Heavy methane to explain the unexplained recent methane growth ?

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Background information - 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, thermogenic and pyrogenic **(see Figure 1)**
- 1 major sink : oxidation by the radical hydroxyl, OH
- + 260% increase since 1750
- 1980s-1990s : + 13 ppb/year
- 2000-2006 : stable concentrations
- Since 2006 : new and unexplained increase

Kirschke et al., 2013

Nisbet et al., 2014

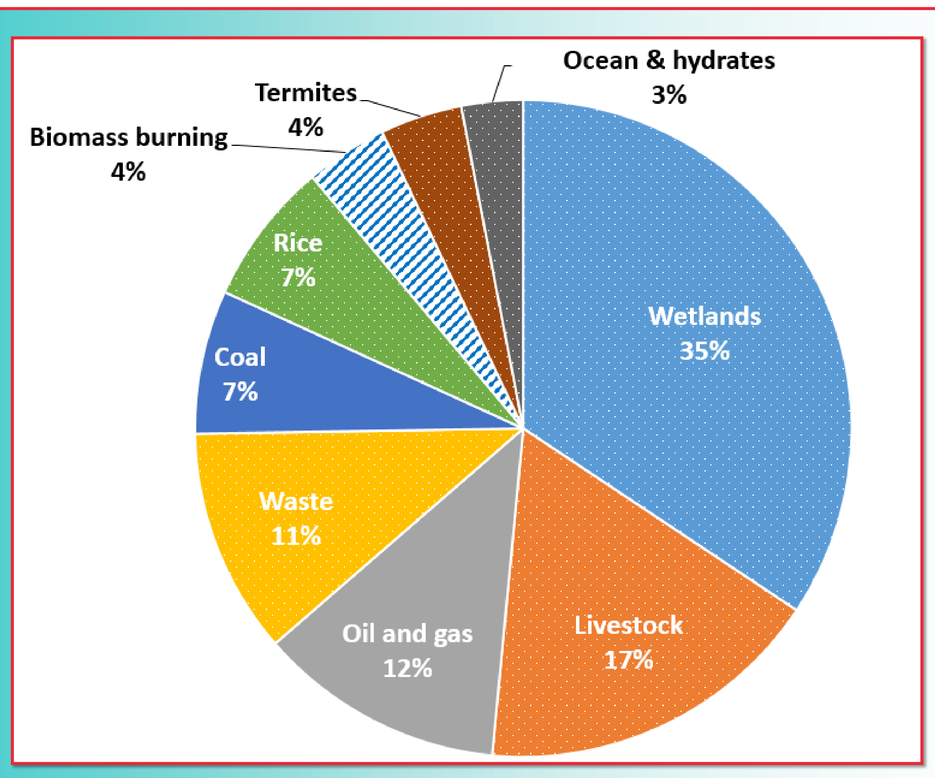

Figure 1 : Sources of atmospheric methane, sorted by biogenic (dotted area), pyrogenic (plain area), and thermogenic processes (hatched area).

Instrumentation & Database

Toronto, ON, Canada

- Bomem DA8 Fourier Transform Spectrometer (0.004 cm^{-1})

  ~1430 days of observations since May 2002

Eureka, NU, Canada

- Bruker IFS-125 HR Fourier Transform Spectrometer (0.0035 cm^{-1})

  ~760 days of observations since July 2006

- PARIS-IR (0.02 cm^{-1})

  Portable Atmospheric Research Interferometric Spectrometer for the InfraRed

  ~240 days of spring observations at Eureka since 2004

Jungfraujoch, Switzerland

- Bruker 120-HR (0.004 cm^{-1})

  ~2590 days of observations since 1990

Complementary : ACE-FTS

- Solar occultations

  ~35 000 occultations since February 2004

A one-year project : timeline (from 07-2016 to 07-2017)

Nov-2016 : Strategy for $^{13}CH_4$ developped and optimized for all stations* + time series production

Mar-2017 : Strategy for CH_3D developped and optimized for all stations* + time series production

May-2017* : Dataset intercomparisons + ACE-FTS

Jul-2017* : Focus on increase since 2006

***lead to publication of results**

What is heavy methane ?

- The main **isotopologues** of $^{12}CH_4$, heavier molecules with one additional neutron either on a carbon or on one hydrogen atom, to form ^{13}C or Deuterium, respectively.

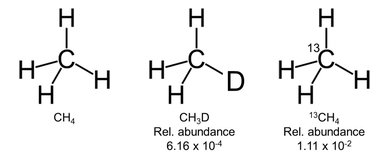

Figure 2 : Main isotopologues of methane

- **Delta values** : Unit used to express the $^{13}C/^{12}C$ or the D/H ratio with respect to a reference value, the Vienna Pee Dee Belemnite (VPBD) for ^{13}C and the Vienna Standard Mean Ocean Water (SMOW) for Deuterium.
- Both isotopologues are emitted with different **isotopic ratios** depending on the emission sources (**see Figure 3**) and show specific delta values.

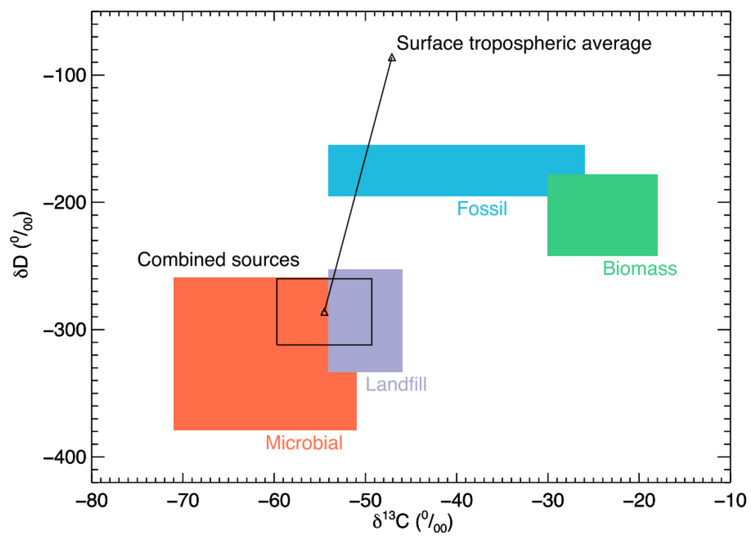

Figure 3 : The $\delta^{13}C$ and δD for the four major sources whose emissions were estimated in Rigby et al. (2012). (Figure 2 from Rigby et al., 2012).

- **Kinetic Isotope Effect (KIE)** : Ratio of the rate constants for uptake of isotopically light and heavy methane. Each removal pathway is associated to a KIE (Saueressig et al., 2001 & Snover and Quay, 2000).
- Determining the $^{13}C/^{12}C$ and D/H content of atmospheric methane is therefore a unique tracer of its budget and can provide additional constraint on the regional, hemispheric and global budgets (Snover and Quay, 2000).

Development of a retrieval strategy from FTIR observations

- Identification of absorption lines of the target species : $^{13}CH_4$ & CH_3D
- Determination of the best combination of spectral windows, spectroscopic line parameters, a priori mixing ratio profile,…

GOAL

- Limit interferences
- Minimize residuals
- Maximize information content.

⇒ Error analysis

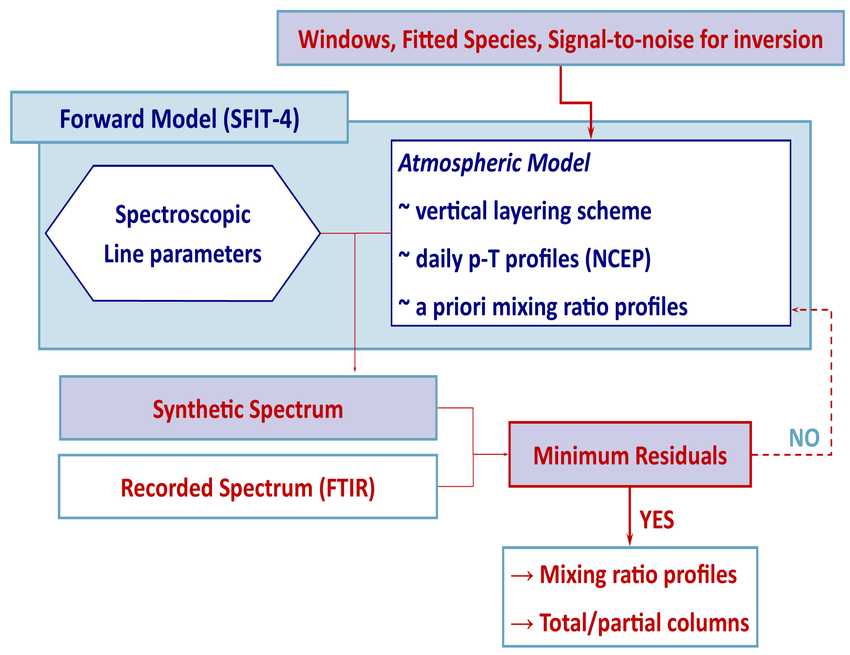

Figure 4 : Operating principle of the SFIT-4 algorithm.

Acknowledgments

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References

Kirschke S., et al.: Three decades of global methane sources and sinks. Nat. Geosci., 6, 813-23, 2013; Nisbet E.G., et al.: Methane on the rise—again. Science, 343, 493-5, 2014; Rigby M., et al.: The value of high-frequency, high-precision methane isotopologue measurements for source and sink estimation. J. Geophys. Res. Atmos., 117, 2012. Saueressig G., et al.: Carbon 13 and D kinetic isotope effects in the reactions of CH4 with O(1D) and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane. J. Geophys. Res., 106, 23127, 2001; Snover A.K. and Quay P.D.: Hydrogen and carbon kinetic isotope effects during soil uptake of atmospheric methane. Global. Biogeochem. Cycles, 14, 25–39, 2000.