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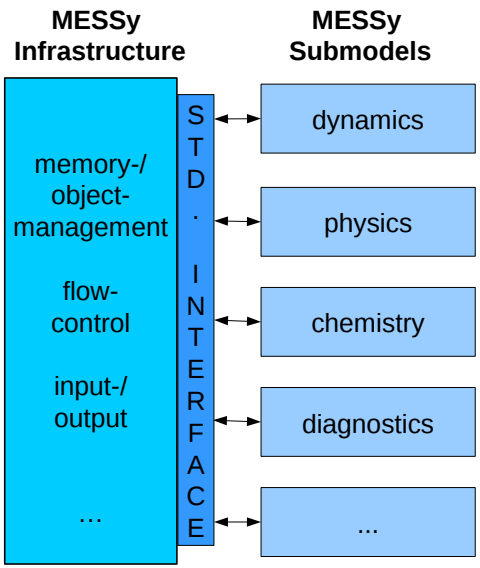
Methane and its isotopologues simulated with a chemistry-climate model to evaluate the atmospheric burden and the uncertainty of emissions

Franziska Frank*, Patrick Jöckel*, Florian Arfeuille**, Dominik Brunner**

* DLR, Oberpfaffenhofen
** EMPA, Zürich

The chemistry climate model EMAC



The ECHAM/MESSy Atmospheric Chemistry (EMAC) model

The Modular Earth Submodel System (MESSy) couples the General Circulation Model ECHAM5 with process based modules
– so called **submodels** – to simulate atmospheric chemistry.
⇒ The GCM is expanded into a **Chemistry Climate Model**.

Our Motivation:

- Up to now: methane was simulated in EMAC with predefined boundary conditions
- We introduced a simplified methane chemistry with isotopologues to improve our knowledge of methane emissions

⇒ First step towards the interactive simulation of methane and its sources

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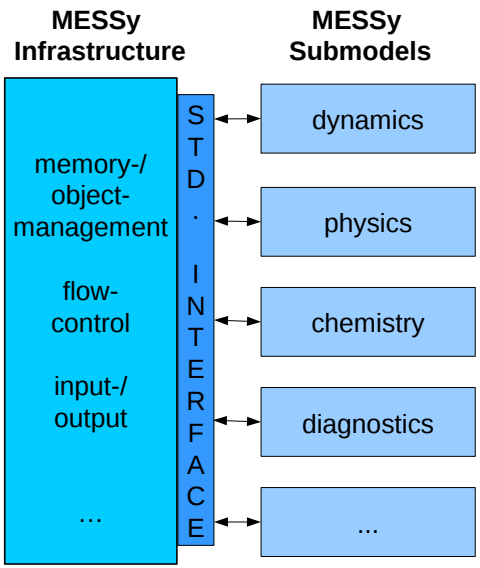

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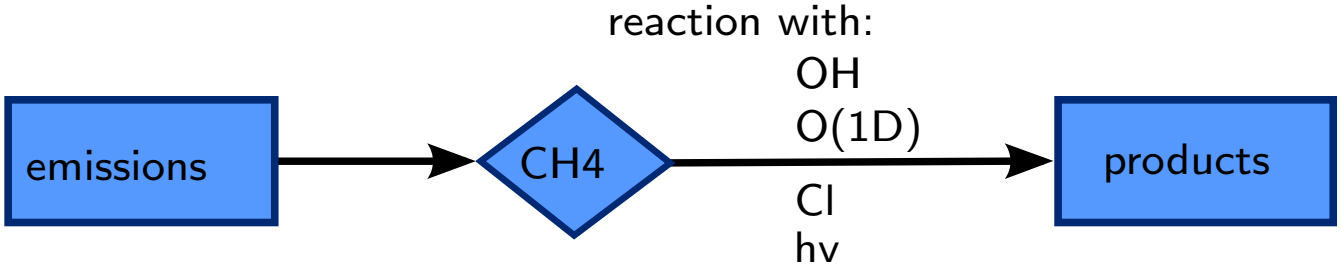
Simplified methane chemistry with isotopologues

The submodel

- simulates the simplified methane chemistry
- uses **predefined** reaction partners and emission fields

Simplified methane chemistry:



Bsp with OH: $\Rightarrow \frac{d[CH_4]}{dt} = -k_{OH} \cdot [OH] \cdot [CH4] + emis$

with [CH4], [OH]: concentrations, k_{OH}: reaction rate, and *emis*: methane emissions.

The extension for isotopologues

simulates the isotopologues:

- CH_4 and CH_3D
- $^{12}CH_4$ and $^{13}CH_4$

Higher substituted isotopologues are neglected.

The submodel accounts for the **kinetic isotope effect** with an altered reaction rate:

e.g. $k_{^{13}CH_4} = KIE^{-1} \cdot k_{^{12}CH_4}$

KIE values in the simulation were taken from [Röckmann 2011]

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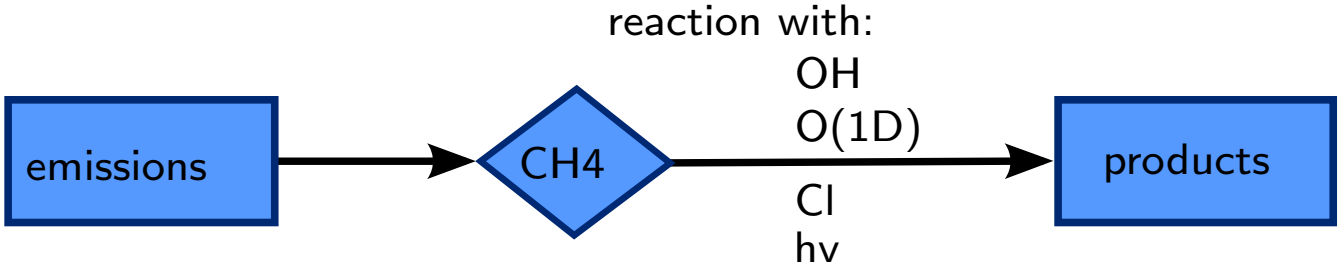

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Simulation Set-up

Parameter of model

- Grid: approx. $3^\circ \times 3^\circ$ on 90 levels up to 0.01 hPa
- Newton relaxation with ERA-Interim data
- Initialization with a spin-up of 10 years

Evaluation approach

- Evaluated time period: Jan 1990 - Dec 1999
- Climatology of the evaluation time period, zonally averaged as indicated
- First results – detailed statistical analysis is still in progress

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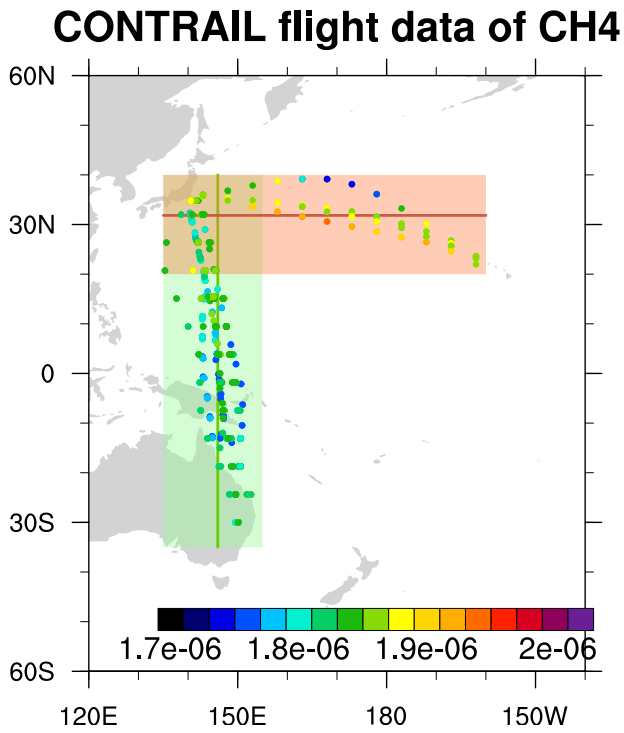
Evaluation with airborne measurements

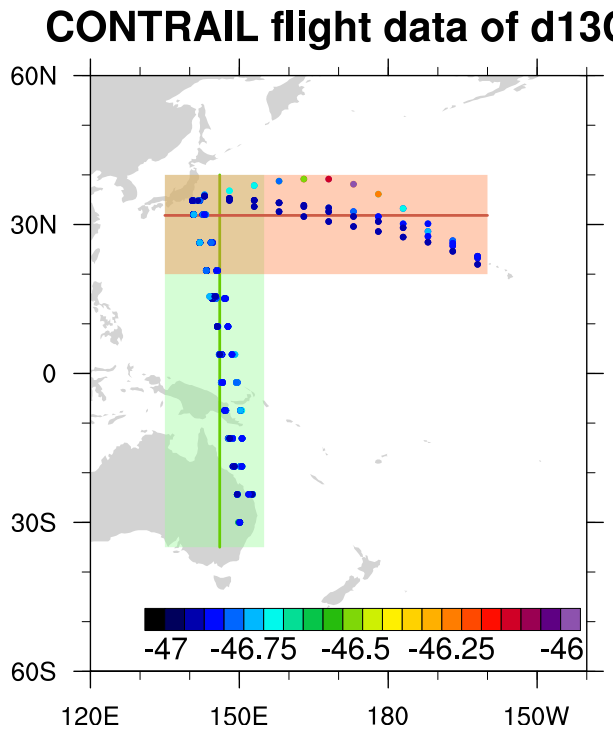
Used data:

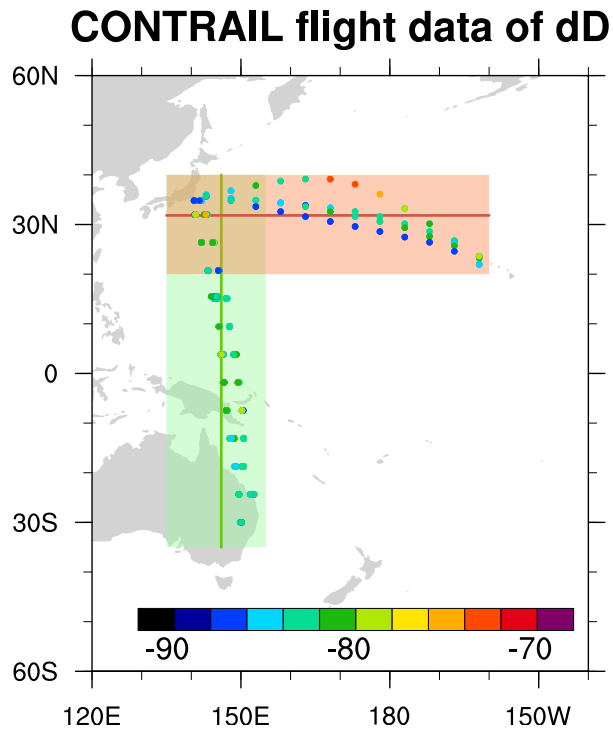
Airborne flask measurements of CH_4, $\delta^{13}C(CH_4)$ and $\delta D(CH_4)$ by mass spectrometry during the CONTRAIL* project.
Period: 2006 - 2010.

* Reference: [Umezawa et al. 2012]

Flight routes

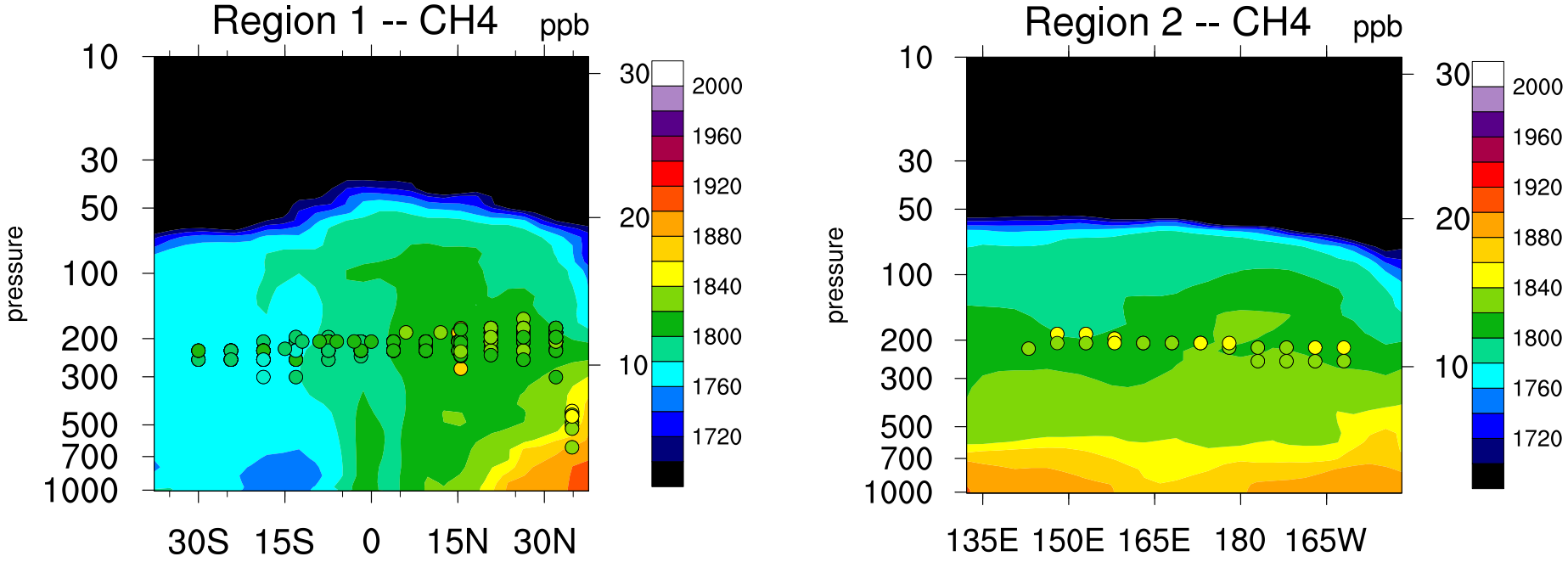






- Separating data in two regions: region 1 (green) and region 2 (red)
- Averaging simulation results over indicating region
- Excluding outliers in region 2 due special meterological conditions as stated in [Umezawa 2012]

Evaluation with airborne measurements



Model results shifted by + 160 ppb

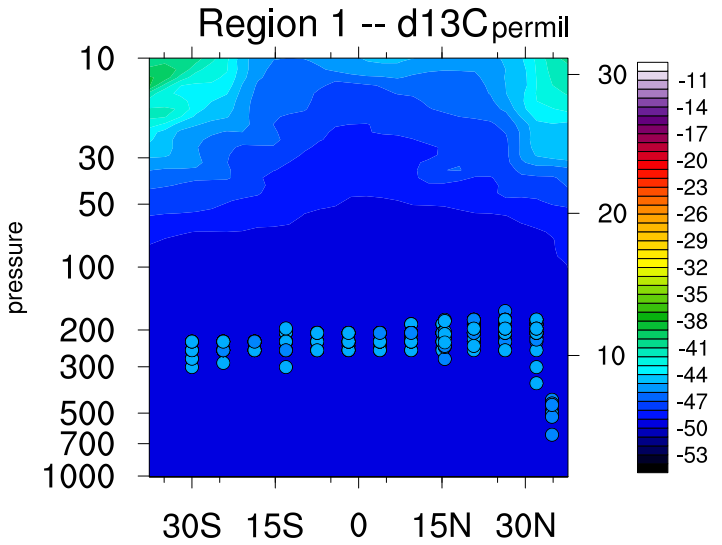
Remark

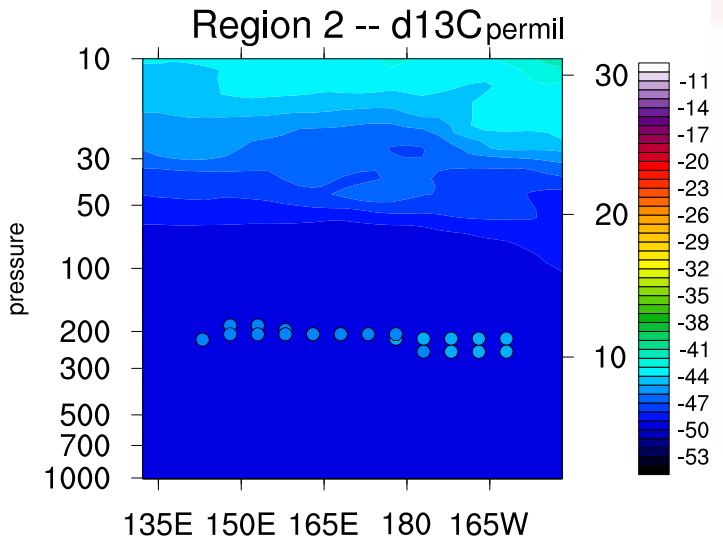
Methane concentration is circa 160 ppb lower

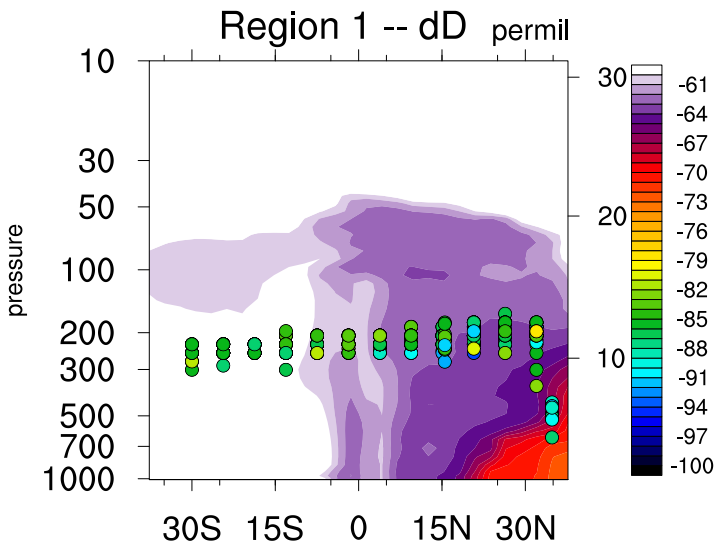
⇒ Simulation covers time period of about 10 years before measurements.

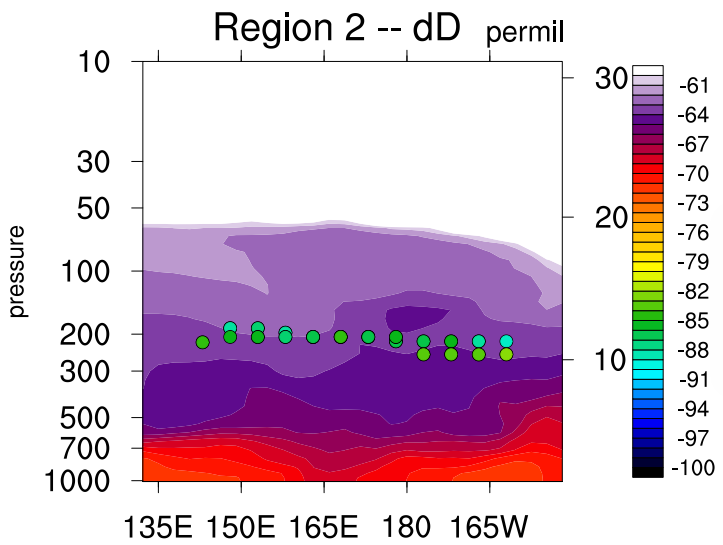
Methane increased about 5 - 15 ppb yr^{-1} between 1990 - 2000.

Vertical profile along flight paths









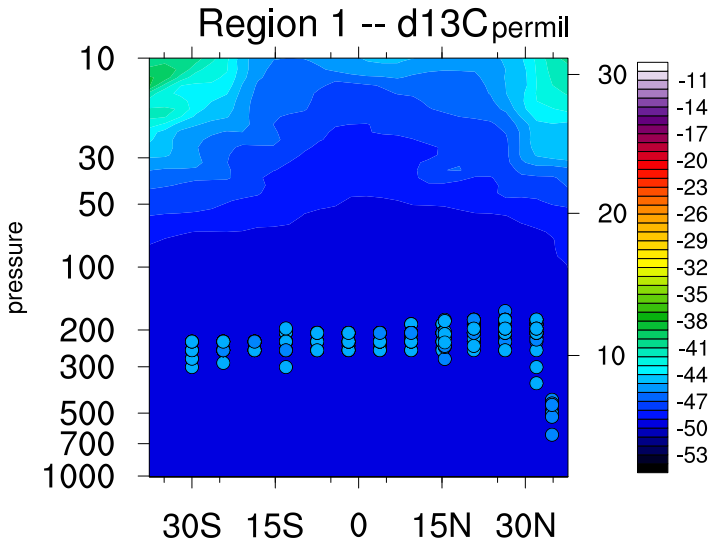
Remark

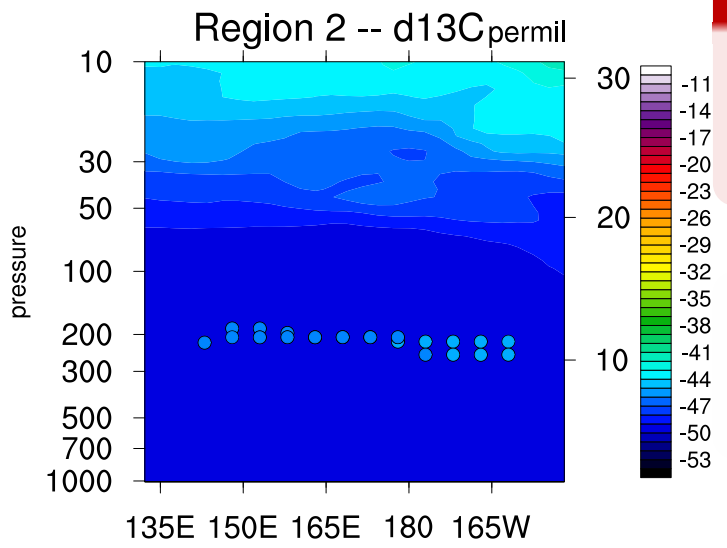
The simulated results deviate from the observations

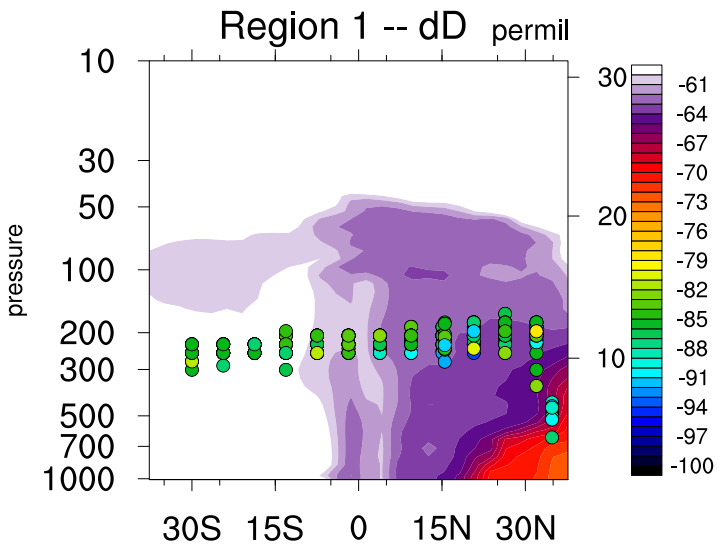
Simulated $\delta^{13}C(CH_4)$ is about 4.2 ‰ lower.

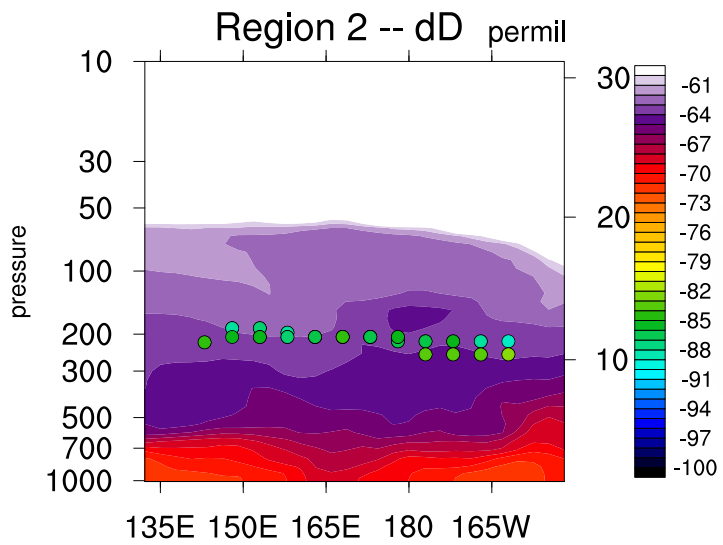
Simulated $\delta D(CH_4)$ is about 25 ‰ higher.

Vertical profile along flight paths









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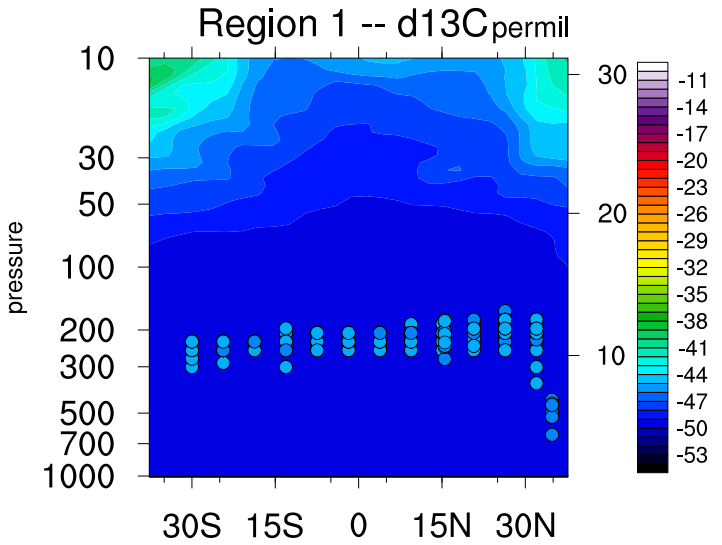

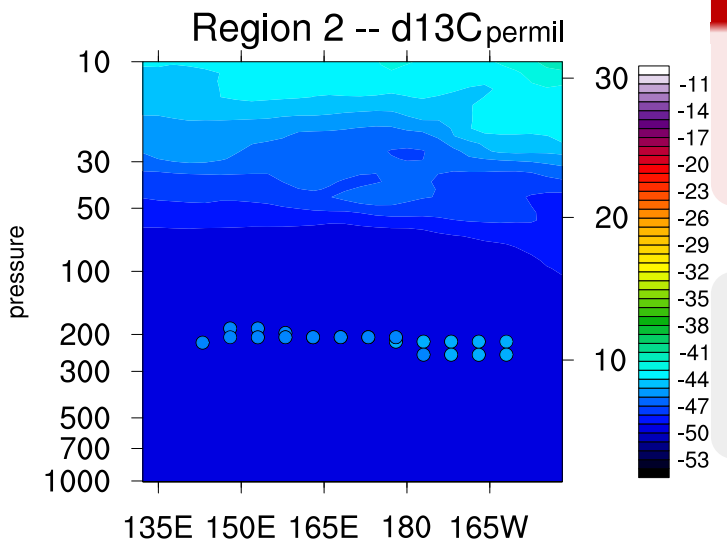

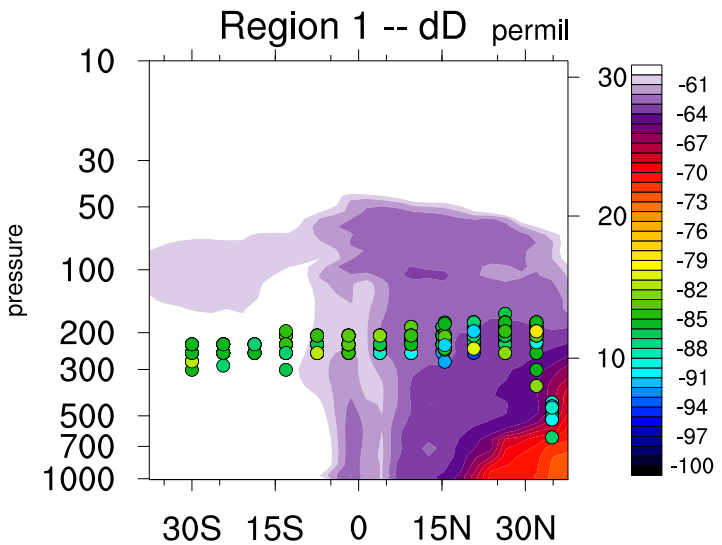

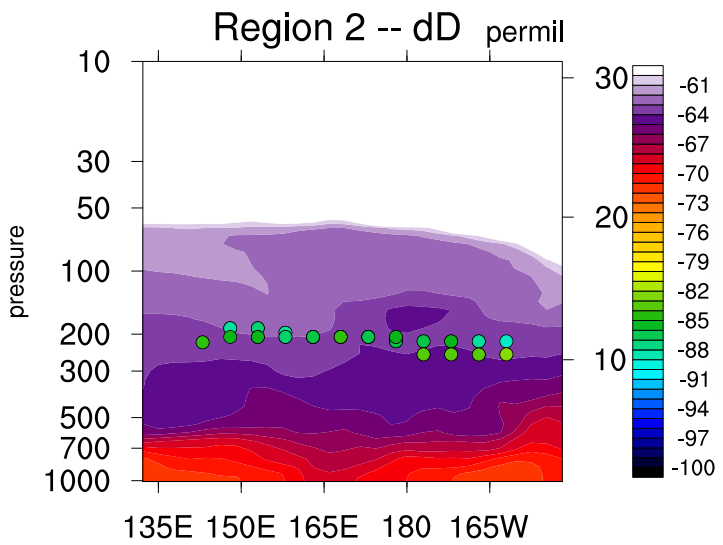

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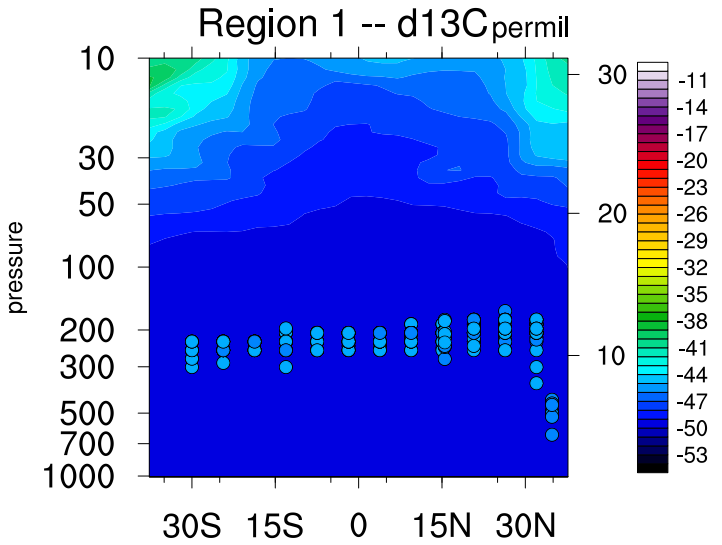

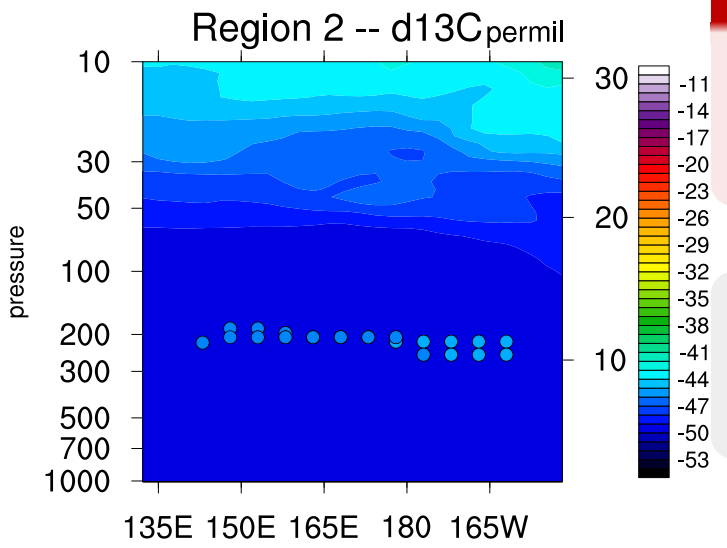

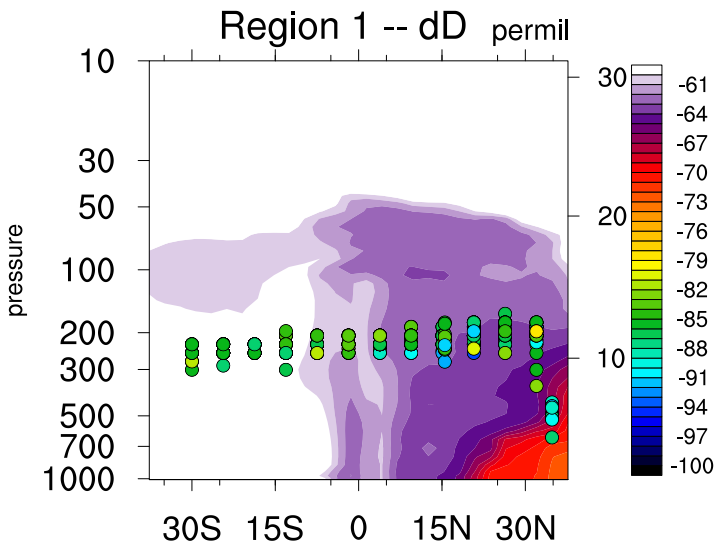

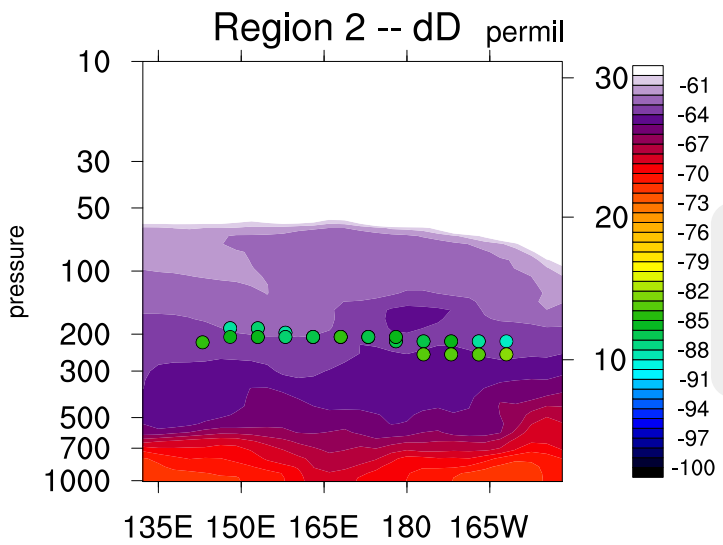

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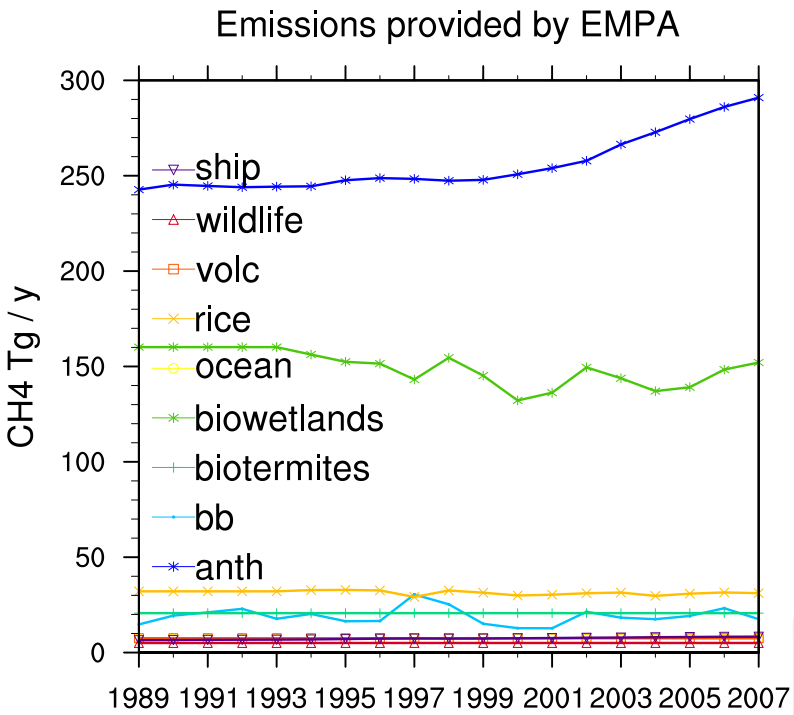

Isotopic ratios of methane sources (in ‰)

Emission-class	$\delta^{13}C(CH_4)$	range	$\delta D(CH_4)$	range
biomass burning	-23.9	2	-213.0	3 - 12
anthropogenic	-49.9	–	-215.1	0 - 2
ocean	-59.0	1	-220.0	–
wetlands	-59.4	1.5	-336.2	20 - 30
termites	-63.3	6	-390.0	–
wildanimals	-61.5	0.5	-319.0	–
rice	-63.0	0 - 2	-324.3	5
volcanoes	-40.9	0.9	-253.4	50

Isotopic ratios were calculated by combining estimates from seven references. [Kiyosu 1982] [Quay 1999] [Snover 2000] [Fletcher 2004] [Whiticar 2007] [Monteil 2011] & [Rigby 2012]

Uncertainties in

- the δ signature of sources
- the relative contribution of different sources
- the kinetic isotope effect

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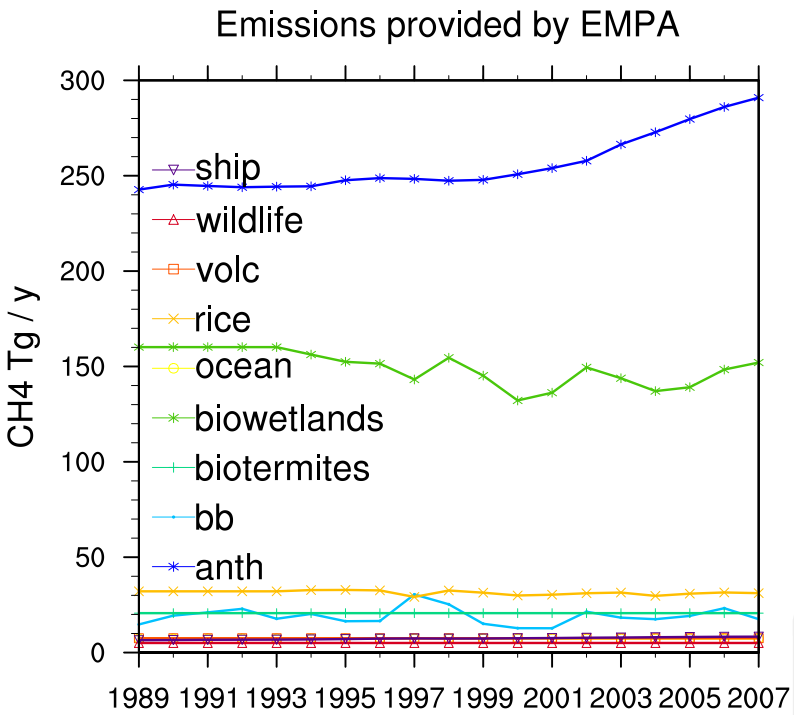

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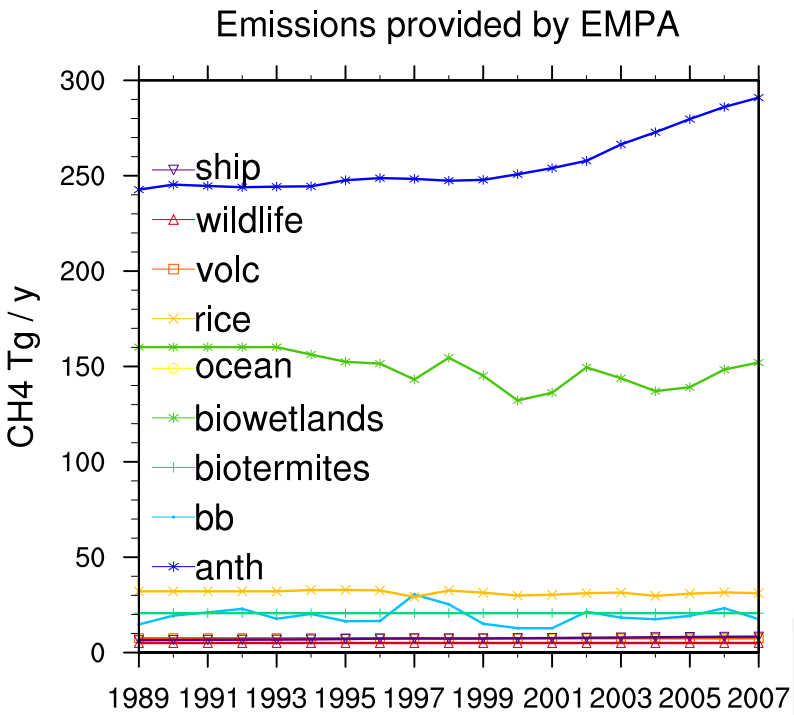

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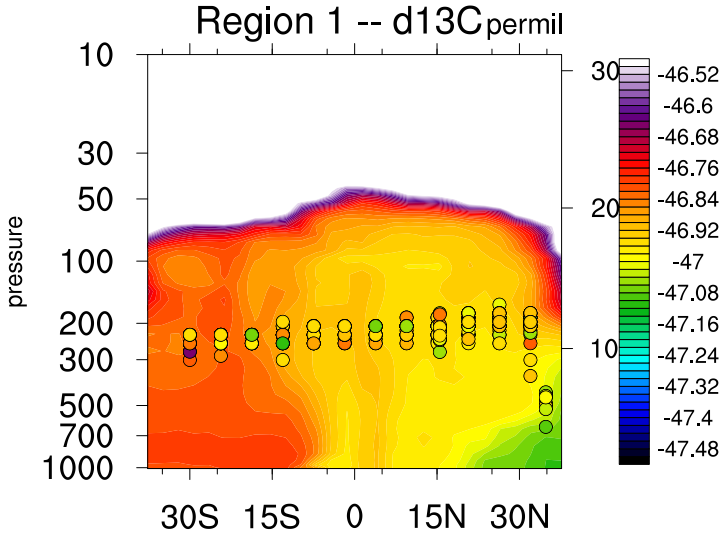
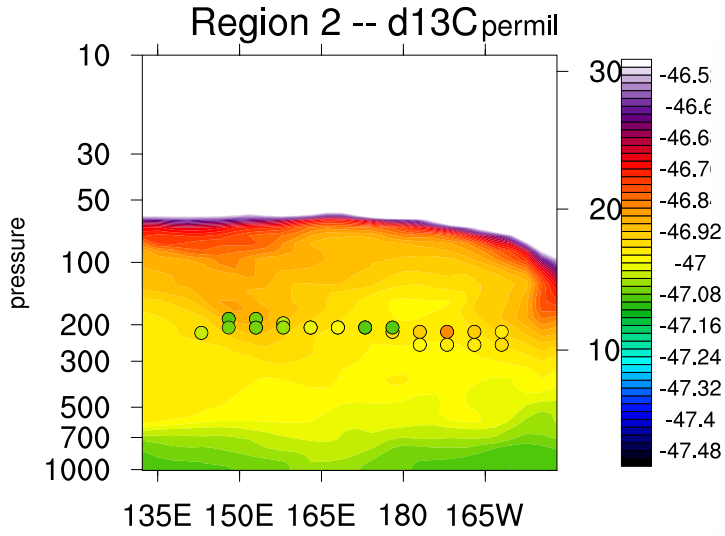
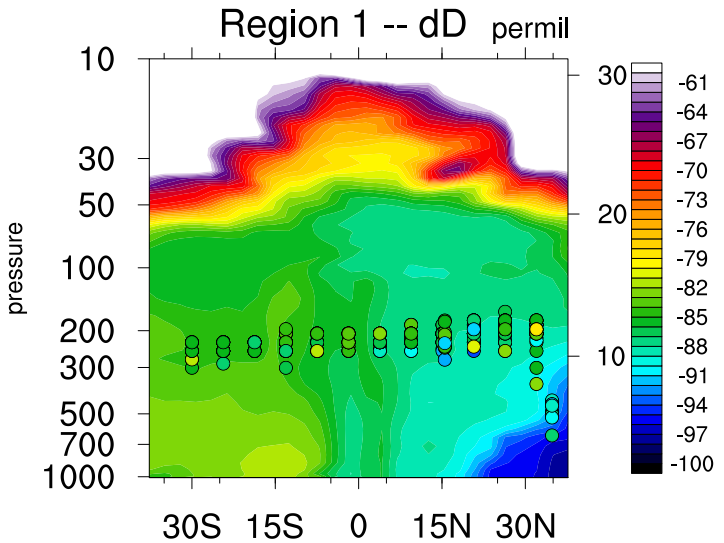
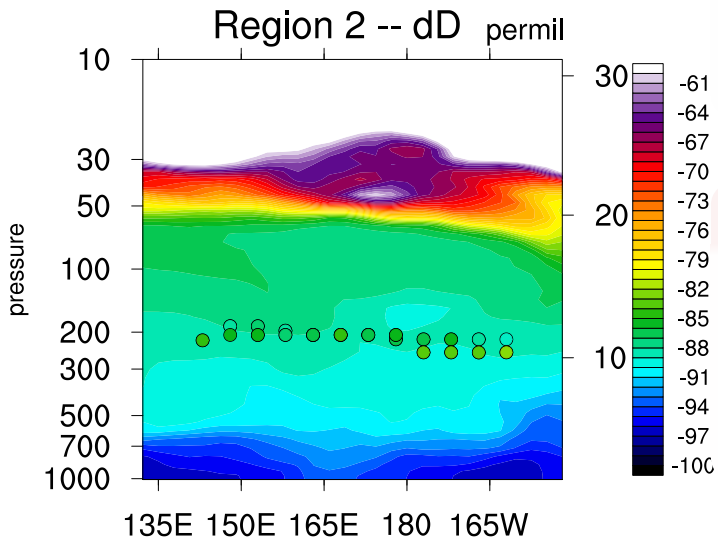
DLR

Vertical profile along flight paths – Corrected









Simulated $\delta^{13}C(CH_4)$ shifted by + 2.4 ‰.

Simulated $\delta D(CH_4)$ shifted by - 25 ‰.

Remark

Observed latitudinal gradient is reproduced by the model.

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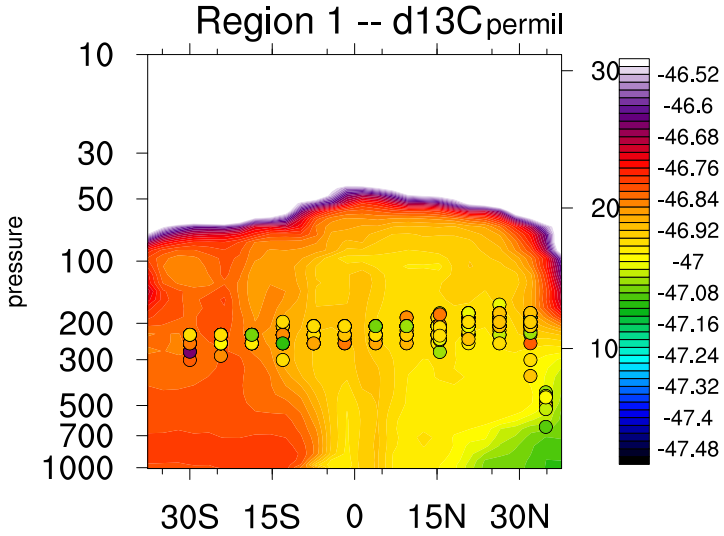

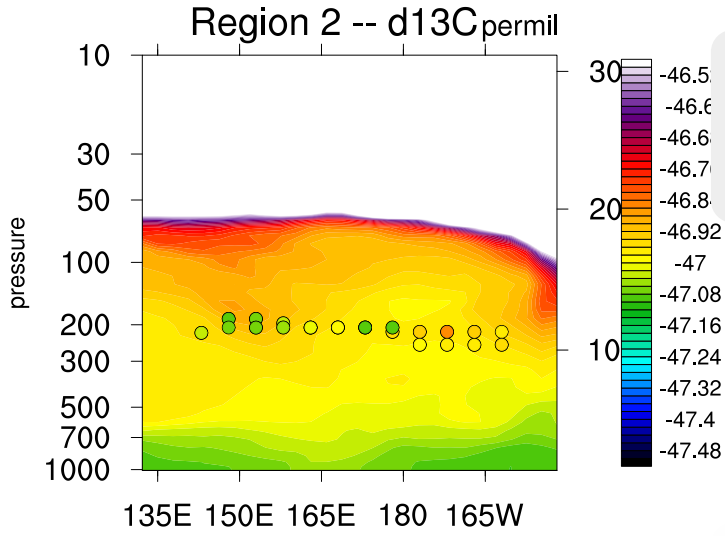

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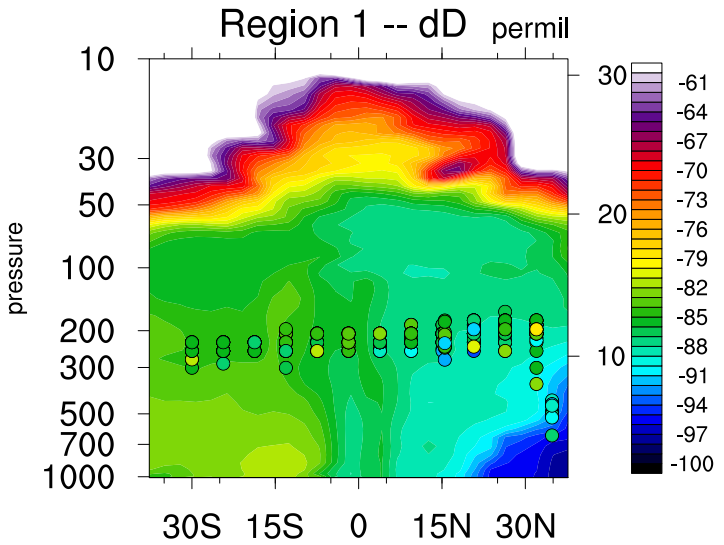

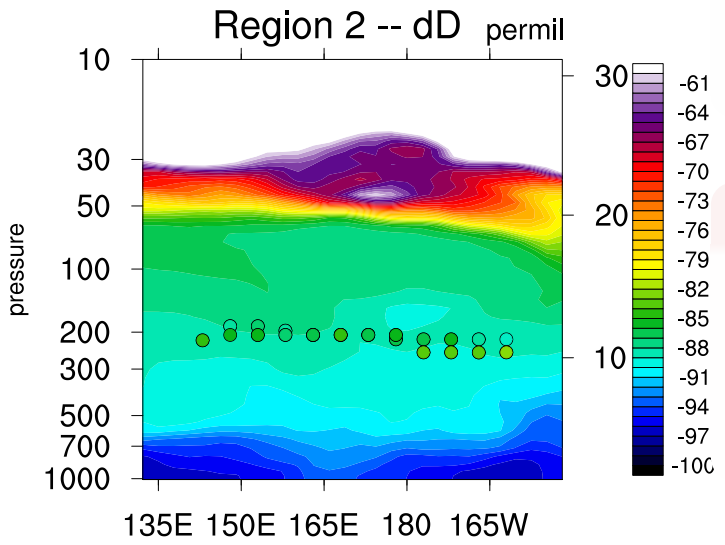

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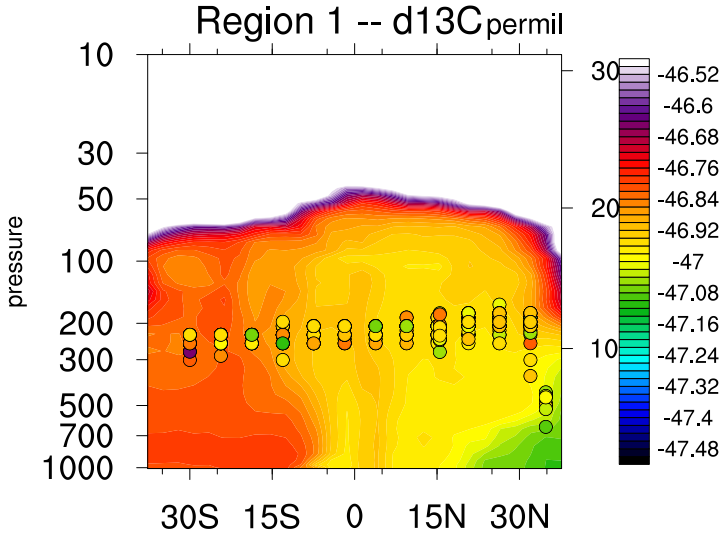

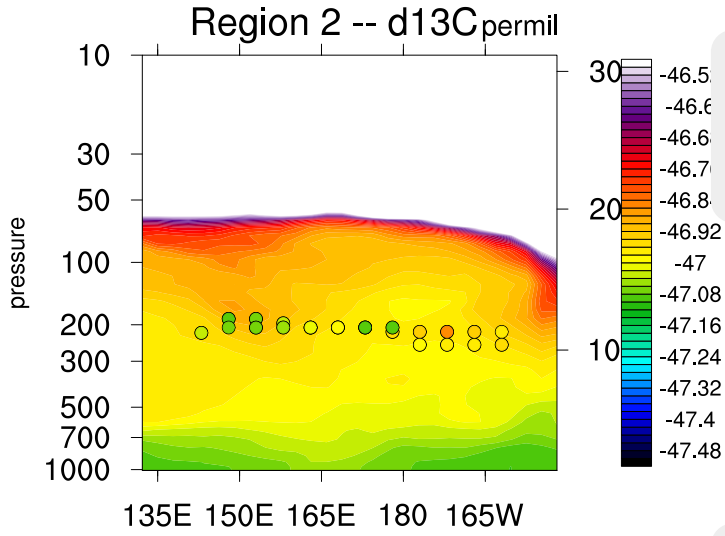

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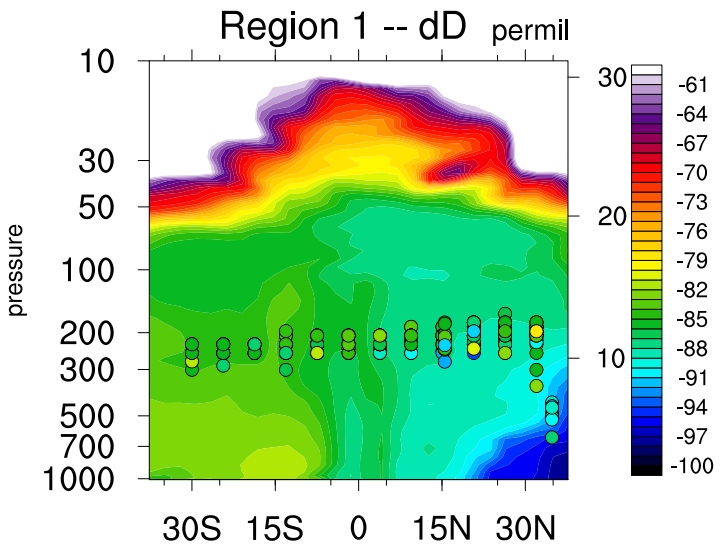

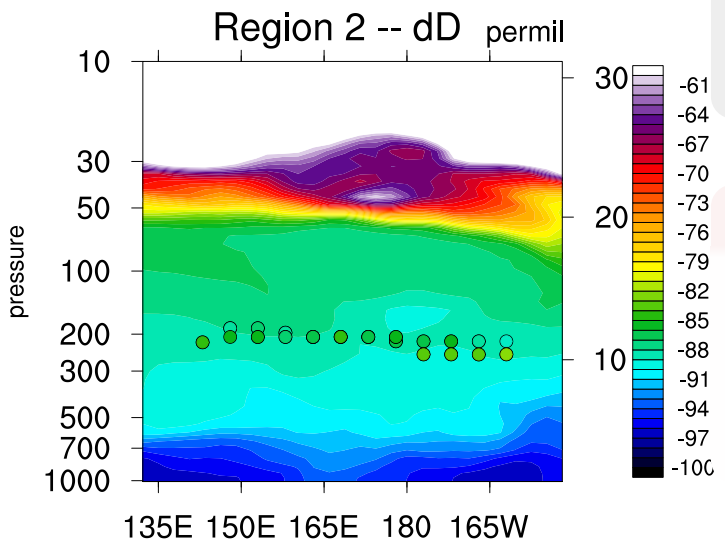

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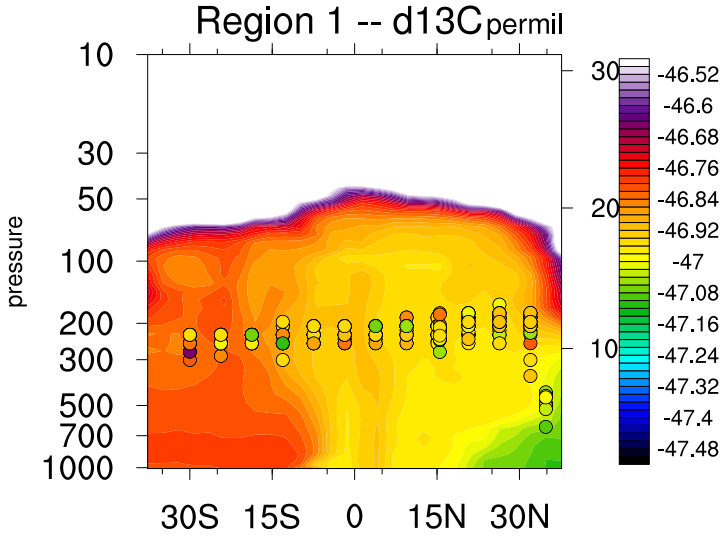
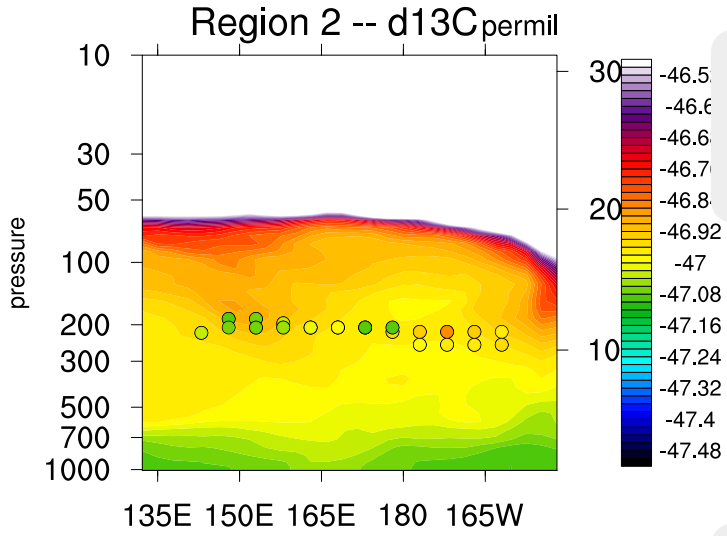
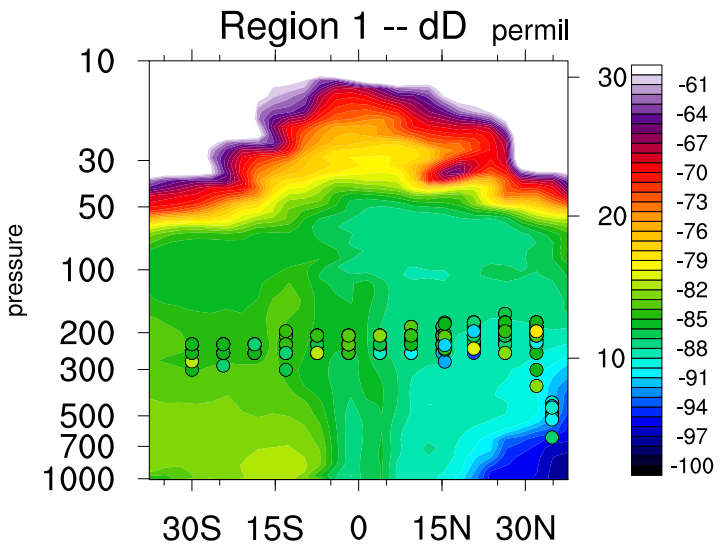
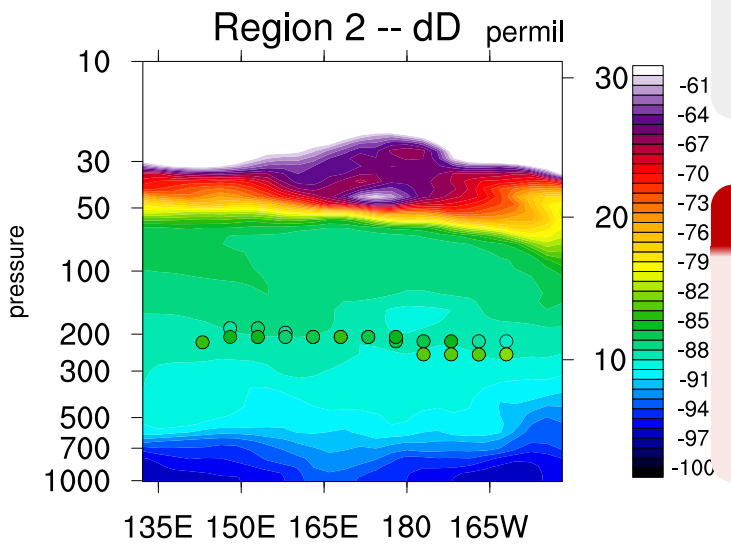




Simulated $\delta^{13}C(CH_4)$ shifted by + 2.4 ‰.





Simulated $\delta D(CH_4)$ shifted by - 25 ‰.

Remark

Observed latitudinal gradient is reproduced by the model.

Evaluation with balloon borne measurements

Used data:

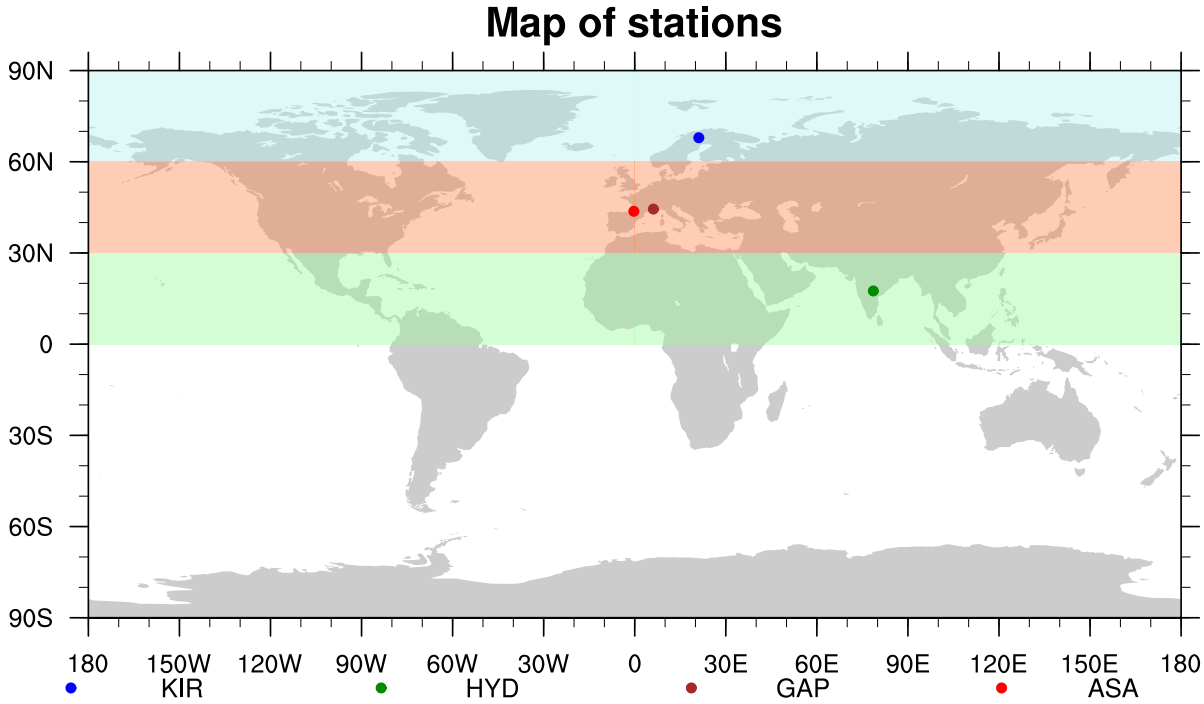
Balloon borne measurements of CH_4, $\delta^{13}C(CH_4)$ and $\delta D(CH_4)$ *
Period: 1987 - 2003

Launchsites

Kiruna (Sweden, KIR), Aire sur l'Adour (France, ASA), Gap (France, GAP) and Hyderabad (India, HYD).

* Reference: [Röckmann et al. 2011]

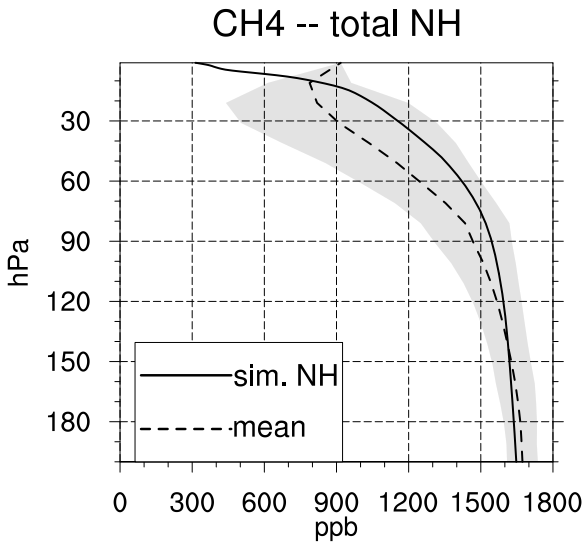
Regions of balloon launches

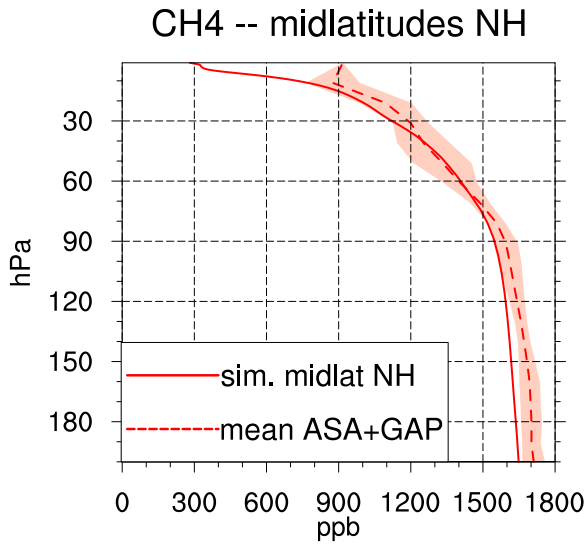


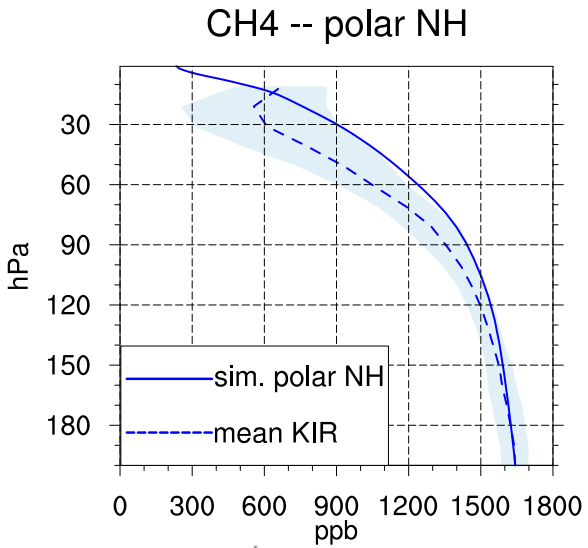
Evaluation approach

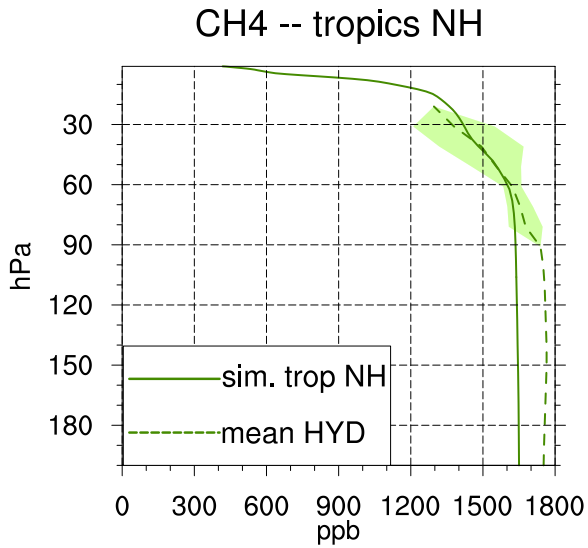
Simulation data was averaged over corresponding latitudinal band and compared to the measurements.

Evaluation of the vertical profile of CH_4

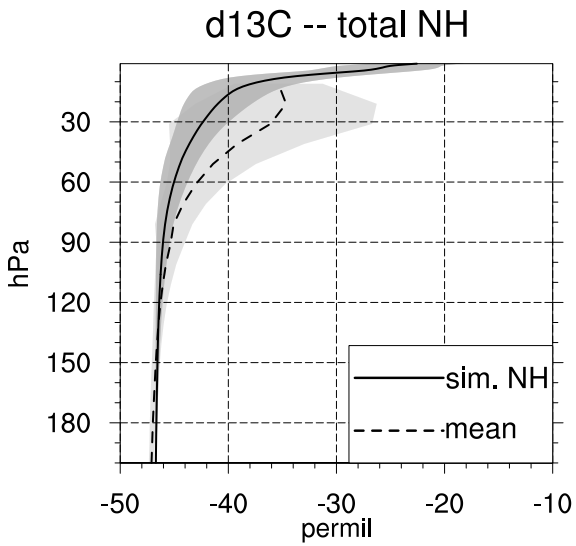


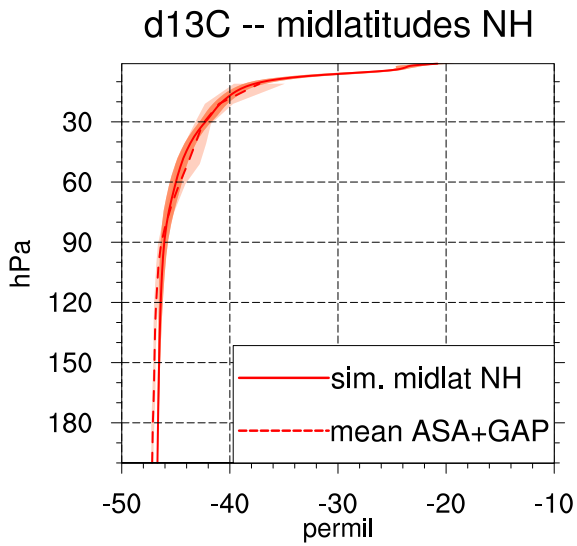


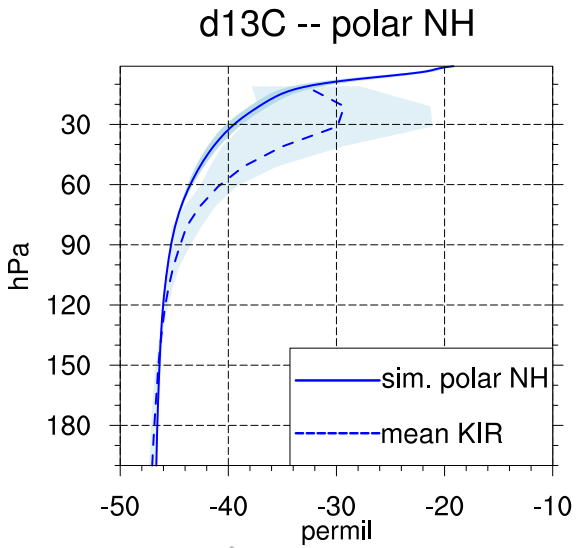


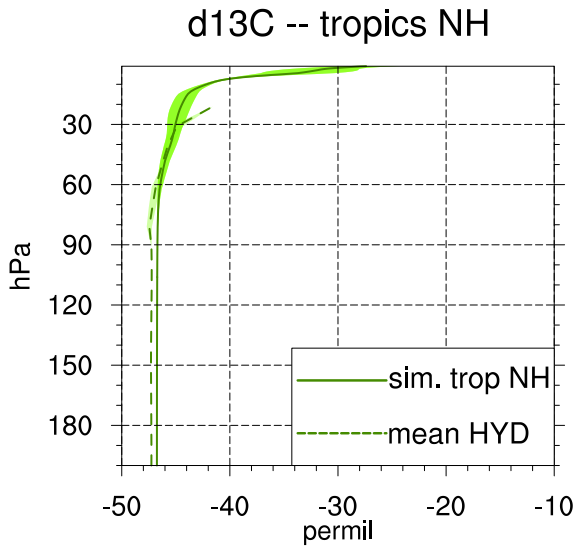


Evaluation of the vertical profile of $\delta^{13}C(CH_4)$







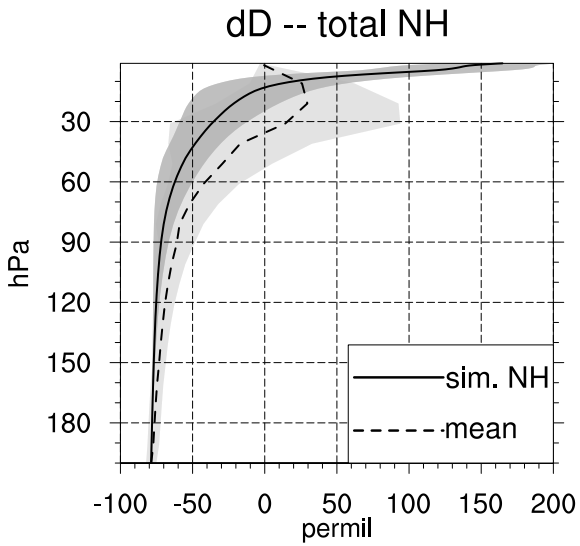


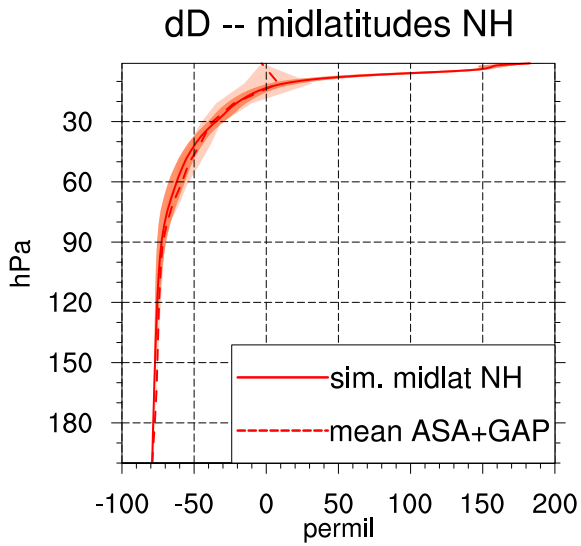
Remark

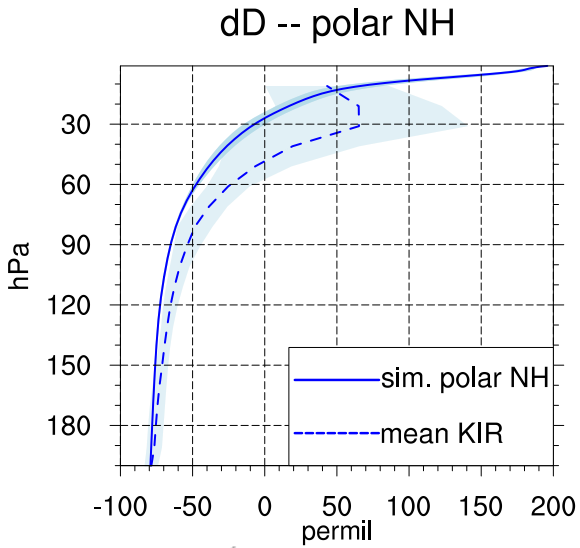
Results corrected by $+2.6‰$.

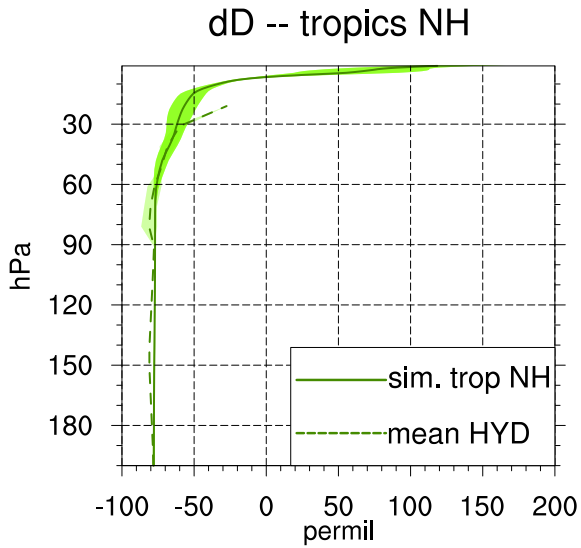
$\Rightarrow$ Emissions are presumably isotopically too light concerning $^{13}CH_4$

Evaluation of the vertical profile of $\delta D(CH_4)$









Remark

Results corrected by $-15‰$.

$\Rightarrow$ Emissions are presumably isotopically too heavy concerning CH_3D

Summary & Outlook

Summary

- Simulation results are affected by the uncertainties of:
  - the estimated methane sources
  - the isotopic ratio of distinct sources
  - the kinetic isotope effect
- The simulation reproduces the observed **latitudinal gradient** of methane and its isotopologues.
- Observed **vertical profiles** of methane and its isotopologues are well reproduced by the simulation.

Outlook

- Optimizations of methane emissions and its isotopic ratios by inversion
- Further evaluations of seasonal/annual changes in $\delta^{13}C(CH_4)$ and $\delta D(CH_4)$
- On the long view: Further simulations with the full chemistry and interactive methane emissions instead of prescribed boundary layer.

DLR

Thank you for your attention!

[Emma Green, "The Case for Shale Gas in 5 Charts", The Atlantic, 2013]

References

1. Miller, J. B., Mack, K. A., Dissly, R., White, J. W. C., Dlugokencky, E. J. and Tans, P. P. 2002. Development of analytical methods and measurements of 13C/12C in atmospheric CH4 from the NOAA/CMDL global air sampling network. J. Geophys. Res. 107, doi: 10.1029/2001JD000630.
2. Project CONTRAIL: CONTRAIL website: http://www.cger.nies.go.jp/contrail/
3. Umezawa, T., T. Machida, K. Ishijima, H. Matsueda, Y. Sawa, P. K. Patra, S. Aoki and T. Nakazawa (2012) Carbon and hydrogen isotopic ratios of atmospheric methane in the upper troposphere over the western Pacific, Atmospheric Chemistry and Physics, 12, 80958113, doi:10.5194/acp-8095-2012
4. Röckmann, T., Brass, M., Borchers, R., and Engel, A.: The isotopic composition of methane in the stratosphere: high-altitude balloon sample measurements, Atmos. Chem. Phys., 11, 13287-13304, doi:10.5194/acp-11-13287-2011, 2011.

DLR

Used values of the kinetic isotope effect:

Reaction partner	for $^{13}CH_4$		for CH_3D	
	A	B	A	B
OH	1.0039	0.000	1.097	49.00
O(1D)	1.0130	0.000	1.066	0.00
Cl	1.0430	6.455	1.278	51.31

values taken from [Röckmann 2011]

with $KIE(T) = A \cdot \exp(B/T)$; $T :=$ temperature

1. Evaluation: Ground-based measurements

Used data:

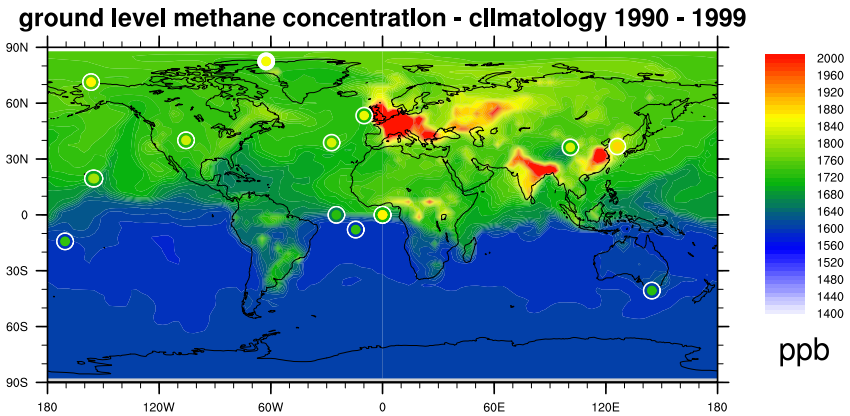
Stationary flask measurements of CH_4 and $\delta^{13}C(CH_4)$ by mass spectrometry of NOAA/ESRL*
Period: 2000 - 2007.

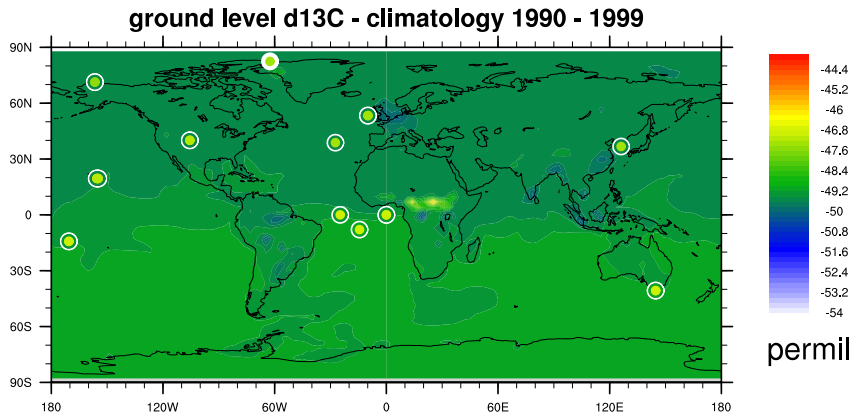
At the Stations:

Alert, Ascension Island, Barrow, Cape Grim, Cape Kumukahi, Mace Head, Mauna Loa, Mt. Waliguan, Niwot Ridge, South Pole, Tae-ahn Peninsula, Tutuila (Cape Matatula)

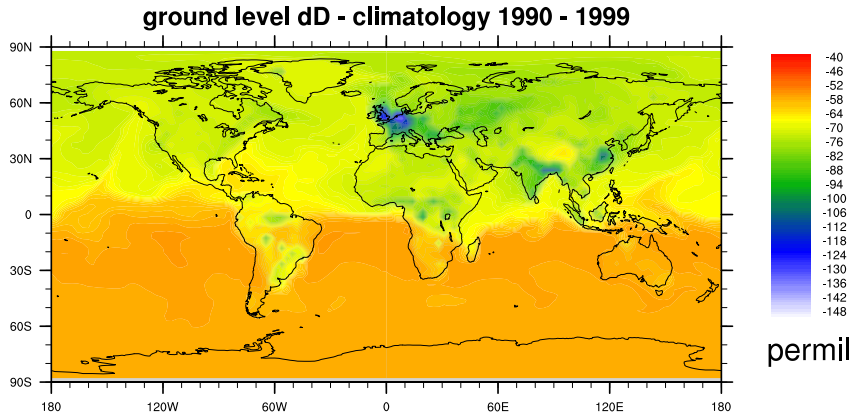
* Reference: [Miller et al. 2002]

1. Evaluation: Ground-based measurements



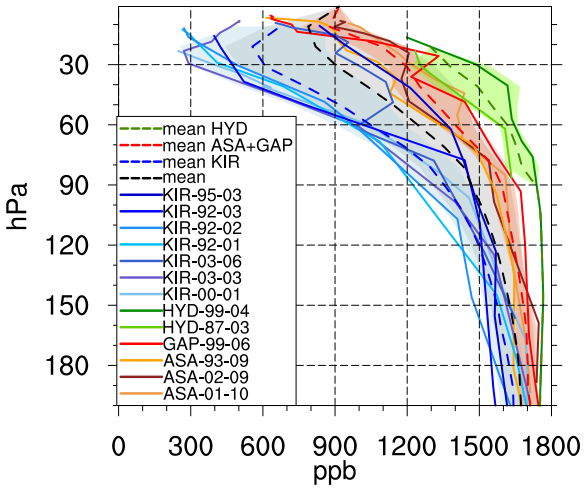


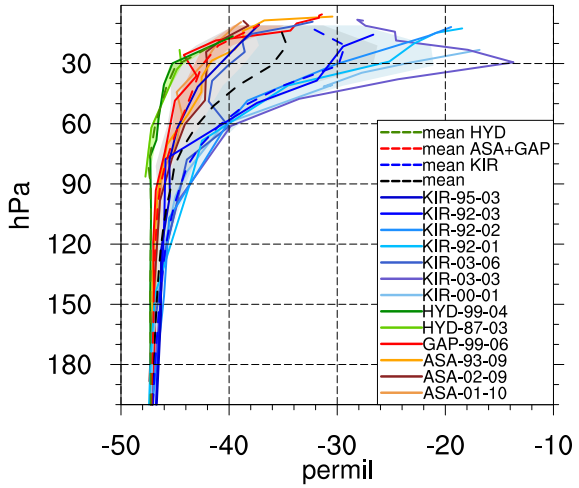
- methane concentration about 100 ppb lower ⇒ simulation covers time period 10 years before measurements
- $d^{13}C$ is about 3 ‰ lower ⇒ Possible reasons: Shift in relative contribution of different sources **or** uncertain isotopic ratios of methane emissions.



NOAA/ESRL did not include dD in the measurements.

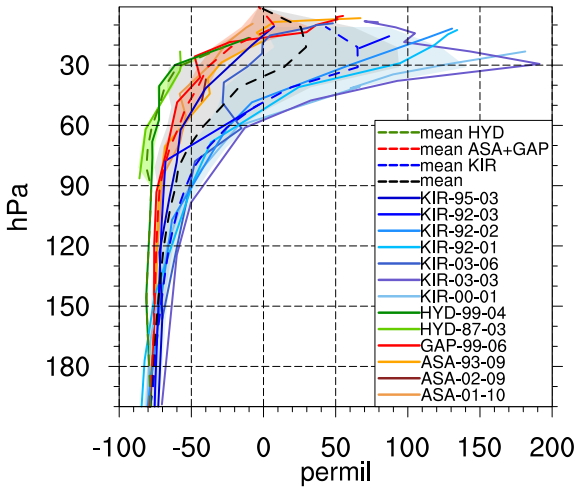
Vertical profile of measurements



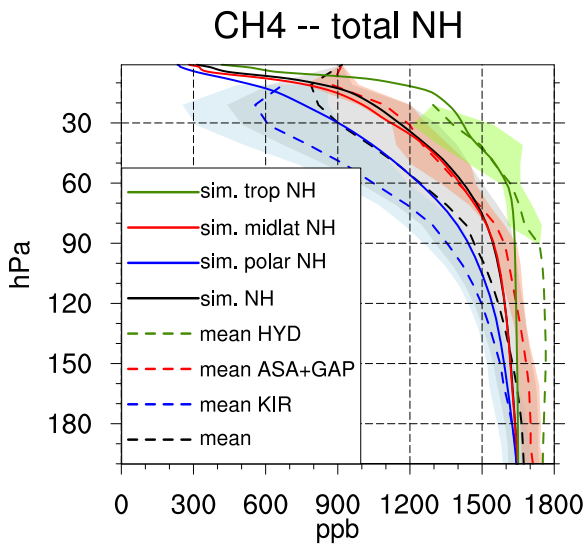


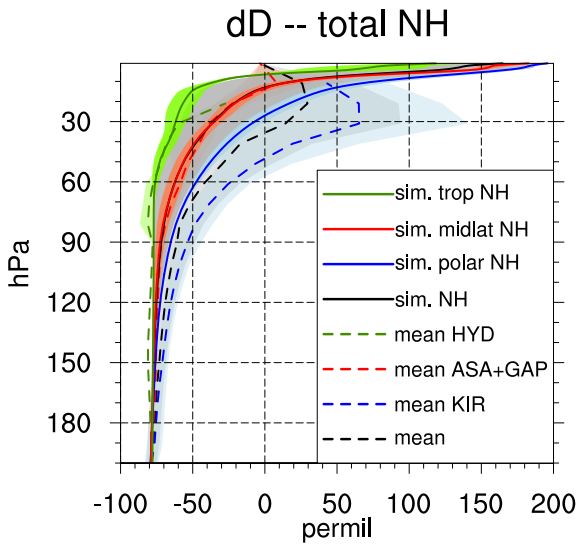
- Polar: KIR - Kiruna - bluish line
- Mid-latitude: ASA - Aire sur l'Adour & GAP - Gap - reddish line
- Tropics: HYD - Hyderabad - greenish line

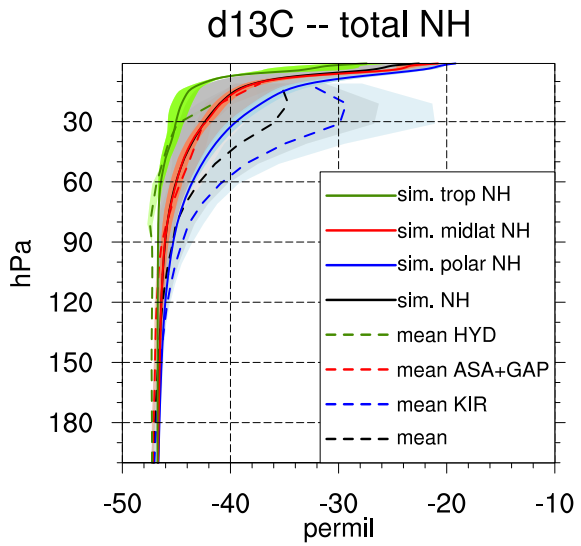
Dashed lines represent the average across all launches in the same region.



Evaluation of the vertical profiles







- δ-values corrected to account for shifted isotopic ratios of sources.
- Simulation results lay within standard deviation of measurements.
- The results sufficiently reproduce the latitudinal and vertical gradient.