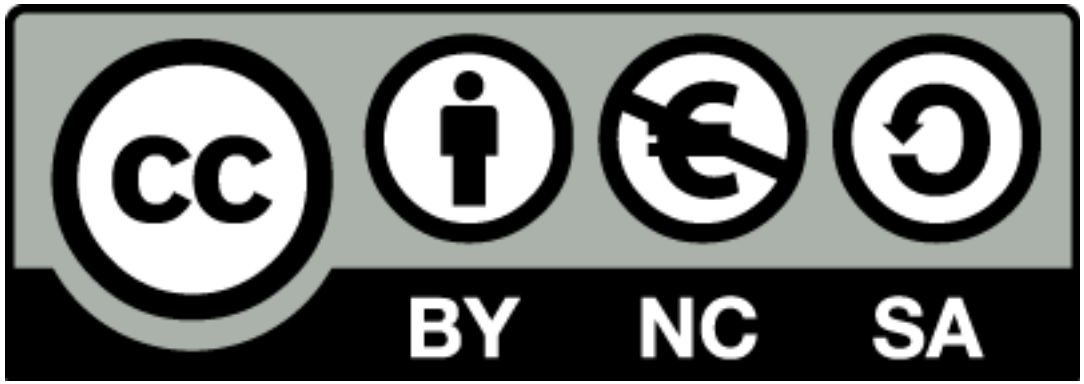
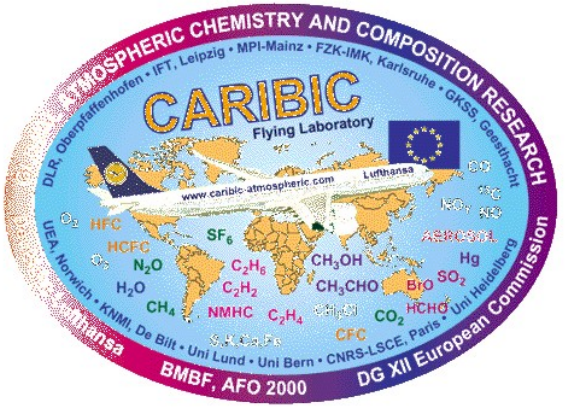
The material that was presented in this presentation was later published in a discussion paper in ACPD, that can be found on:
http://www.atmos-chem-phys-discuss.net/12/589/2012/acpd-12-589-2012.html



CARIBIC based D/H measurements for understanding the molecular hydrogen (H_2) cycle

A.M. Batenburg, T.J. Schuck, A.K. Baker, A. Zahn, C.A.M. Brenninkmeijer, T. Röckmann

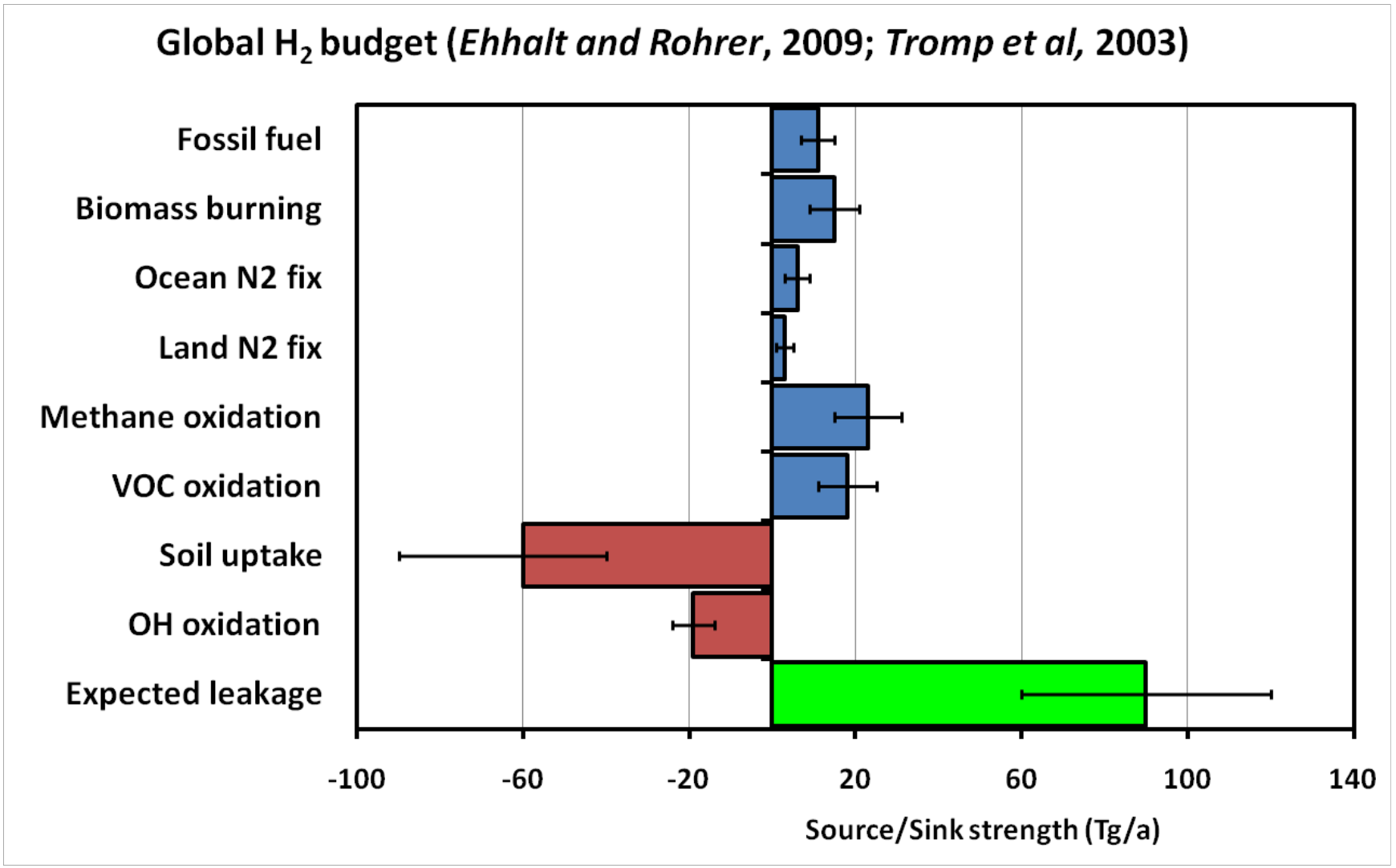
IMAU
Institute for Marine and Atmospheric research Utrecht



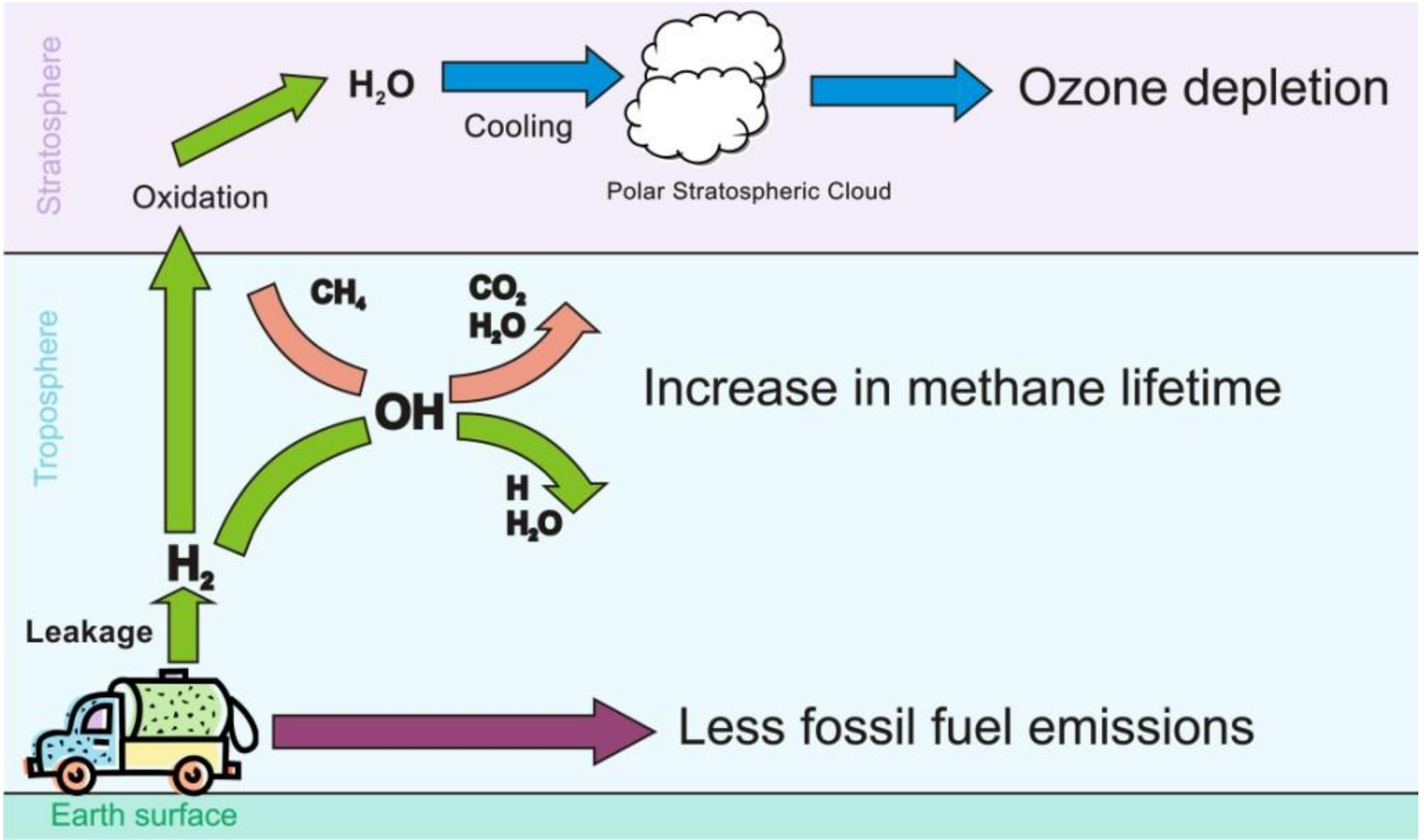
Presentation overview

- **Introduction**
  - * Hydrogen (H_2)
  - * Hydrogen isotopes
  - * Ground station data
- **Results & Discussion**
  - * A first look
  - * Pollution signatures
  - * Lower stratosphere
  - * Summer monsoon
- **Summary**

The atmospheric H_2 budget



Effects of a Hydrogen Economy

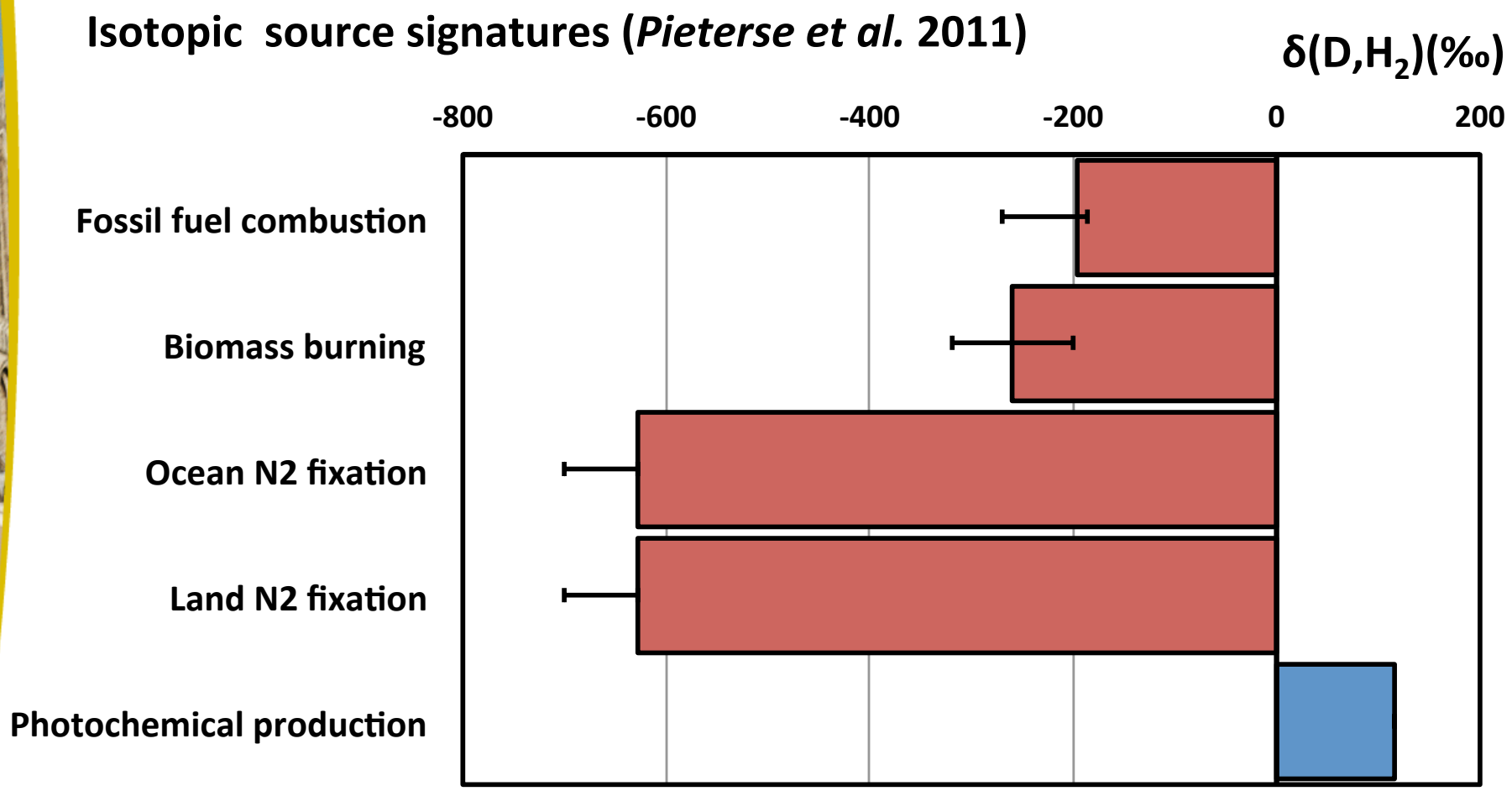


Isotope δ-notation

$$\delta(\mathrm{D},\mathrm{H_2}) = \left(\frac{\left(\frac{\mathrm{D}}{\mathrm{H}}\right)_{\mathrm{Sample}}}{\left(\frac{\mathrm{D}}{\mathrm{H}}\right)_{\mathrm{VSMOW}}} - 1 \right) \cdot 1000‰$$

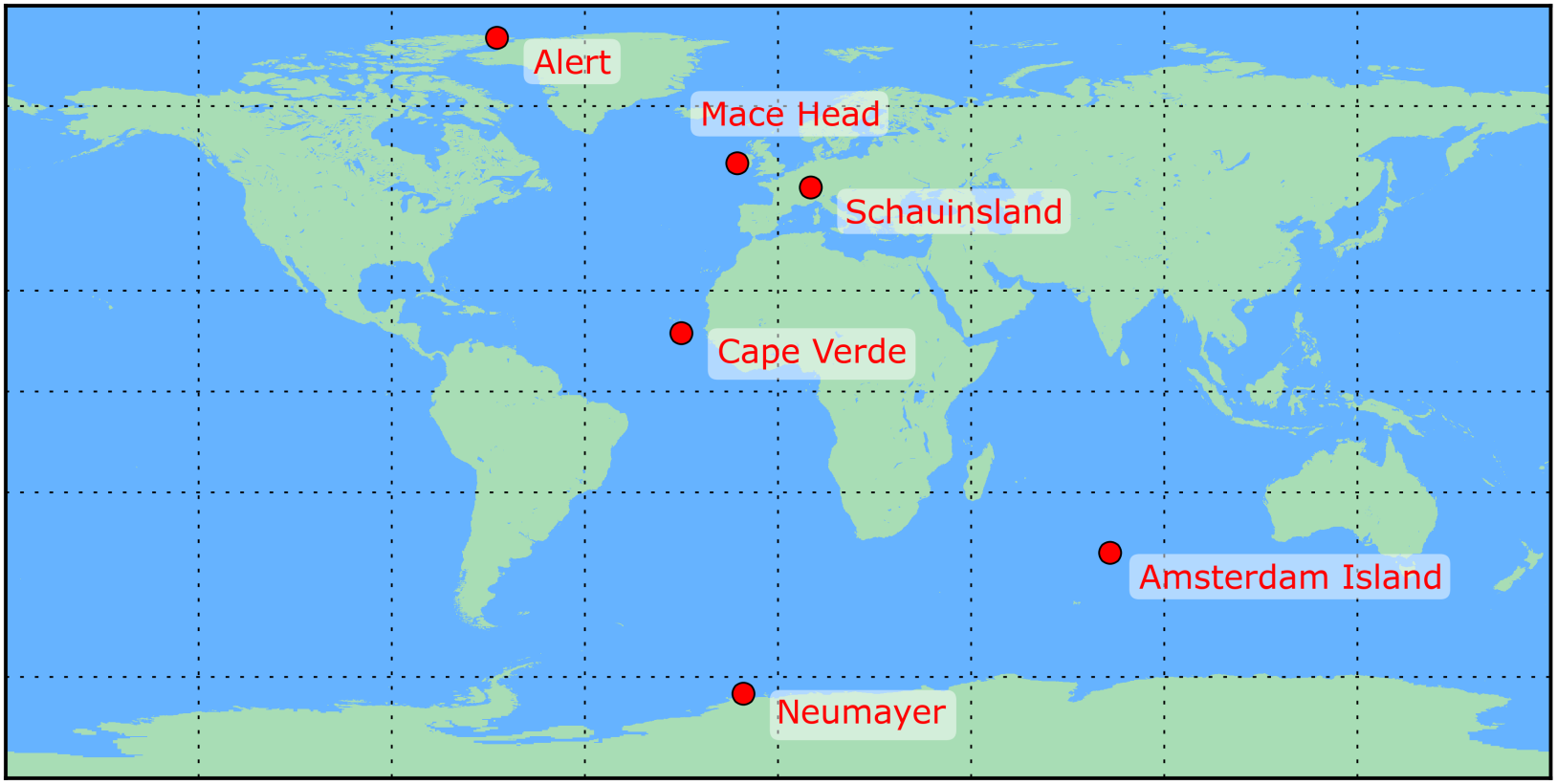
The $\delta(\mathrm{D},\mathrm{H_2})$ value represents the deuterium-to-hydrogen ratio in the $\mathrm{H_2}$ relative to a standard (Vienna Standard Mean Ocean Water (VSMOW))

Isotopic source signatures



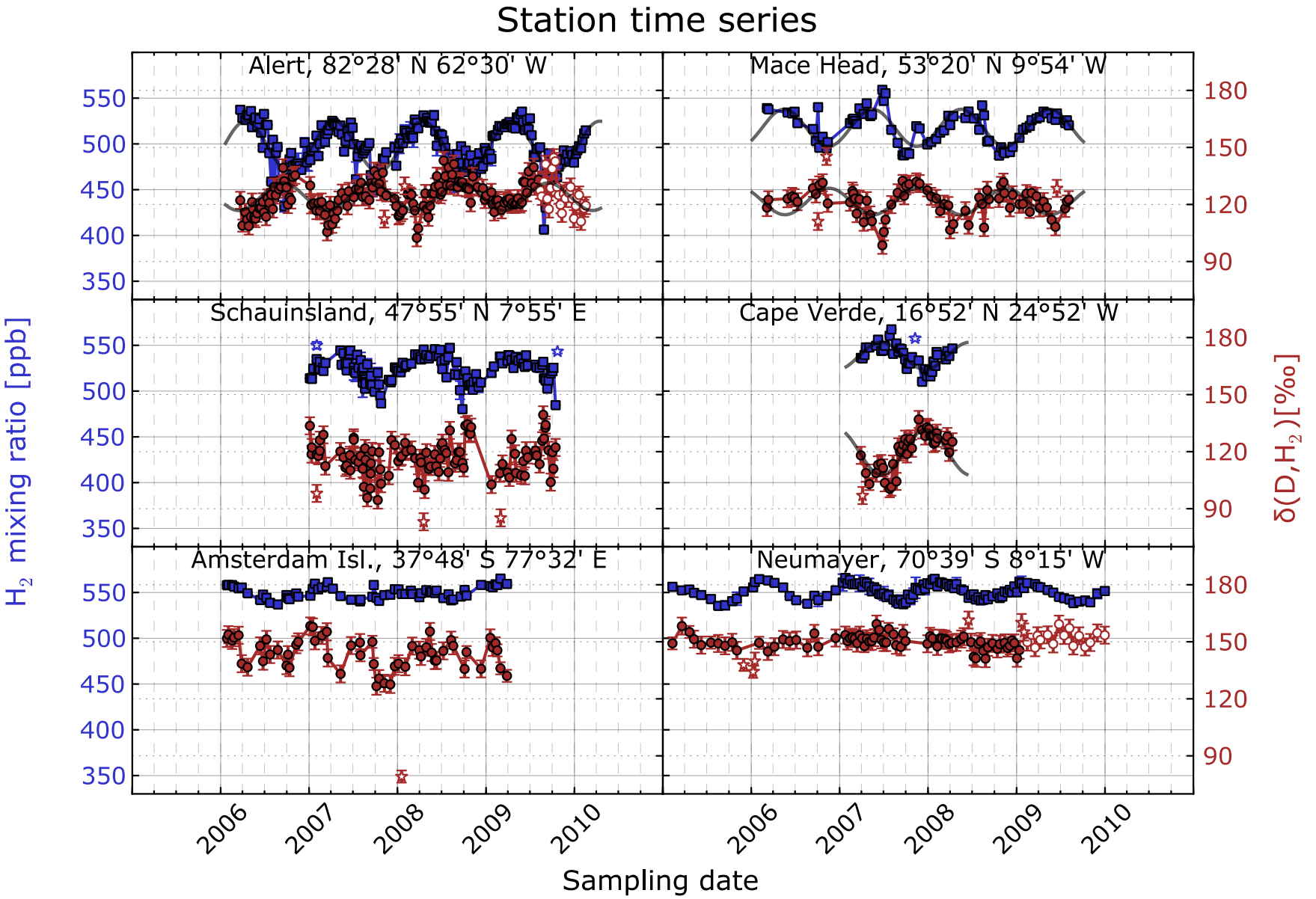
Isotopes can be used to gain information about different sources and sinks.

The EUROHYDROS network



Batenburg et al., 2011
http://www.atmos-chem-phys.net/11/6985/2011/acp-11-6985-2011.html

EUROHYDROS data



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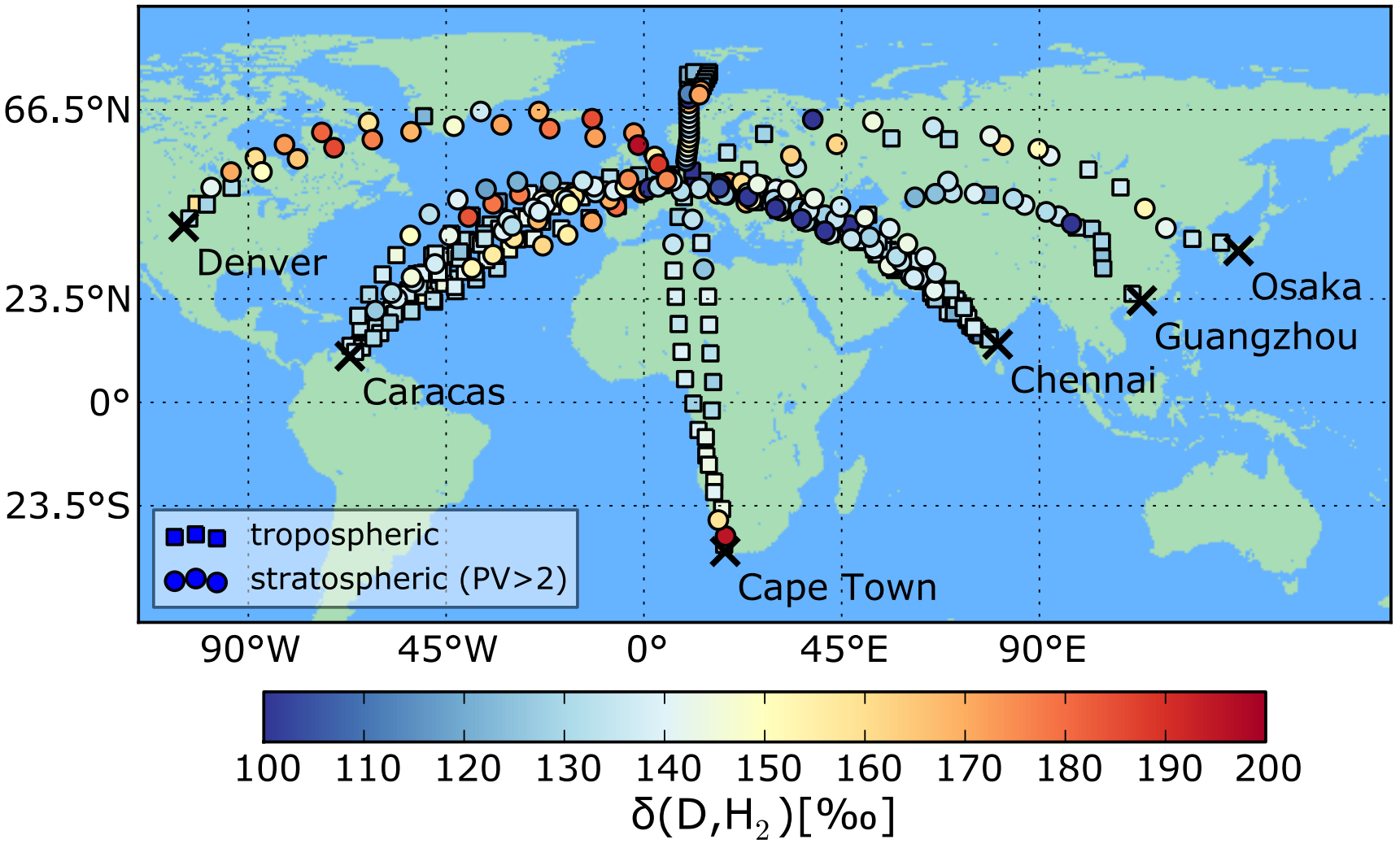
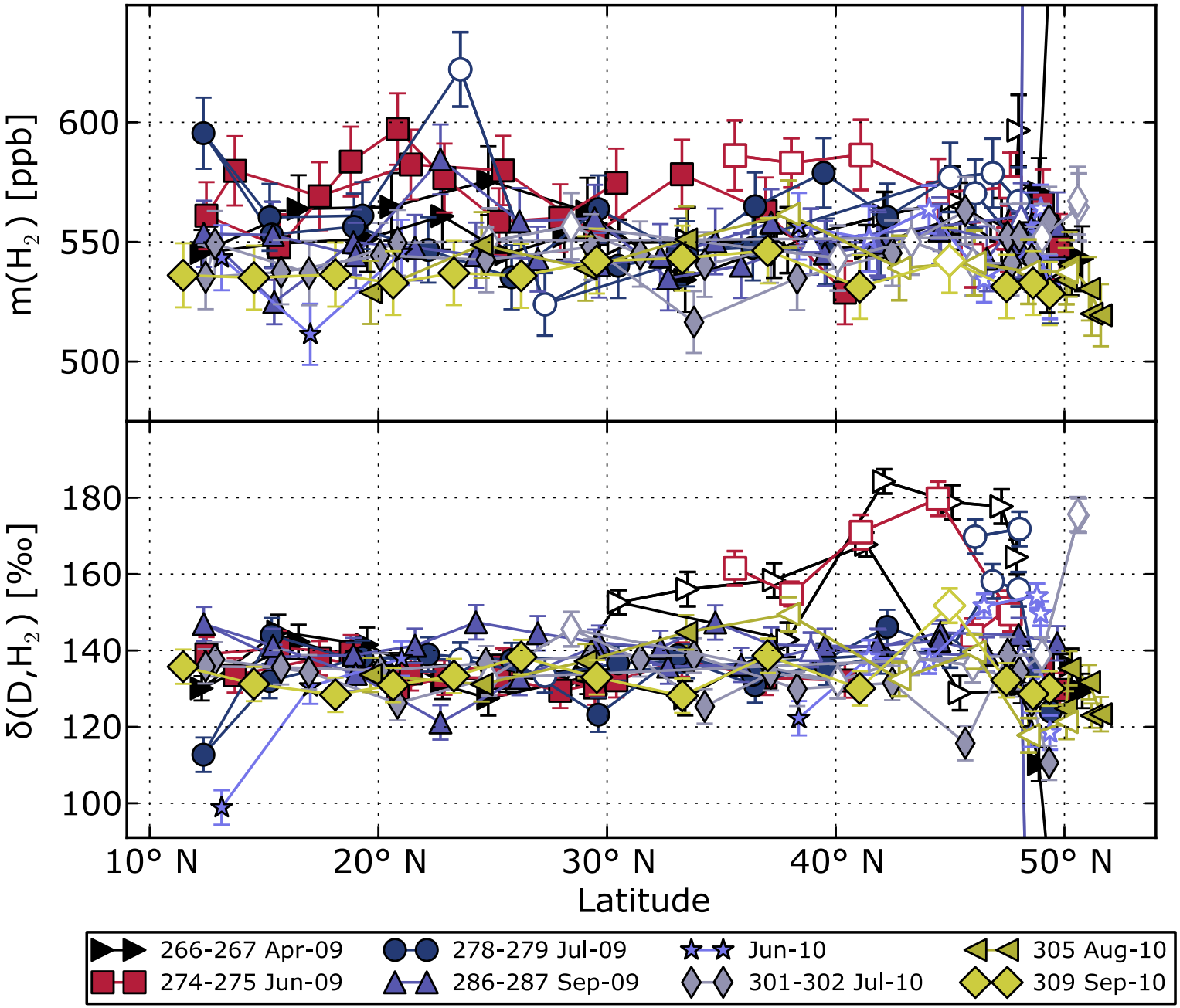
Results: a first look

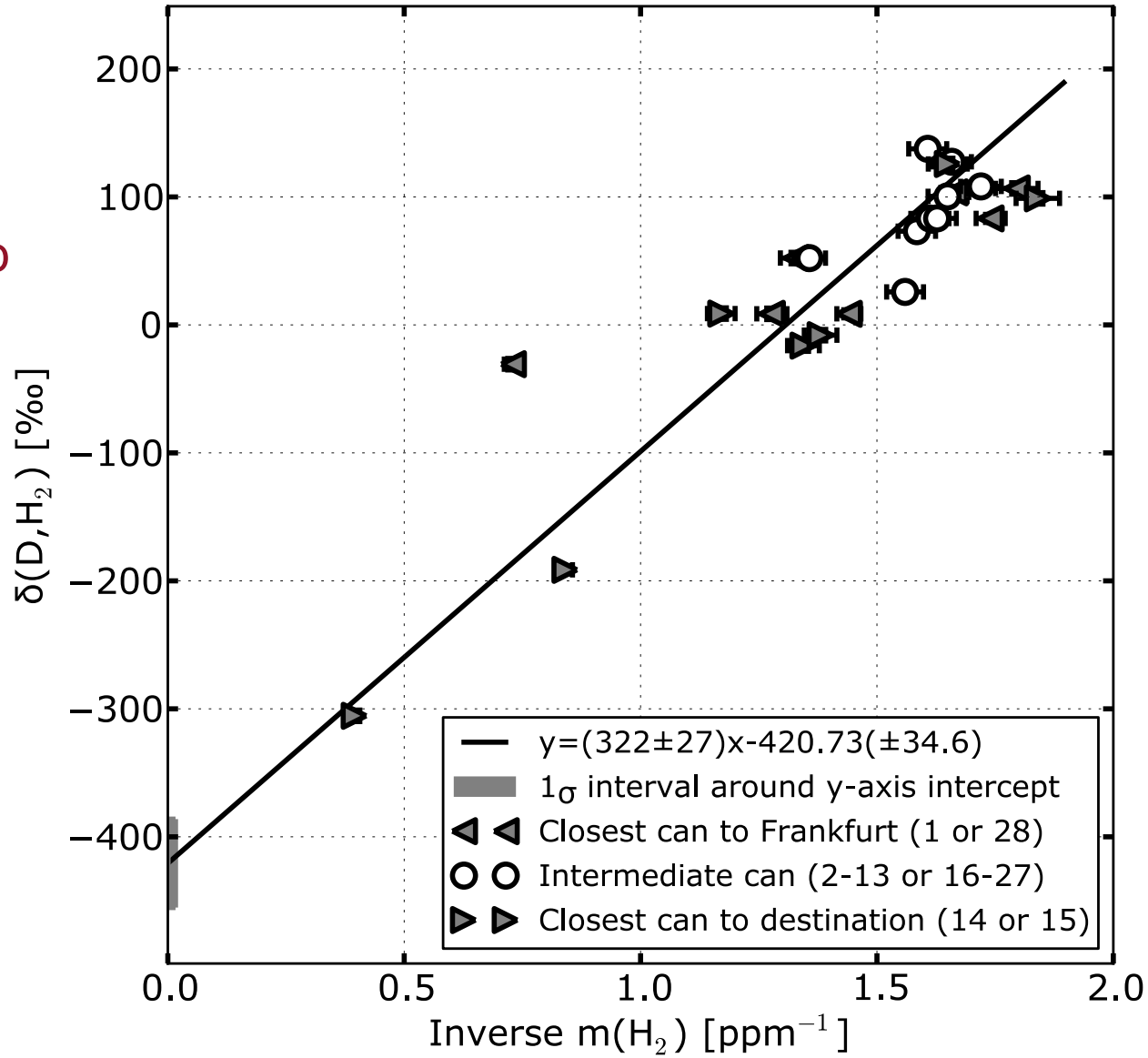


A first look: Caracas flights



"Polluted" samples

- Strong depletions
- Tendency to occur close to airports: Contrails?
- Source signature lower than expected for fossil fuels
- No clear relation with other species



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Stratospheric H_2 cycle

CH_4

Source: Hydrocarbon oxidation

Enriched in D

H_2

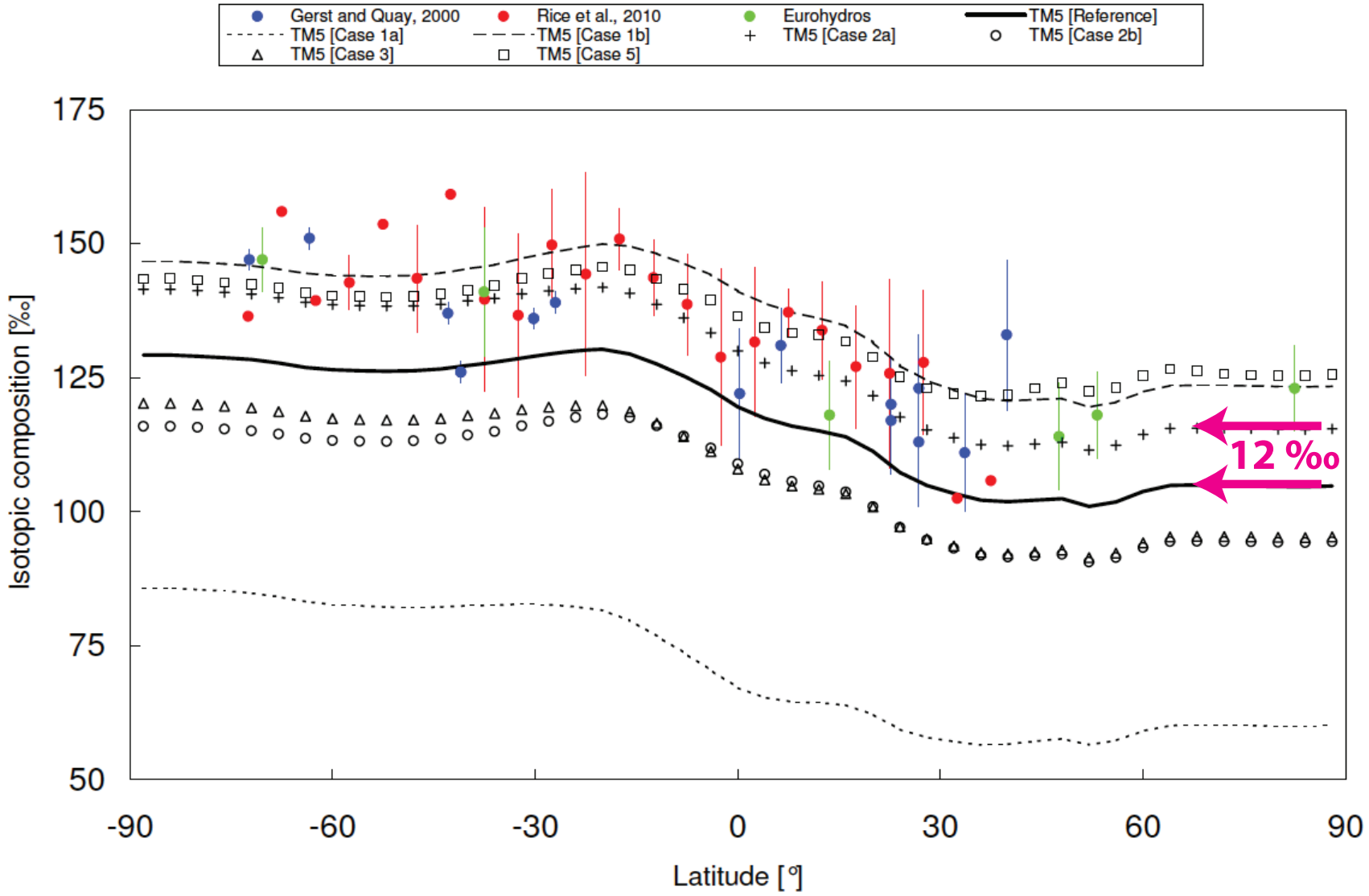
Sink: Oxidation by OH

Preferentially removes H

H_2O

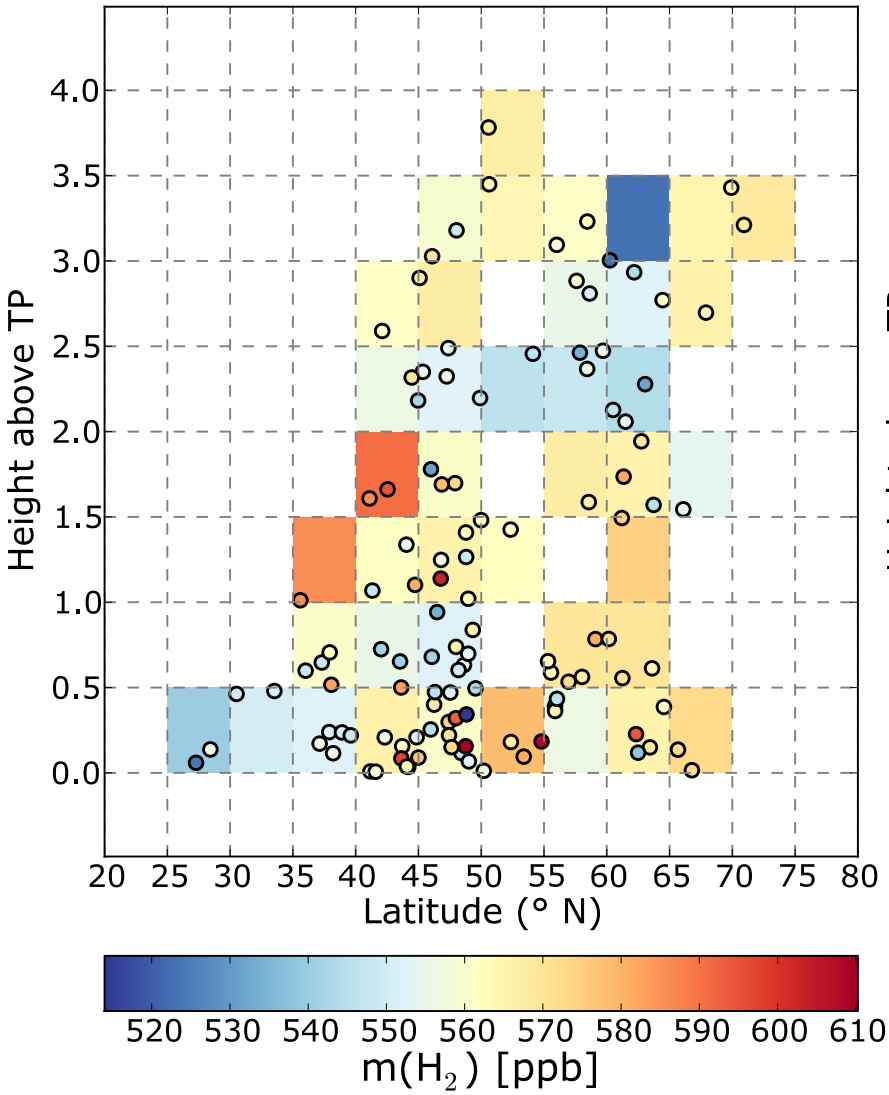
Result of stratospheric processing: H_2 mixing ratio changes little, while δD increases dramatically.

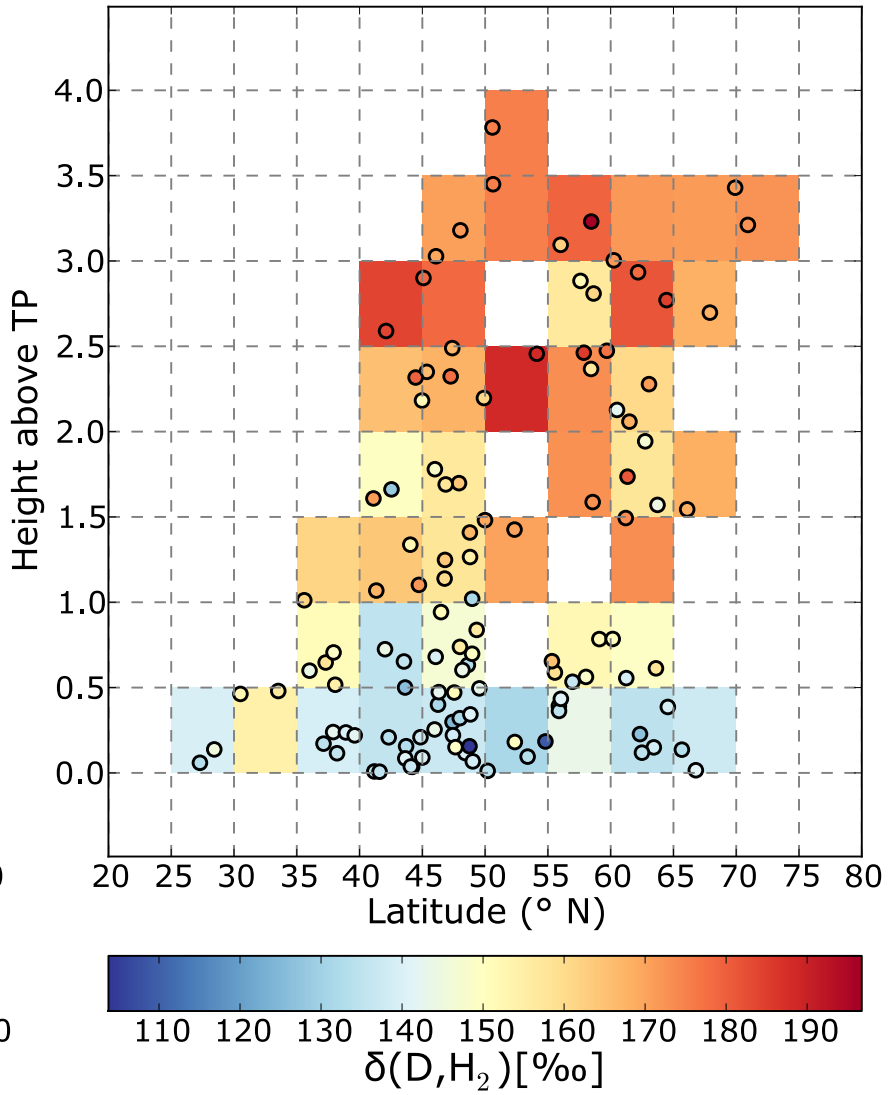
Stratospheric input



Pieterse et al., 2011
http://www.atmos-chem-phys.net/11/7001/2011/acp-11-7001-2011.html

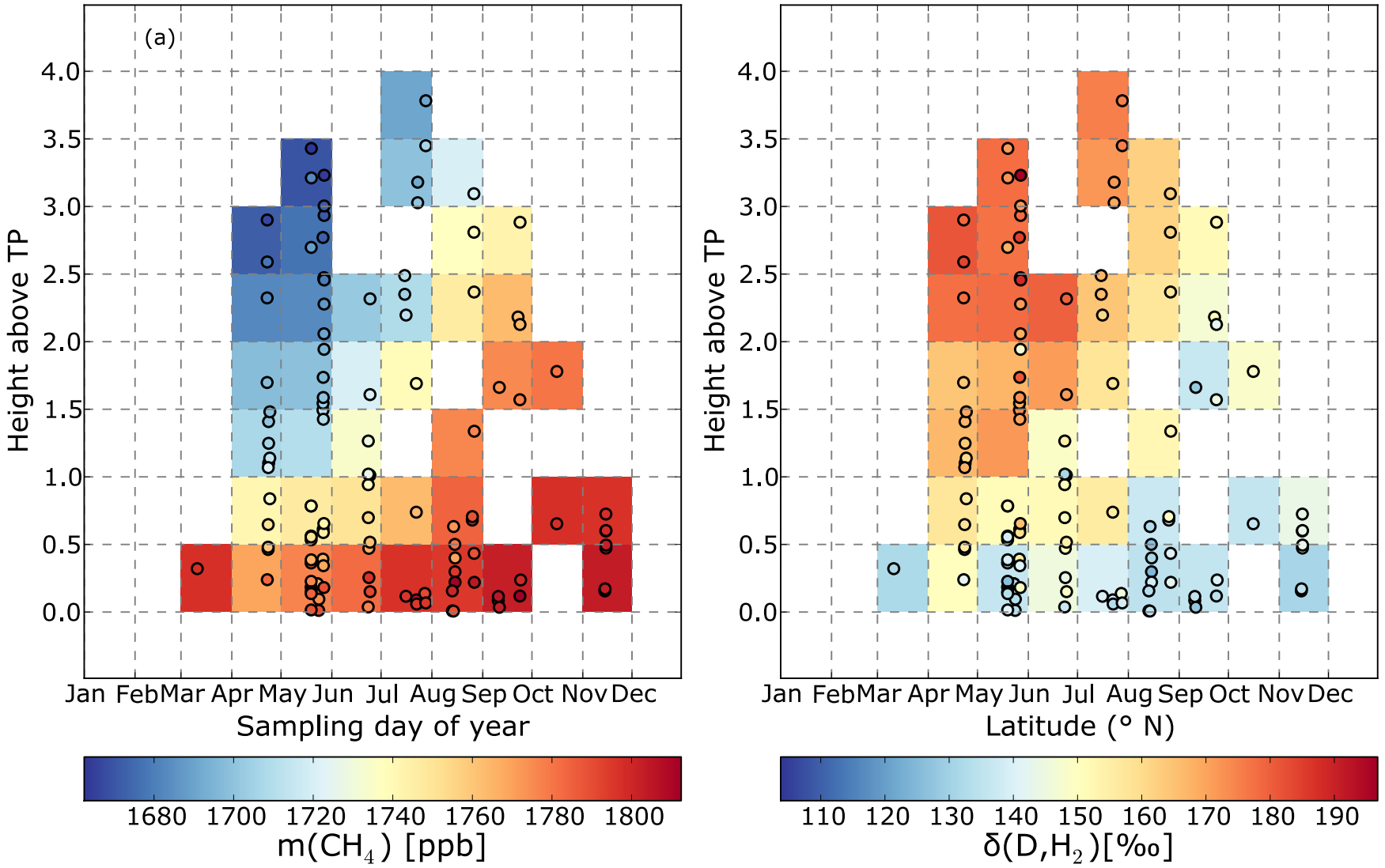
Stratospheric samples





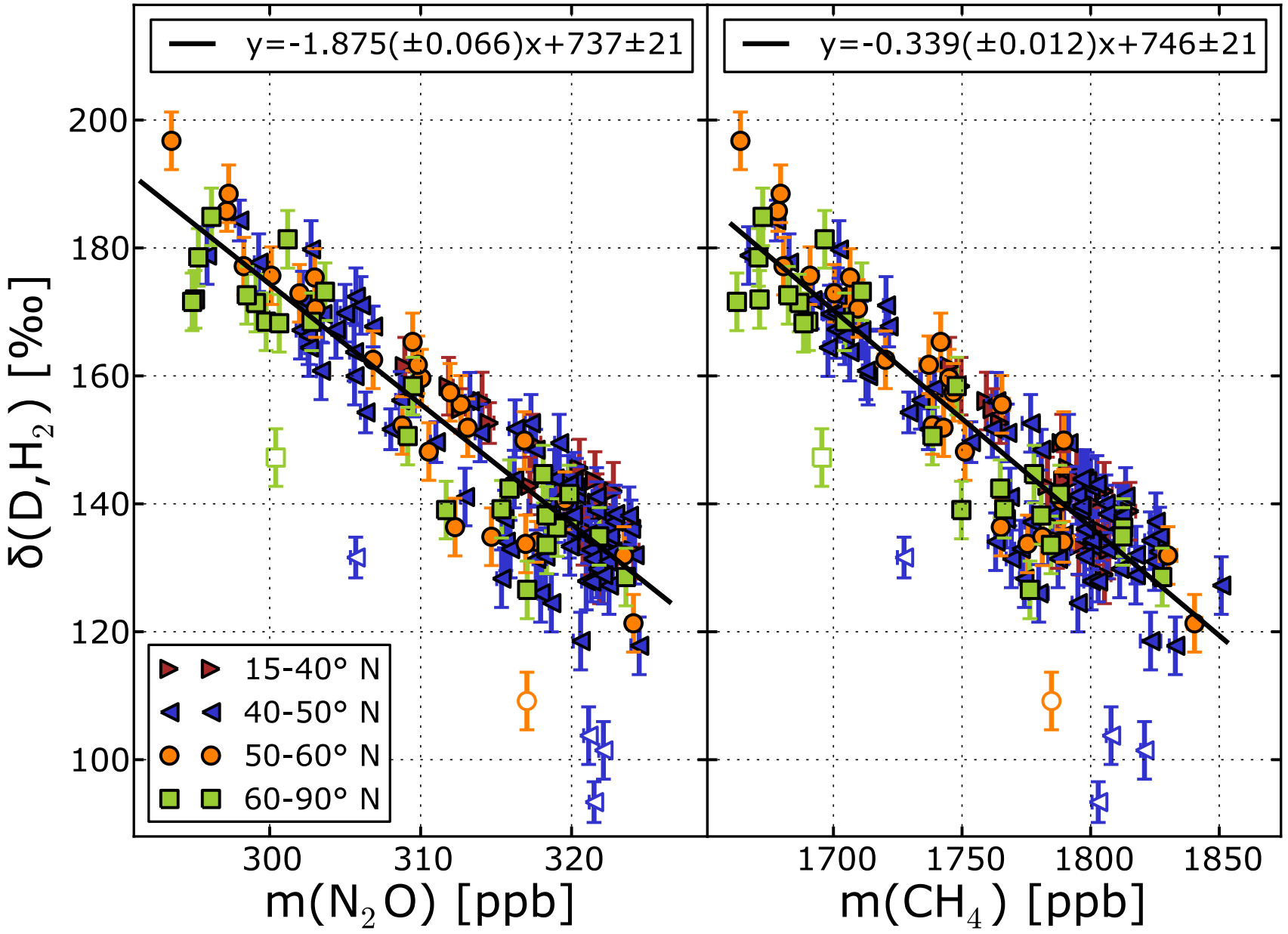
Vertical gradient in $\delta D(H_2)$, but not in mixing ratio

Stratospheric samples

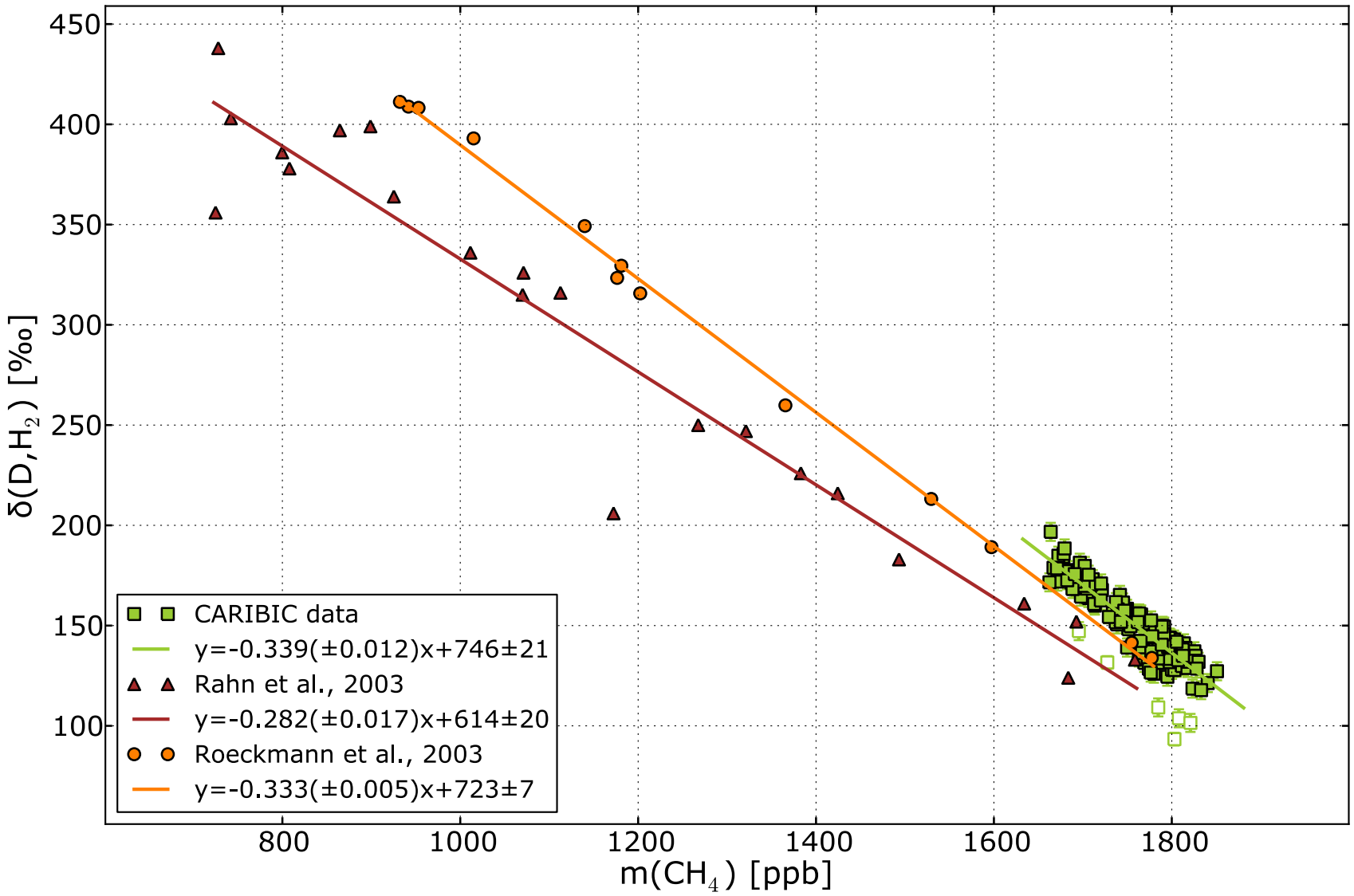


$\delta D(H_2)$ `mirrors' methane

Stratospheric correlations



Comparison to previous work



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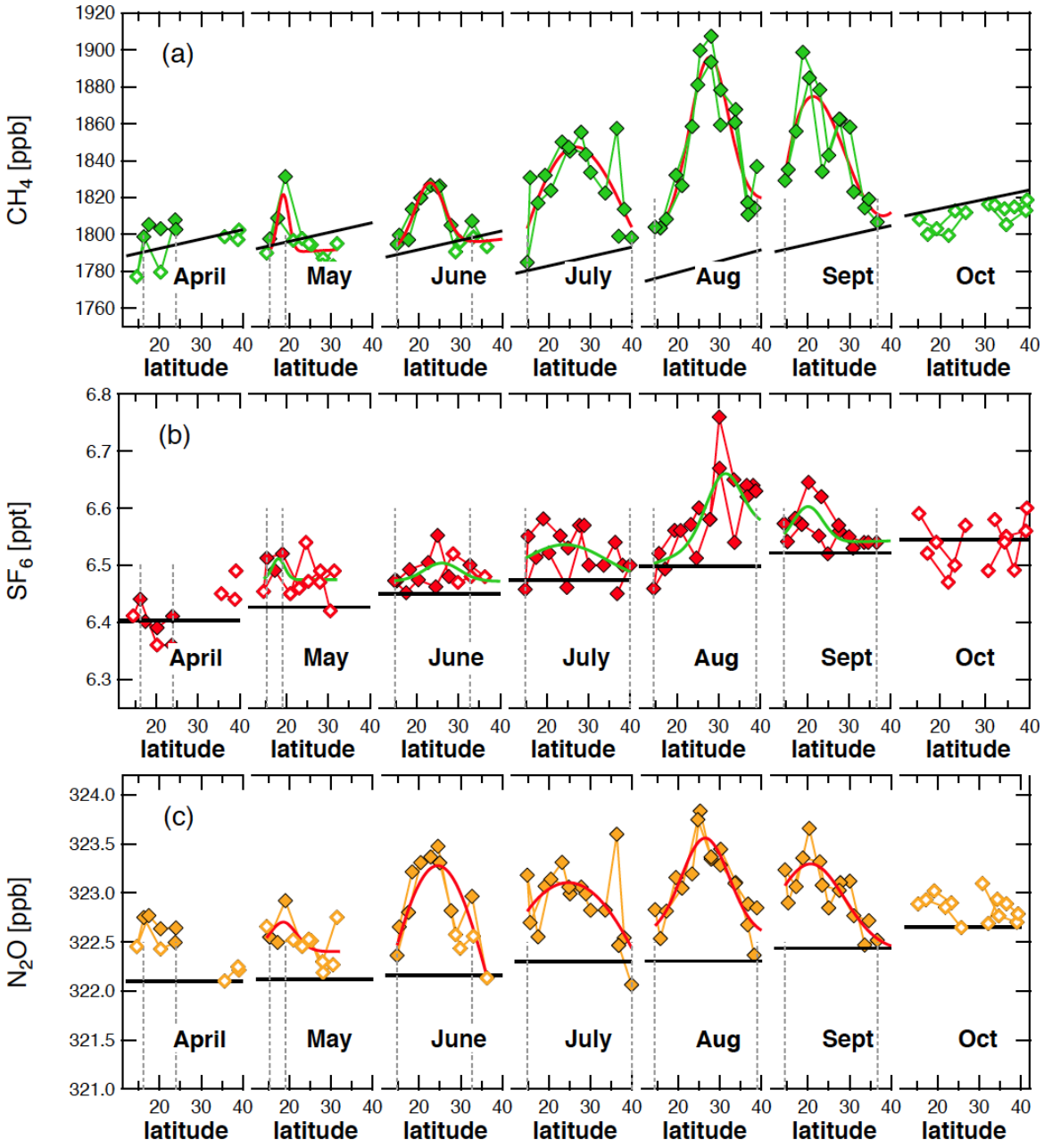
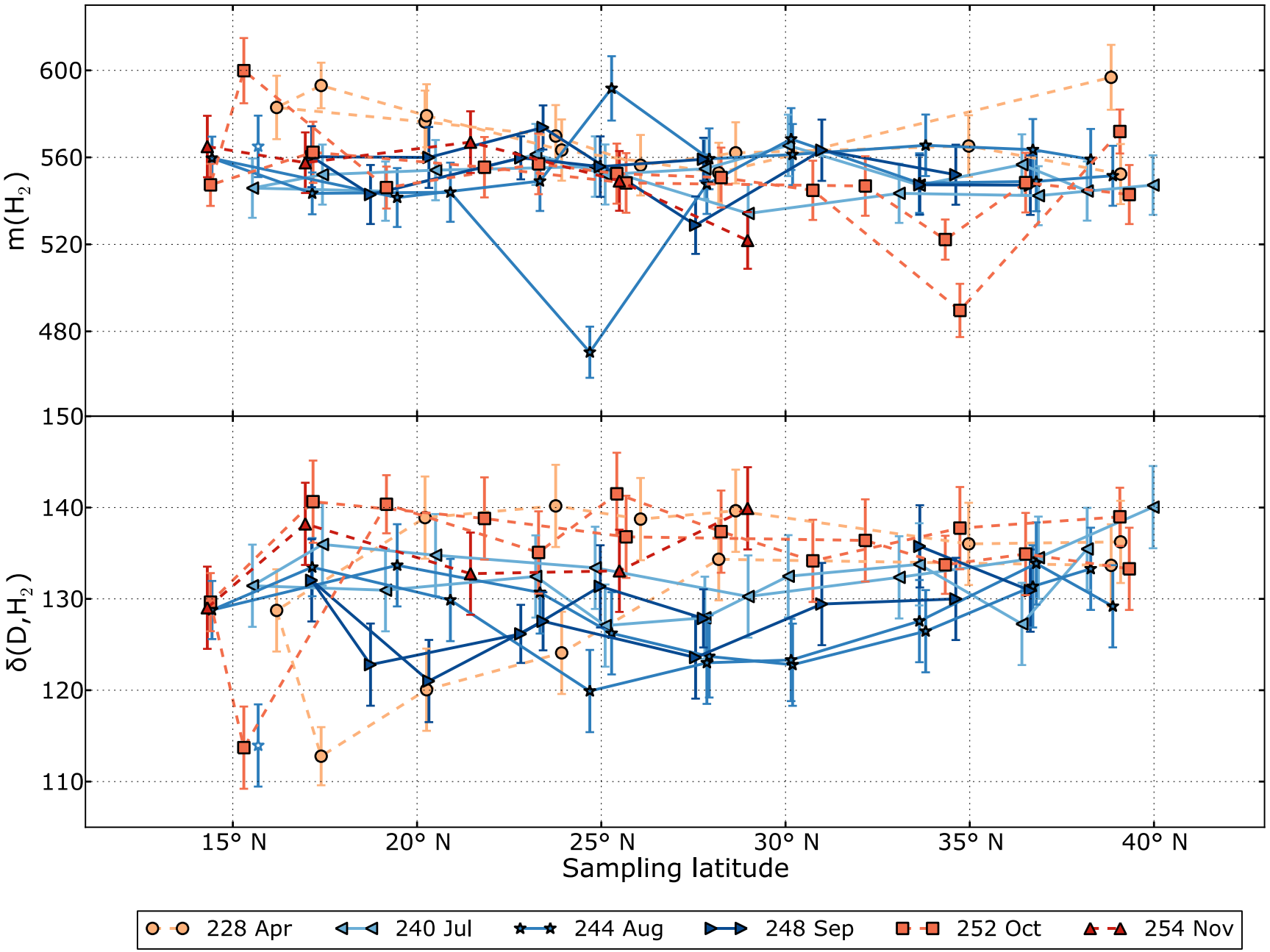
Summer monsoon GHG data

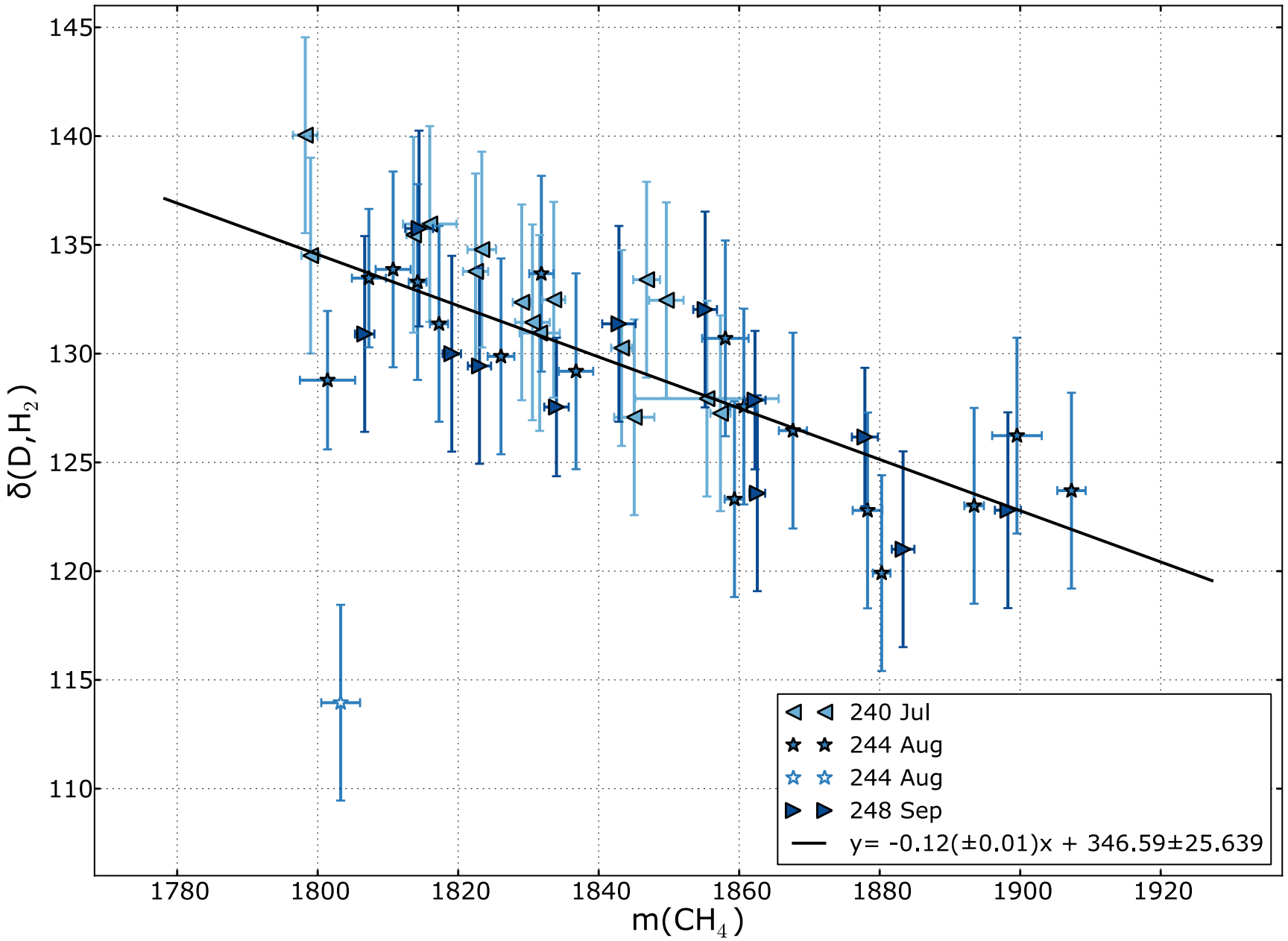


Enhanced mixing ratios of Greenhouse gases occur in from May until September, with a maximum in August. (*T.J. Schuck et al.* 2010)

δD lowering in monsoon



Correlation with methane



Some estimates

The mass conservation formula:

$$(p + bg)\delta\mathrm{D}_{p+bg} = p \cdot \delta_p\mathrm{D} + bg \cdot \delta_{bg}\mathrm{D}$$

can be used to calculate how much H_2 is needed to lower the background δD from ≈137‰ to ≈122‰ at a background m(H_2) of 560 ppb.

- With δD_p=-260‰ (biomass burning): ≈ 21 ppb
- With δD_p=-628‰ (microbial): ≈ 11 ppb

Our m(H_2) uncertainty is about 560*2.5%=14 ppb.

➔ Microbial production likely contributed to the D-depletion during summer monsoon

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Summary

- A large δD dataset was collected in the UTLS region
- Some samples appear **polluted by an unknown, very D-depleted source**
- **In the LS, a strong correlation is found between CH_4 and δD**, that can be used to improve δD in models
- **A lowering of δD values appears over India during summer monsoon**, correlated to the CH_4; possibly microbial sources