40 years of observations of atmospheric methane from a remote European site
(among other things...)

Whitney Bader
Brewer-Wilson Seminar
November 4th, 2016
Overview


- PhD Thesis: "Long-term study of methane and two of its derivatives from solar observations recorded at the Jungfraujoch station."
  - Increase of CH$_4$ since 2005 based on FTIR observations and GEOS-Chem tagged simulation, ACPD, in review, 2016.

- Postdoc project: "Atmospheric content of the most abundant of $^{12}$CH$_4$ isotopologues from ground-based and satellite infrared solar observations and development of a methane isotopic GEOS-Chem module."
Jungfraujoch station

- Swiss Alps (46.5°N, 8.0°E)
- 3 580 m a.s.l.
- Weak local pollution: no major industries within 20 km
- Very high dryness: high-altitude + Aletsch Glacier in its immediate vicinity
Instrumentation and retrievals
Jungfraujoch station

Instrumentation timeline

1950'
1 m focal length
grating
spectrometer

1976 - 1989
7.3 m focal
length Double
Pass Grating
Spectrometer

1985
Homemade
Fourier
Transform
Spectrometer

1991
Bruker 120HR
Fourier
Transform
Spectrometer

Network for the
Detection of
Atmospheric
Composition
Change -
NDACC

1950:
Pioneering infrared
solar observations
CH4: Nielsen and
Migeotte, 1952
CO: Migeotte and
Neven, 1950
+ solar atlas

1975:
Detection of HF in
the atmosphere by
R. Zander
Zander et al., 1989

1985:
Atmospheric
observations
resumed and
haven't stopped
since then.

1991:
Network for the
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Database of 45 000 spectra (grating + homemade + Bruker)
→ 40 years of continuous observations
Jungfraujoch station

Instrumentation timeline

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Network for the Detection of Atmospheric Composition Change - NDACC

pioneering infrared solar observations
CH4 : Nielsen and Migeotte, 1952
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1975 Detection of HF in the atmosphere by R. Zander
Zander et al., 1989

Atmospheric observations resumed and haven't stopped since then.

Database of 45 000 spectra (grating + homemade + Bruker)

→ 40 years of continuous observations
"Extension of the long-term total column time series of atmospheric methane above the Jungfraujoch station: analysis of grating infrared spectra between 1977 and 1989."

Master's thesis
Grating spectrometer

- Telescope
- Monochromator
- Rapid Scanning System
- Double Pass Spectrometer
- Computer(s)
- Ω-meter
- Detector

→ wavelength
→ diffraction order

wavenumber (cm⁻¹)

Intensity

Inversion

4th Nov 2016

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Inversion strategy (SFIT-2)

Forward Model (SFIT-2)
- Spectroscopic Line parameters

Atmospheric Model
- vertical layering scheme
- daily p-T profiles (NCEP)
- a priori mixing ratio profiles (scaling)

Windows, Fitted Species, Signal-to-noise for inversion

Synthetic Spectrum

Recorded Spectrum (FTIR)

Minimum Residuals
- YES
  → Mixing ratio profiles
  → Total/partial columns

NO
Datasets and harmonization

2700 spectra - 9 datasets
9 different combinations of diffraction orders, windows, spectroscopy,…

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Micro-windows and Fitted species

1. 2913.4 → 2914.25 CH4; HDO
2. 2924.17 → 2924.99 CH4; H2O; HDO + solar lines
3. 2962.8906 → 2963.7003 CH4; H2O; HCl
Datasets and harmonization

Different spectra quality, signal-to-noise ratio

|------|------|------|------|------|------|------|------|------|------|------|------|------|------|

- **1979**
  - Iter: 7

- **1983**
  - Iter: 3

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Datasets and harmonization

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**Micro-windows and Fitted species**

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Averaging

B & C

B & D

Micro-windows and Fitted species

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Days in common: 85
Ratio: 1.086

E & I

Days in common: 19
Ratio: 1.005

F, G & H

Homemade - FTS

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Methane (CH$_4$) above Jungfraujoch

**Random error:** 1.17%
**Systematic error:** 11.98% - 15.08% - 9.04%

**Daily means total columns**
- Averaged DPGS (μw2 - μw3)
- Grating spectrometer (μw 1)
- Grating instrument (μw 2)
- Homemade FTS (NDACC strategy)

**TOTAL COLUMN (molec./cm$^2$)**

**DATE**

1.68e+19

Zander et al., 1989

COLUMN IN 1950-51
Jungfraujoch station

Instrumentation timeline

1950':
- 1 m focal length grating spectrometer

1976 - 1989:
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Database of 45,000 spectra (grating + homemade + Bruker) → 40 years of continuous observations

pioneering infrared solar observations
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Network for the Detection of Atmospheric Composition Change - NDACC

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Fourier Transform Spectrometer

2 Detectors
HgCdTe and InSb
650 à 4500 cm\(^{-1}\)
High resolution
between 0.00285 cm\(^{-1}\)
and 0.006 cm\(^{-1}\)
Inversion strategy (SFIT-2)

Windows, Fitted Species, Signal-to-noise for inversion

Forward Model (SFIT-2)

Atmospheric Model
- vertical layering scheme
- daily p-T profiles (NCEP)
- a priori mixing ratio profiles

Spectroscopic Line parameters

Synthetic Spectrum

Recorded Spectrum (FTIR)

Minimum Residuals

YES
- Mixing ratio profiles
- Total/partial columns

NO

covar matrix
"Long-term study of methane and two of its derivatives from solar observations recorded at the Jungfraujoch station."

PhD thesis
Part I – Optimization of retrieval strategies
Inversion strategy (SFIT-2)

Forward Model (SFIT-2)

Windows, Fitted Species, Signal-to-noise for inversion

Atmospheric Model

- vertical layering scheme
- daily p-T profiles (NCEP)
- a priori mixing ratio profiles

Synthetic Spectrum

Recorded Spectrum (FTIR)

Minimum Residuals

YES

Methane, methanol, ethane

→ Mixing ratio profiles
→ Total/partial columns

NO
Long-term evolution and seasonal modulation of methanol above Jungfraujoch (46.5° N, 8.0° E): optimisation of the retrieval strategy, comparison with model simulations and independent observations

W. Bader¹, T. Stavrakou², J.-F. Muller³, S. Reimann¹, C. D. Boone⁴, J. J. Harrison¹, O. Flock¹, B. Bovy¹, B. Franco¹, B. Lejeune¹, C. Servais¹, and E. Mahieu¹

¹Institute of Astrophysics and Geophysics of the University of Liège, Liège, Belgium
²Belgian Institute for Space Aeronomy, Avenue Circulaire 3, 1180, Brussels, Belgium
³Laboratory for Air Pollution and Environmental Technology, Swiss Federal Laboratories for Materials Testing and Research (Empa), Dübendorf, Switzerland
⁴Department of Chemistry, University of Waterloo, Ontario, Canada
⁵Department of Chemistry, University of York, York, UK
Inversion strategy

Rinsland et al., 2009
992 – 998.7 cm\textsuperscript{-1}

Atmospheric Chemistry Experiment, 2011
984.9 – 1005.1 cm\textsuperscript{-1}

Mahieu et al., 2012

CH\textsubscript{3}OH

Stavrakou et al., 2011
1029 – 1037 cm\textsuperscript{-1}

Simulated windows for Jungfraujoch, SZA : 80°, 6.1 mK, HITRAN08
Inversion strategy

- Solar zenith angle 65 et 80°
- Contrasting absorptions features
  \( \text{O}_3 \) 93% and 98%
  \( \text{CH}_3\text{OH} \) 1.7% and 1.8%
- Improved vertical sensitivity range
  Low troposphere [surface - 7 km]
  UTLS [7 - 15 km]
Retrieval of ethane from ground-based FTIR solar spectra using improved spectroscopy: recent burden increase above Jungfraujoch


*Institute of Astrophysics and Geophysics, University of Liège, B-4000 Liège (Sart-Tilman), Belgium
Jet Propulsion Laboratory, California Institute of Technology, Pasadena California, 91109, USA
CEA, DEN, DPC, F-91191 Gif-sur-Yvette, France
Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA-UMR7583) CNRS, Universités Paris Est Créteil and Paris 7 Diderot (IPSL), F-94010 Créteil cedex, France
Department of Atmospheric Science, Colorado State University, Fort Collins, CO USA
Graduate School of Environmental Studies, Nagoya University, Nagoya, Japan
Department of Environmental Geochemical Cycle Research, Japan Agency for Marine-Earth Science and Technology, Yokohama, Japan
Department of Chemistry, University of Waterloo, Ontario, Canada
Inversion strategy - Interferences

Simulation for Jungfraujoch
Solar Zenith Angle: 60°

Dry conditions

Humid conditions
Inversion strategy - Spectroscopy

- Combination of 3 windows & updated spectroscopic parameters included
- Improved vertical sensitivity range
  - Low tropospheric < 8.5 km
  - UTLS 8.5 - 22 km

**Hitran 2008**

- Pseudolines
- \( C_2H_6 \)
- \( CH_3Cl \)
40 years of observations of atmospheric methane from a remote European site

(among other things...)

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Brewer-Wilson Seminar
November 4th, 2016
Atmospheric methane

- 2nd most important anthropogenic greenhouse gas
- 1/5 of anthropogenic radiative forcing since 1750 is due to methane
- 3 types of emission processes:
  - biogenic (dotted)
  - thermogenic (plain)
  - pyrogenic (hatched)
- 1 major sink
  - oxidation by OH

+ 260% since 1750
Harmonized long-term time series of CH$_4$ above Jungfraujoch
CH$_4$ : 1977 - 2015

Harmonized long-term time series of CH$_4$ above Jungfraujoch

Total Column (molec./cm$^2$)

+ 6.96 %
Between 1978 and 1983

0.72 ± 0.11
0.37 ± 0.07
-0.04 ± 0.07
...
"The recent increase of methane from 10 years of NDACC ground-based FTIR observations."

Jungfraujoch station

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resumed and
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Database of 45 000 spectra (grating + homemade + Bruker)
→ 40 years of continuous observations
Unexplained increase since ~2005

CH$_4$ above Jungfraujoch (46.5°N, 3.58 km a.s.l.)

- 0.04 ± 0.08 %
- 0.35 ± 0.09 %
- 0.31 ± 0.04 %
10 years of NDACC FTIR observations

1- Eureka (80 °N)
2- Kiruna (68 °N)
3- Zugspitze (47 °N)
4- Jungfraujoch (47 °N)
5- Toronto (44 °N)
6- Tsukuba (37 °N)
7- Izaña (28 °N)
8- Wollongong (34 °S)
9- Lauder (45 °S)
10- Arrival Heights (78 °S)

2005-2014
10 years of NDACC FTIR observations

Anomaly with respect to 2005.0
Averaged increase : 0.31 ± 0.03 %/year

0.26 ± 0.02 %/year : Wollongong
0.39 ± 0.09 %/year : Toronto

4th Nov 2016
GEOS-Chem v9-02. Tagged simulation

- Resolution: $2^\circ \times 2.5^\circ$ and $4^\circ \times 5^\circ$
- 47 vertical levels - Output: 3 hours
- Meteo fields: GEOS5
  (Dec 2003 - May 2013)
- Spin-up over 2004
  (70 spins for initialization)
- Emission inventories
  - Anthropogenic emissions: EDGAR v4.2
  - Biomass burning: GFED3 (8h)
  - Wetland model [Pikett-Heaps, 2011]
  - Termites [Fung et al., 1991]
  - Biofuels [Yevich and Logan, 2003]
  - Soil absorption [Fung et al., 1991]
- Main sink: 3D OH monthly
  [Park et al., 2004]
- Lifetime: 8.9 years

Each tracer represents the contribution of each source to the simulated total column of methane

<table>
<thead>
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<th>Tracers</th>
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<tr>
<td>1- Total</td>
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<td>2- Gas and oil</td>
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<td>3- Coal</td>
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<td>4- Livestock</td>
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<td>5- Waste management</td>
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<tr>
<td>6- Biofuels</td>
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<td>7- Rice cultures</td>
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<tr>
<td>8- Biomass burning</td>
</tr>
<tr>
<td>9- Wetlands</td>
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<tr>
<td>10- Other natural</td>
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<tr>
<td>11- Other anthropogenic</td>
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<tr>
<td>12- Soil absorption</td>
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</tbody>
</table>
FTIR vs GEOS-Chem

- Maximum bias $4.8 \pm 3.5\%$ (Arrival Heights) ≈ FTIR systematic error
  
  Anomaly with respect to 2005.0
FTIR vs GEOS-Chem

Averaged increase over 2005-2012

FTIR: $0.30 \pm 0.04 \%$/year

GEOS-Chem: $0.35 \pm 0.03 \%$/year
Methane since 2005

![Graph showing methane annual change at various latitudes.](image)

- Eureka
- Kiruna
- Zugspitze
- Jungfraujoch
- Toronto
- Tsukuba
- Izaña
- Wollongong
- Lauder
- Arrival Heights

**CH₄ annual change (% year⁻¹)**
Yearly relative change in %.

\[ YC (\text{in } \%) = \frac{\mu_n - \mu_{n-1}}{\mu_{\text{tot},n-1}} \]

\( \mu_n \): annual mean of CH\(_4\), year n.

The year-to-year relative changes are computed so that when we assume a relative change of a tracer for the year n, it is expressed wrt to the previous year (n-1) as reference.

\( \mu_{\text{tot},n-1} \): annual mean of the simulated cumulative methane for the year (n-1)
GC tagged simulation: Analysis

- Yearly relative change (%)
- Natural sources mainly responsible for the interannual variation
- e.g. Wollongong

![Graph showing various sources of methane emissions and their contributions over years](chart)

**Legend:**
- **Total Methane**
- **Biomass burning**
- **Biofuels**
- **Coal**
- **Livestock**
- **Gas and oil**
- **Other Anthropogenic**
- **Other Natural**
- **Rice Cultures**
- **Waste**
- **Wetlands**
- **Soil absorption (sink)**
GC tagged simulation: Analysis

- Yearly relative change (%)
- Secondary contributors such as coal or gas and oil contribute to the overall increase
- e.g. Izaña

![Graph showing various contributors to methane emissions with a focus on coal, biomass burning, biofuels, and gas and oil.](image-url)
**GC tagged simulation: Analysis**

- Contributors to the cumulative increase: tracer ranking

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- Gas and oil
- Other Anthropogenic
- Other Natural
- Rice Cultures
- Waste
- Wetlands
- Soil absorption (sink)

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*4th Nov 2016*
## Methane increase: Discussion

**Source attribution?**

<table>
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<tr>
<th>Many studies...</th>
<th>Aydin et al., 2011</th>
<th>Kirschke et al., 2013</th>
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<td>Ringeval et al., 2010</td>
<td>Sussmann et al., 2012</td>
<td>Hausmann et al., 2016</td>
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<td>Bloom et al., 2010</td>
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<td>Schaefer et al., 2016</td>
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From GEOS-Chem tagged simulation

Secondary contributors to the global budget of methane play a major role in the increase of methane observed since 2005.
→ coal mining, gas and oil transport and exploitation
Methane increase: Discussion

Source attribution?

From GEOS-Chem tagged simulation

Secondary contributors to the global budget of methane play a major role in the increase of methane observed since 2005.

→ coal mining, gas and oil transport and exploitation

Best emission inventories available → limitations

EDGAR v4.2

- Overestimates the recent emission growth in Asia (Schwietzke et al. 2014, Bergamaschi et al. 2013 and Bruhwiler et al. 2014).
- Chinese coal mining emissions are too large by a factor of 2 (Turner et al. 2015, from a global GOSAT inversion)
- EDGAR v4.2 vs global GOSAT inversion (Turner et al., 2015)
  - increase in wetland emissions in South America
  - increase in rice emissions in Southeast Asia
Methane increase: Discussion

Source attribution?

Gas and oil use and exploitation (GAO)

underestimated by current emission inventories (incl. EDGAR)

Franco et al., 2015, 2016; Turner et al., 2015, 2016
Methane increase: Discussion

Source attribution?

Gas and oil emissions: the use of $C_2H_6$ as a proxy

$CH_4$ and $C_2H_6$ share a source of emissions

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane’s atmospheric budget (Logan et al., 1981; Rudolph, 1995)
Methane increase: Discussion

Source attribution?

Gas and oil emissions: the use of \( \text{C}_2\text{H}_6 \) as a proxy

\( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \) share a source of emissions.

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane’s atmospheric budget (Logan et al., 1981; Rudolph, 1995)

*Franco et al., 2016*

- Observations: sharp increase of \( \text{C}_2\text{H}_6 \) since 2009 × GEOS-Chem
  \[ \rightarrow \sim 5 \% / \text{year at mid-latitudes}, \sim 3 \% / \text{year at remote sites} \]
- Massive growth of oil and gas exploitation in the North American continent, confirmed by *Helmig et al. 2016*
Methane increase: Discussion

Source attribution?

Gas and oil emissions: the use of $\text{C}_2\text{H}_6$ as a proxy

Production, transport and use of natural gas and the leakage associated to it amounts at ~ 62 % of ethane’s atmospheric budget (Logan et al., 1981; Rudolph, 1995)

Franco et al., 2016

- Observations: sharp increase of $\text{C}_2\text{H}_6$ since 2009 × GEOS-Chem
  → ~5 %/year at mid-latitudes, ~3 %/year at remote sites

Methane increase? From $\text{C}_2\text{H}_6/\text{CH}_4$ ratio derived from GOSAT measurements

→ from 20 Tg in 2008, to 35 Tg in 2014

Confirming the influence of GAO on the observed methane increase
Methane increase: Discussion

Source attribution?

Gas and oil emissions: the use of $C_2H_6$ as a proxy $\rightarrow C_2H_6/CH_4$

**Hausmann et al. 2016**: GAO contribution of 39% to the renewed methane in Zugspitze between 2007 and 2014

**BUT**

The strength of the $C_2H_6/CH_4$ relationship associated to GAO strongly depends on the studied region and/or production basin

Variability rarely taken into account (Kort et al. 2016, Peischl et al. 2016)
Methane increase: Discussion

Source attribution?

The problem of the use of \( C_2H_6 \) as a proxy \( \rightarrow C_2H_6/CH_4 \)

- Emissions from GAO well pads may be missing from most bottom-up emission inventories. Lyon et al. (2016)
- A horizontal drilling rig for natural gas in the Marcellus formation in eastern, Pennsylvania.

- Emissions differ from one well pad to another and even within the same pad depending on the depth of the extraction.
- e.g. Marcellus Basin that is actually two different overlapping basins.
Methane increase: Conclusion

• FTIR ground-based measurements: 0.31 ± 0.03 %/year wrt 2005.0

Source attribution?

• GEOS-Chem: 0.35 ± 0.03 %/year vs 0.30 ± 0.04 %/year (FTIR)

• Anthropogenic sources, secondary contributors to the global CH$_4$ budget, are first contributors to the observed increase
  • coal mining, gas and oil exploitation, livestock

• While GEOS-Chem agrees with our observations, the repartition between the different sources of methane would greatly benefit from an improvement of the global emission inventories. e.g. EDGAR
  • US oil and gas and livestock are underestimated.
  • Coal emissions are overestimated.
What's the next step?

Postdoc project

- $\text{CH}_4$
- $\text{CH}_3\text{D}$
- $^{13}\text{CH}_4$

Relative abundance:
- $6.16 \times 10^{-4}$
- $1.11 \times 10^{-2}$
How can isotopologues help?  

*Source attribution?*

**In situ $^{13}$CH$_4$ observations**

NOAA Earth System Research Laboratory & Global Atmospheric Watch

**Schwietzke et al. (2016)**

Total fossil fuel = industry activities + natural geological seepage

"Methane emissions from natural gas, oil and coal production and their usage are 20 to 60 percent greater than inventories."

No upward trend of industrial fossil fuel emissions in global CH$_4$ inventories $\rightarrow$ natural-gas industry improvements

**Nisbet et al. (2016)**

"A major cause of increased tropical wetland and tropical agricultural methane emissions, the likely major contributors to growth, may be their responses to meteorological change."
How can isotopologues help?

- Both isotopologues show distinctive $^{13}\text{C}/^{12}\text{C}$ (and D/H) signature depending on the emission process.

- **Kinetic Isotope Effect (KIE)**: Each isotopologue will react at a specific rate constant depending on the removal pathway. $\text{KIE} = \text{Ratio of the rate constants.}$ (Saueressig et al., 2001 & Snover and Quay, 2000).

- Determining the $^{13}\text{C}/^{12}\text{C}$ and D/H content of atmospheric methane is therefore a unique tracer of its budget.

Allen, Rebalancing the global methane budget, Nature, 46, 538, 2016. (Fig. 1)
Two year project – Part I

- Development of a retrieval strategy for $^{13}\text{CH}_4$ and CH$_3$D from infrared observations

**Instrumentation & Database**

- **Fourier Transform Spectrometers**
  - *Toronto*: ~1430 days since 2002, resolution: 0.004 cm$^{-1}$
  - *Eureka*: ~760 days since 2006 (0.0035 cm$^{-1}$)
  - *Jungfraujoch, Switzerland*: 2590 days since 1990 (0.004 cm$^{-1}$)

- **PARIS-IR (0.02 cm$^{-1}$)** ~240 days since 2004
  - Portable Atmospheric Research Interferometric Spectrometer for the InfraRed

- **Complementary**: ACE-FTS solar occultations
  - ~35 000 occultations since February 2004
Two year project - Part II

• Development of an isotopic module for GEOS-Chem
• CH₄ GEOS-Chem tagged simulation as a starting point
• Supported by the best available emission inventories of CH₄
• + Emission ratios for each isotopologues and source type + KIE

The model will provide a spatially global answer to the question of the methane budget.
Thank you!

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