Thirty years of global atmospheric CH_4 and ethane monitoring:

What can ethane teach us about CH_4?

Isobel Simpson, Donald Blake, Simone Meinardi, Nicola Blake, and F. Sherwood Rowland

Dept. of Chemistry
University of California, Irvine
Irvine, CA 92697-2025
U.S.A.

isimpson@uci.edu

Atmospheric methane (CH_4)

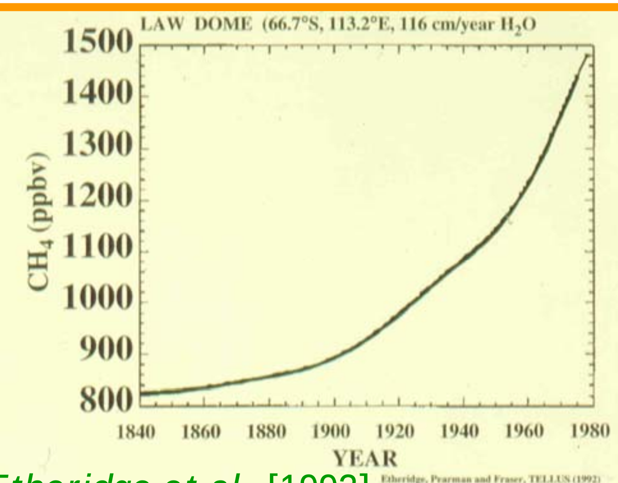
Atmospheric CH_4 levels have more than doubled since the 1700s:

- 400-700 ppbv pre-industrially
- 1780 ppbv currently

Second largest human contribution to climate change after CO_2:

- CO_2: 1.66 W m^{-2}
- CH_4: 0.48 W m^{-2}
- O_3: 0.35 W m^{-2}

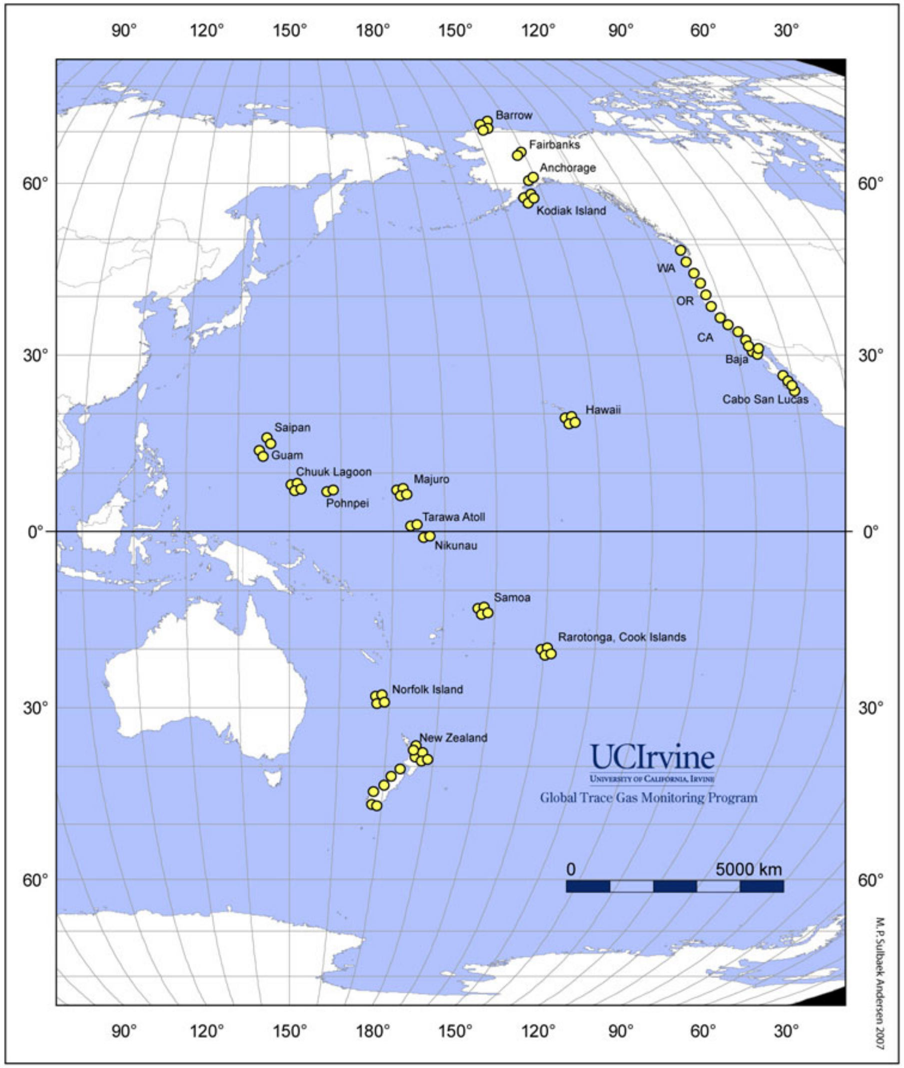
Spahni et al. [2005]; *IPCC* [2007]



Etheridge et al. [1992]

Rice paddy workers, Philippines

UC-Irvine global monitoring



Trace gas monitoring

- 1978 to present

Sampling details

- 4 trips a year (Mar, Jun, Sep, Dec)
- 3-week period
- 40-45 sampling sites
- 80 samples per trip

71ºN to 47ºS

- Alaska
- Pacific Northwest
- Baja California
- Central Pacific
- South Pacific

Whole air sampling (WAS)

Portage Glacier

Rarotonga

Canisters

- 2-L stainless steel
- Conditioned
- Evacuated
- Bellows valve

Site selection

- Along coast
- On-shore wind

Sampling

- 1 minute
- Filled to ambient pressure

GC/FID/ECD/MSD analysis at Irvine

Hydrocarbons

- Methane
- Ethane
- Ethyne
- Propane
- *i*-Butane
- *n*-Butane

Alkyl nitrates

- Methyl nitrate
- Ethyl nitrate
- *i*-Propyl nitrate

Halocarbons

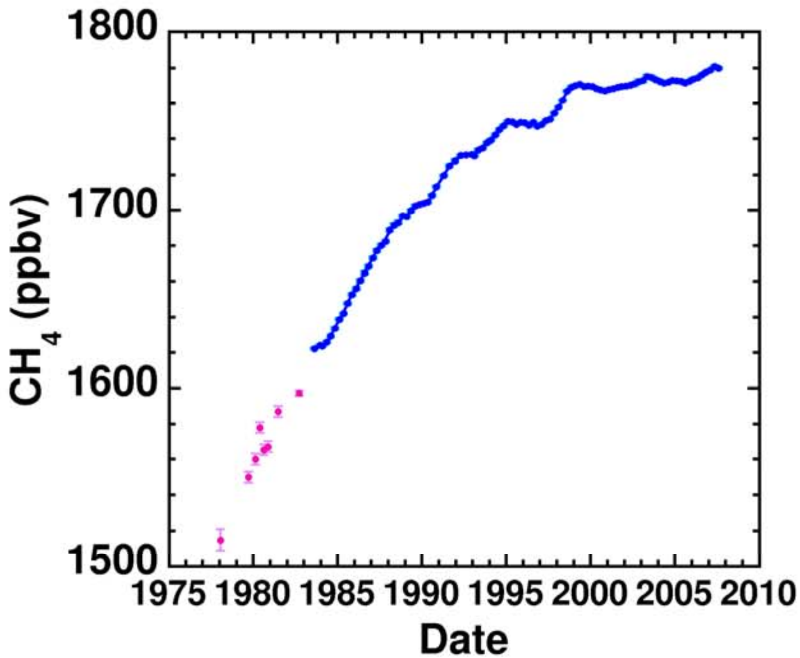
- CFC-11
- CFC-12
- CFC-113
- CCl_4
- CH_3CCl_3
- $CHCl_3$
- C_2Cl_4
- H-1211

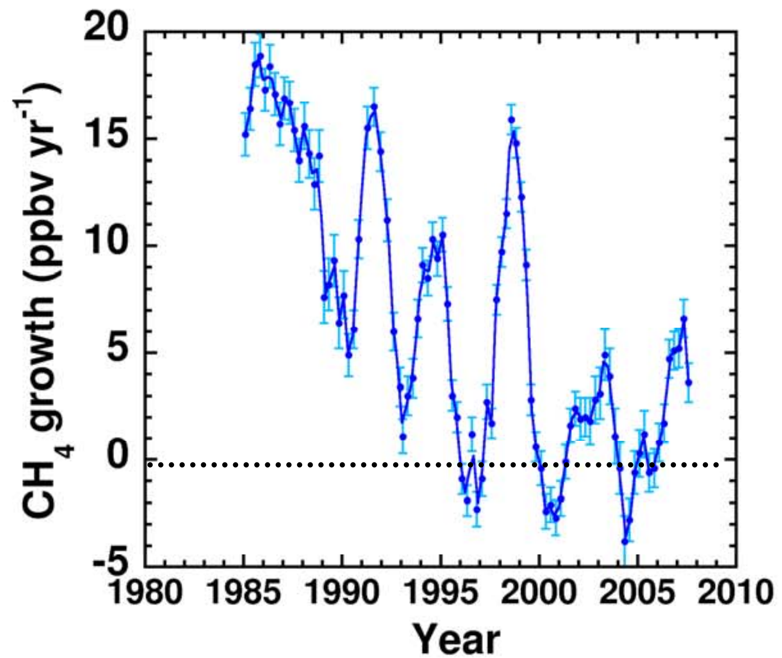
http://cdiac.ornl.gov/tracegases.html

	Accuracy	Precision
CH_4	±1%	1 ppbv
Ethane	±5%	2%
C_2Cl_4	±3-8%	0.05 pptv

UC-Irvine laboratory

Global CH_4 mixing ratio and growth





17% mixing ratio increase since 1978

- 1970s & 80s } Steady growth then slowing growth
- 1990s: Variable growth
- 2000s: Near-zero growth

Long-term growth rate decline with striking anomalies

- Every 3½ -4½ years
- Most recent in 2007

Sources of CH_4

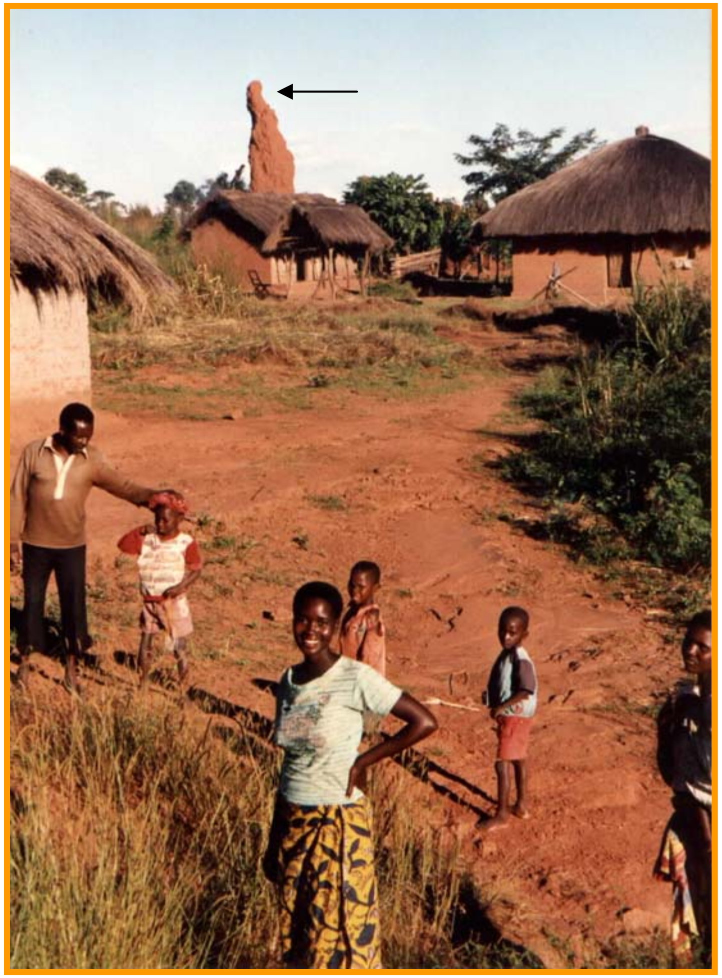
Anthropogenic sources (70 %)

- Fossil fuel 100 Tg CH_4 yr^{-1}
- Ruminant animals 80 Tg CH_4 yr^{-1}
- Rice agriculture 60 Tg CH_4 yr^{-1}
- Landfills 60 Tg CH_4 yr^{-1}
- Biomass burning 50 Tg CH_4 yr^{-1}

Natural sources (30 %)

- Wetlands 100 Tg CH_4 yr^{-1}
- Termites 20 Tg CH_4 yr^{-1}
- Geological 10 Tg CH_4 yr^{-1}
- Hydrates 5 Tg CH_4 yr^{-1}
- Oceans 4 Tg CH_4 yr^{-1}
- Wildfires 2 Tg CH_4 yr^{-1}
- (Vegetation controversy)

Denman et al. [2007] (*IPCC*, Ch. 7)



Termite mound, Democratic Republic of the Congo

Sources of ethane

Anthropogenic sources (70 %)

- Biomass burning 5.6 Tg C yr^{-1}
- Fossil fuel 4.8 Tg C yr^{-1}

Natural sources (30 %)

- Vegetation 4.0 Tg C yr^{-1}
- Oceans 0.8 Tg C yr^{-1}

Total: 15.2 Tg C yr^{-1}

Ehhalt and Prather [2001] (*IPCC*, Ch. 4)

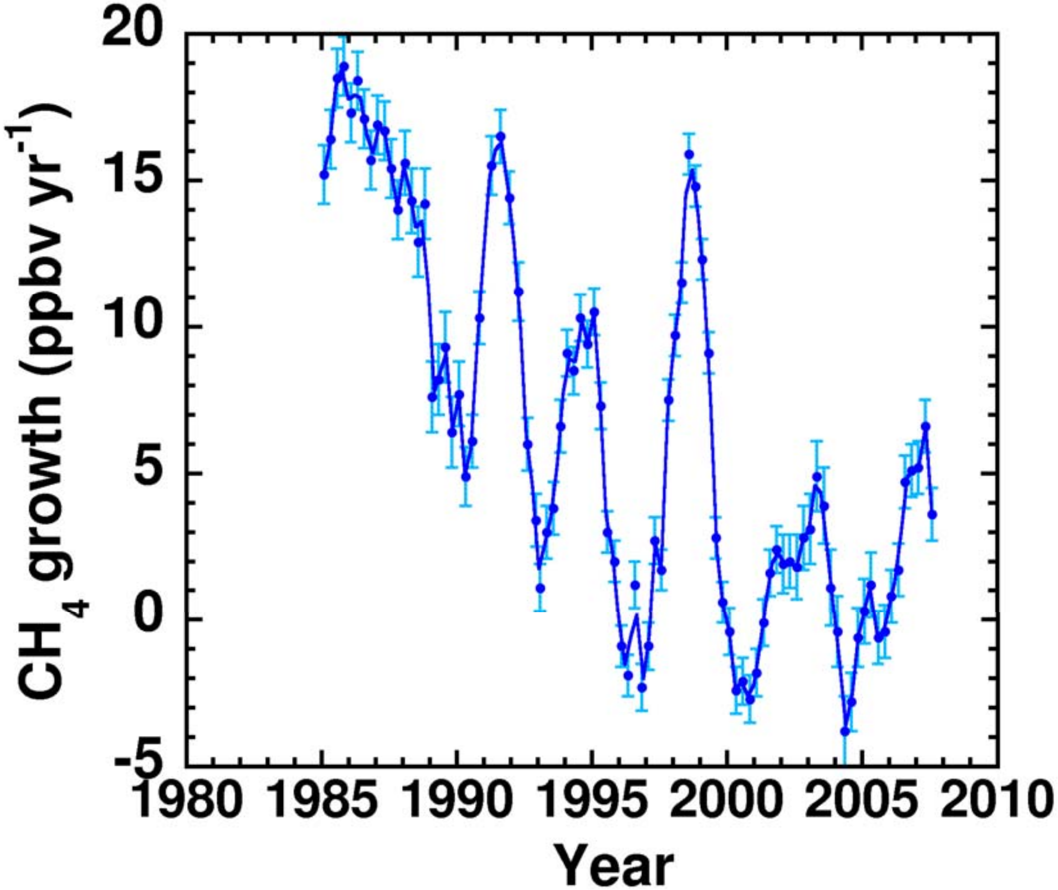
Tapping into a natural gas reserve near Medicine Hat, Alberta

Comparison with C_2Cl_4 and ethane

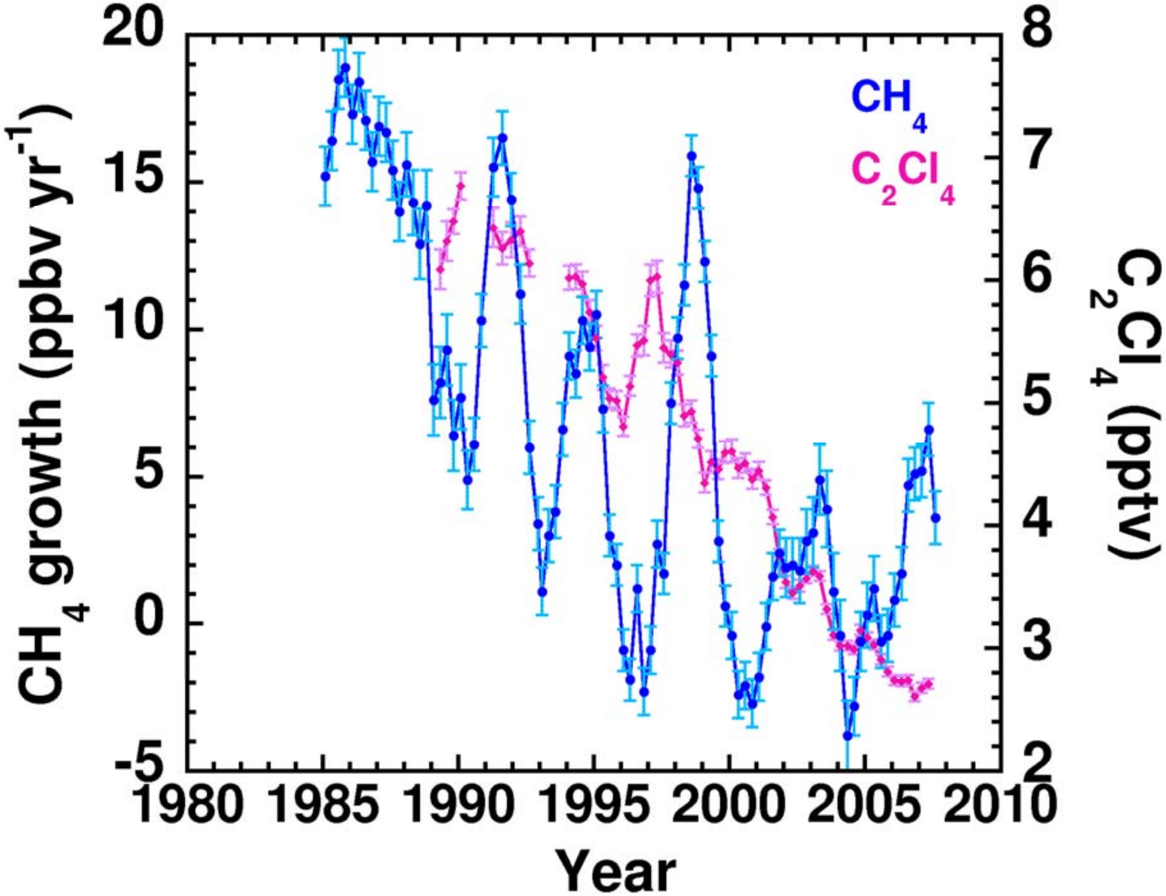
	Sources			Sinks
	Fossil fuel	Biomass burning	Industrial solvent	OH
CH_4	√	√		√
Ethane	√	√		√
C_2Cl_4			√	√

- Test whether CH_4 growth rate fluctuations are **source**-driven or **sink**-driven

Comparison with C_2Cl_4



Comparison with C_2Cl_4

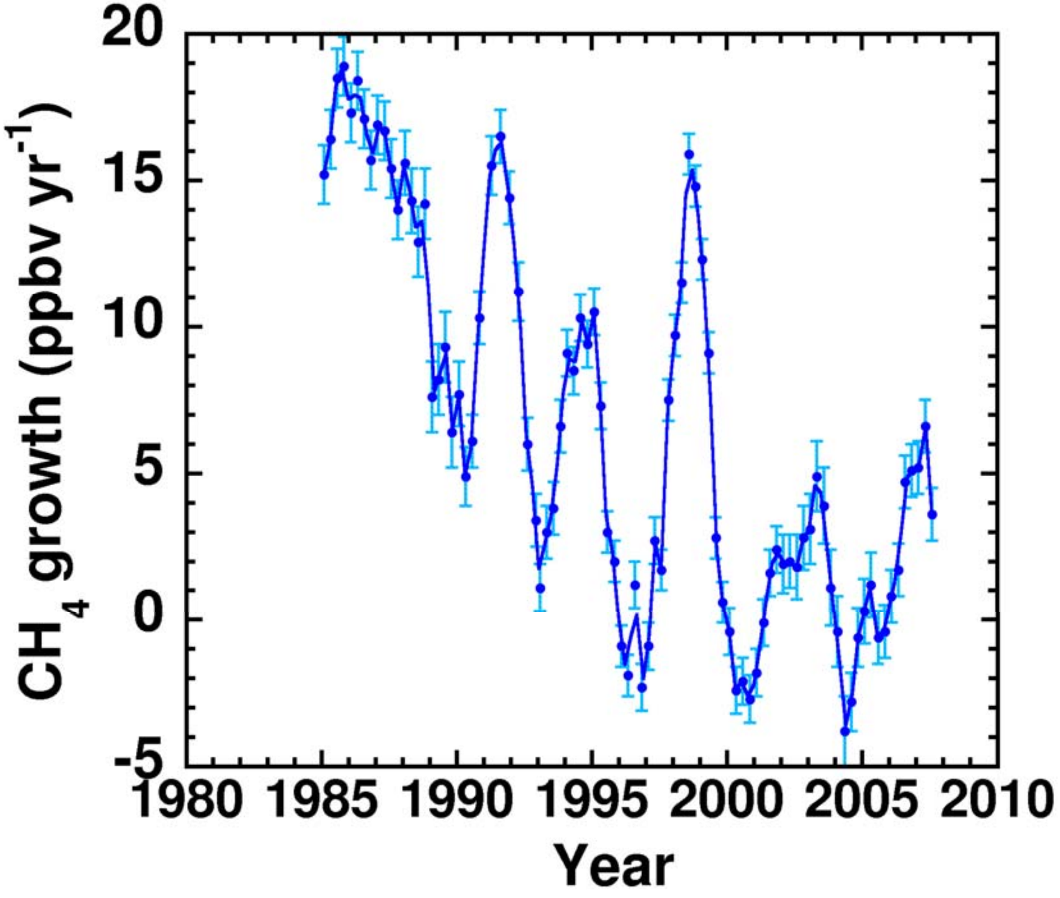


CH_4 and C_2Cl_4
- Do not correlate

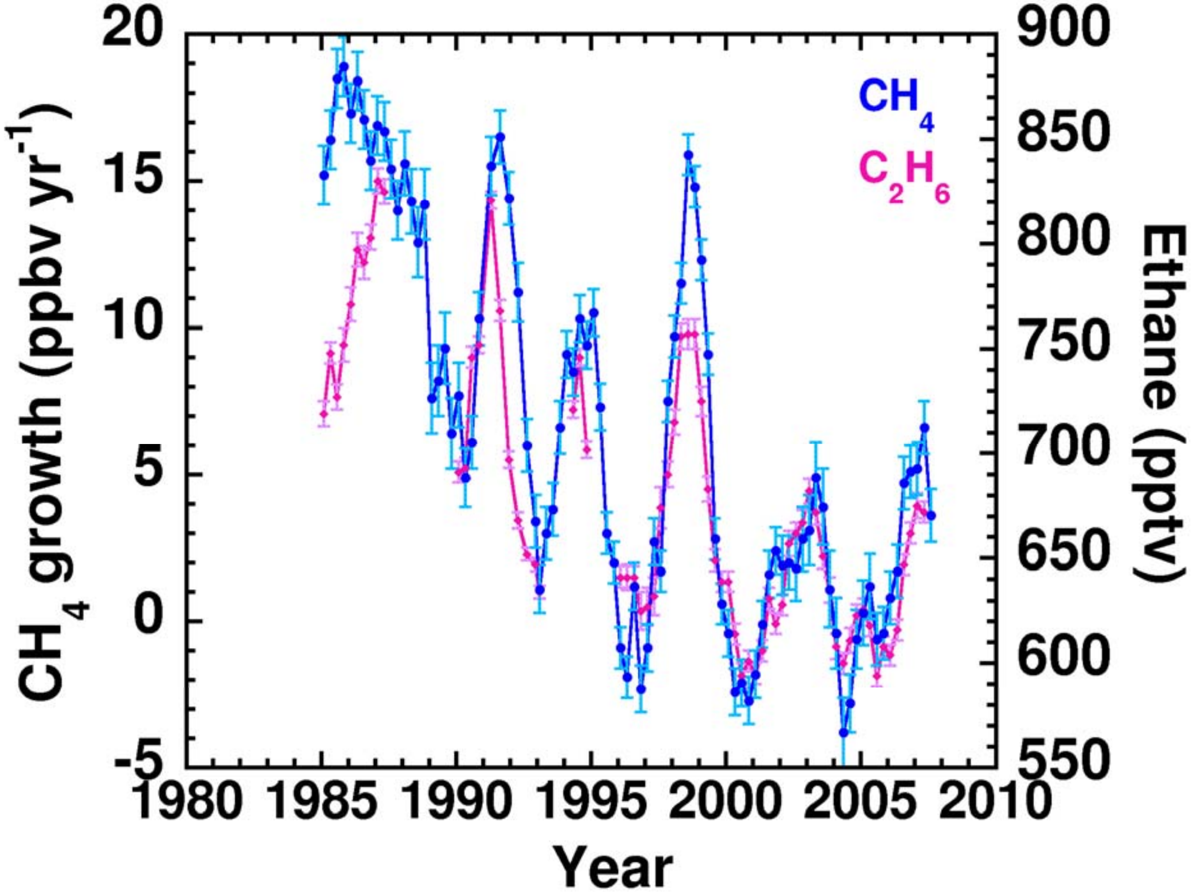
Long-term global C_2Cl_4 decline
- Source-driven
- Decreasing industrial emissions [*Simpson et al.*, 2004]

Short-term
- C_2Cl_4 peak in 1996
  - Montreal Protocol
- Small C_2Cl_4 peak in 2003
- No peak in 1998

Comparison with ethane



Comparison with ethane



CH_4 and ethane

- Correlate remarkably well
- Suggests source-driven CH_4 changes

Long-term global ethane decline

- Consistent with fossil fuel decline

Short-term

- Ethane peaks match CH_4 peaks
- Contributions from biomass burning

Influence of biomass burning

Tropical forest fires...

For every **100 g CO** released,
~7 g CH_4 and **1 g ethane**
are released [*Andreae and Merlet*, 2001]

Indonesian wildfires:
1997

Extratropical forest fires...

For every **100 g CO** released,
~5 g CH_4 and **0.6 g** ethane
are released [*Andreae and Merlet*, 2001]

Boreal forest fires:
1998, 2002-2003

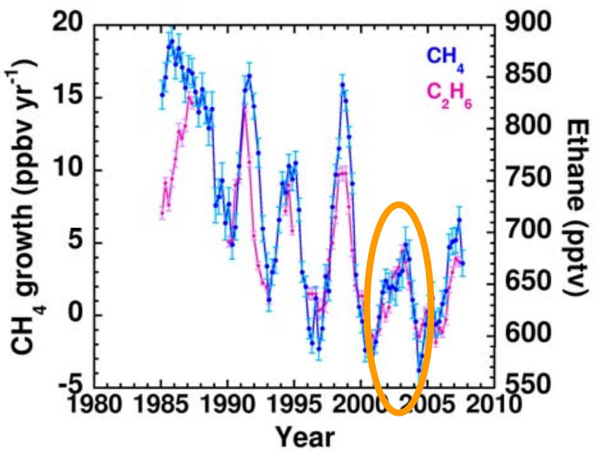
Boreal forest fires: 2002-2003

- **100 g CO: 5 g CH_4: 0.6 g ethane**
- **Estimated CO release:**
  2002: 95 Tg CO [*Yurganov et al*., 2005]
  2003: 130 Tg CO [*Yurganov et al*., 2005]
- **Estimated hydrocarbon release:**
  [*Andreae & Merlet*, 2001; *Yurganov et al*., 2005]

10 ± 4 Tg CH_4
1.2 ± 0.4 Tg ethane

- **Magnitude of the 2002-2003 CH_4 and ethane anomalies** (relative to growth in 1999-2001)**:**

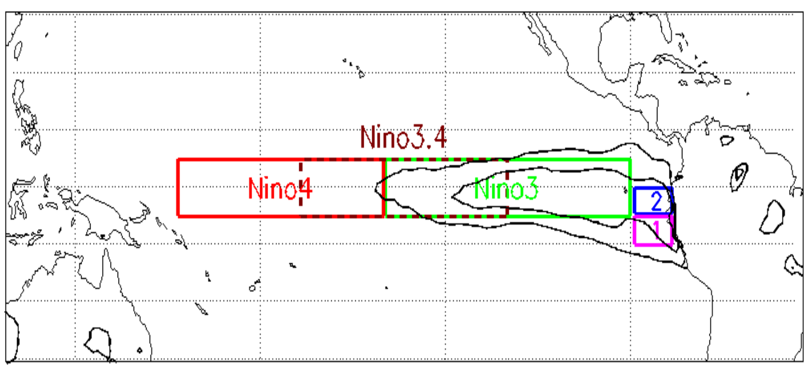
14 ± 5 Tg CH_4
1.0 ± 0.8 Tg ethane

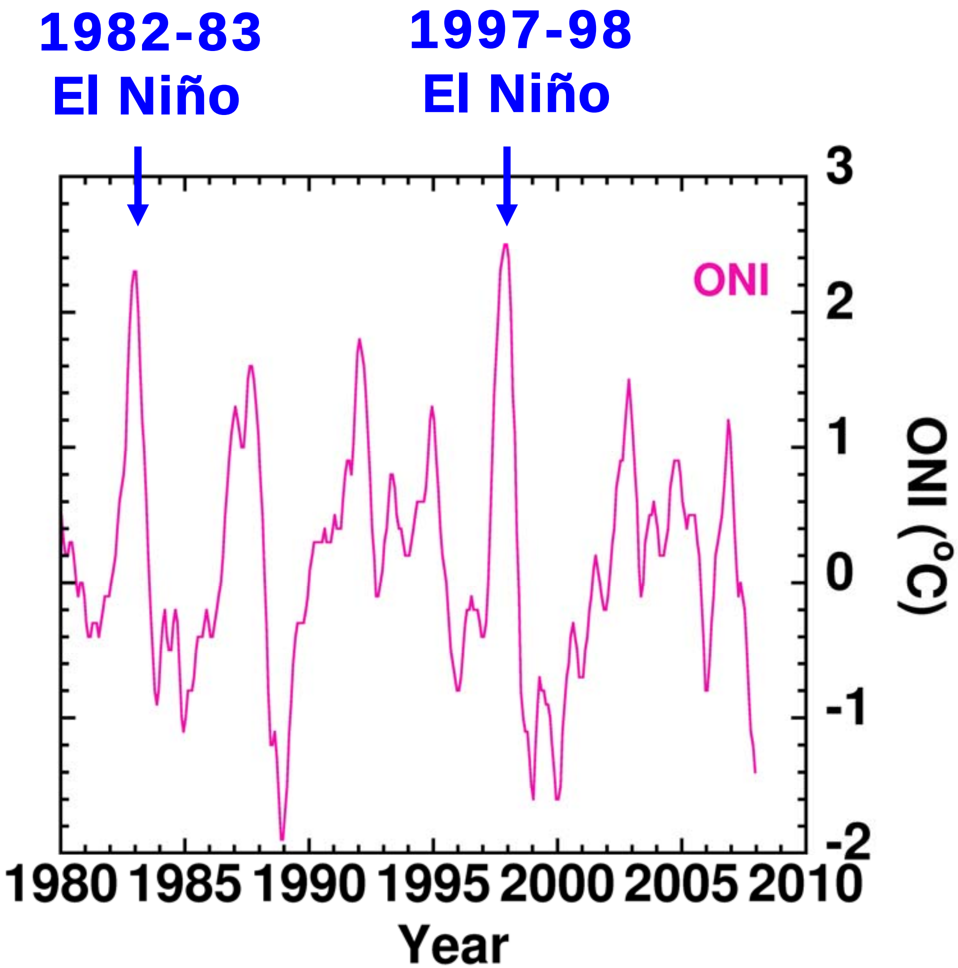


Influence of El Niño

Oceanic Niño Index (ONI)

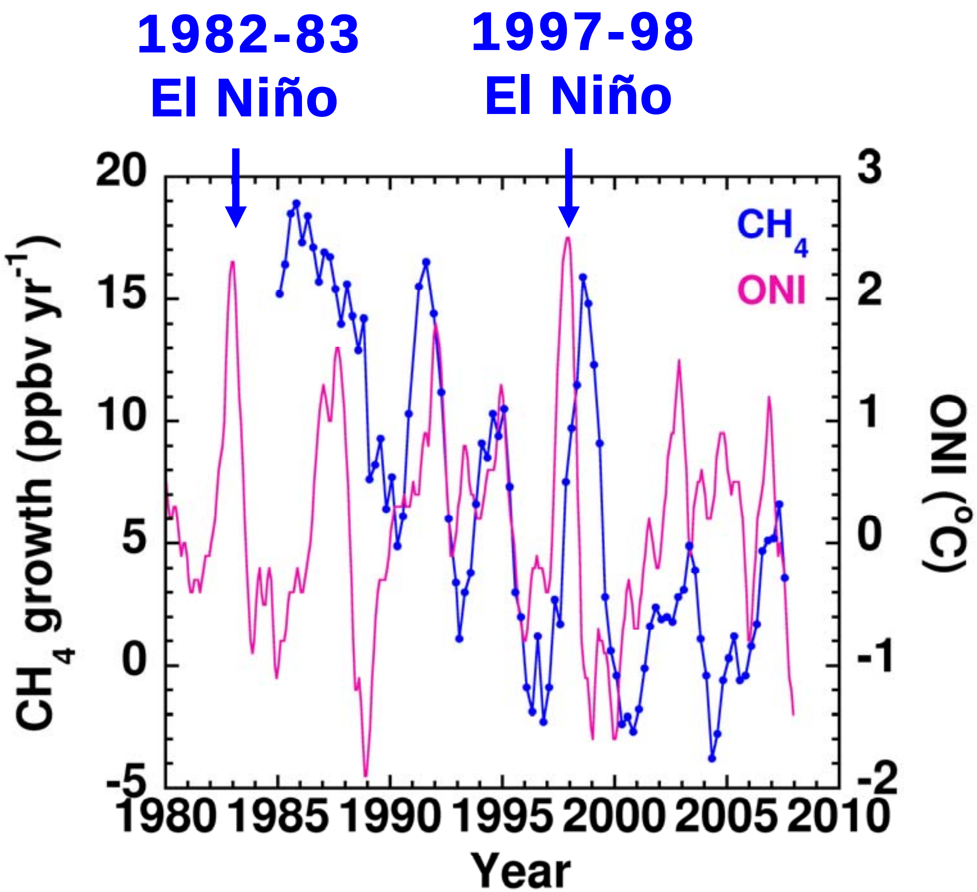
- **Sea surface temperature anomaly** in specific Pacific regions during El Niño and La Niña events
- **Niño3.4 region:** 120-170°W; 5°N-5°S





http://www.cpc.noaa.gov/products/analysis_monitoring/ensostuff/ensoyears.shtml

Influence of El Niño



CH_4 and ethane track ONI (unlike C_2Cl_4)

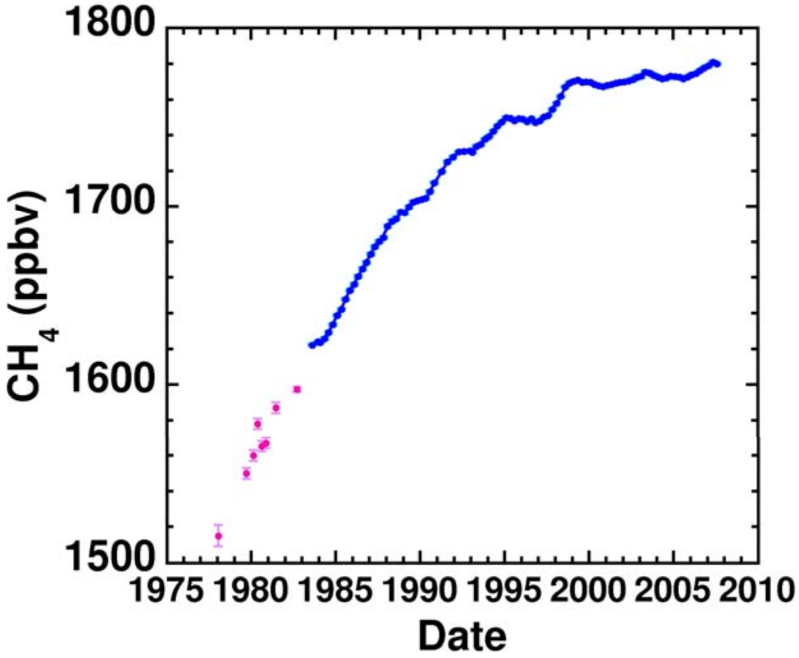
Consistent with a biomass burning source:

Positive Oceanic Niño Index
Increased drought
Increased biomass burning
Increased hydrocarbon release

Looking to the future...

Near-zero net CH_4 growth for the past 8 years

- Increase in 2007
- No evidence for any new Arctic CH_4 sources
  - Permafrost
  - Thaw lakes
  - Wetlands
  - Arctic sea floor



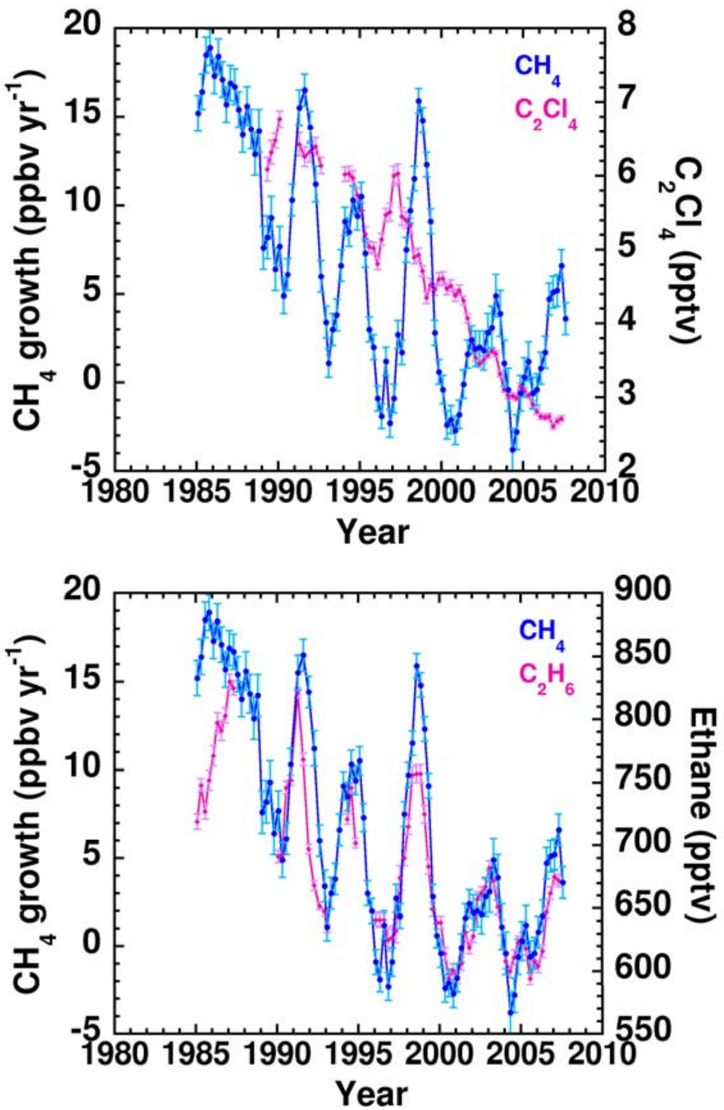
Difficult to predict future CH_4 levels

- The CH_4 budget is easily perturbed
- Potential climate change feedbacks

Summary & conclusions

CH_4, ethane and C_2Cl_4:

- Matching patterns between CH_4 and ethane–but not C_2Cl_4– suggest source influences on the CH_4 growth rate
- Long-term CH_4 decline:
  - Rice agriculture
  - Fossil fuel
- Short-term CH_4 anomalies:
  - 1998: biomass burning + wetlands
  - 2002-2003: biomass burning
  - 2007: biomass burning + wetlands?
- Influence of El Niño

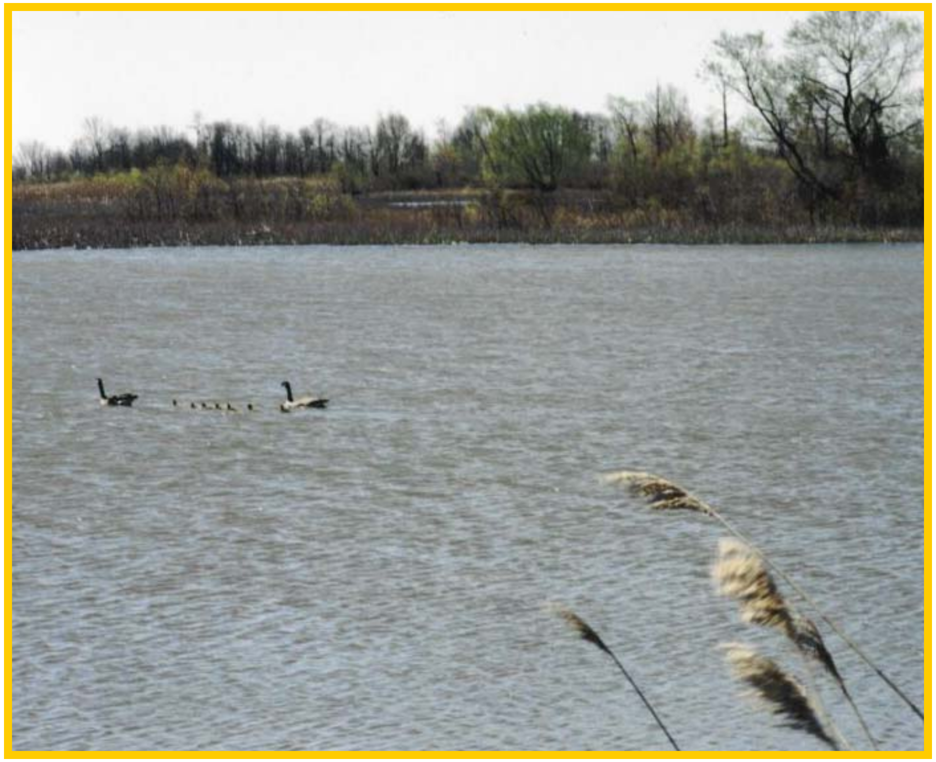


Acknowledgments: UC-Irvine team, David Karoly, NASA contract NAGW-452, Gary Comer Fellowship

Wetlands: CH_4 and ethane

Laboratory measurements of a clayey wetlands soil (550 mV to –150 mV): [*Devai and Delaune*, 1996]

Max CH_4: 20,000 ng CH_4 d^{-1}
Max ethane: 16 ng ethane d^{-1}



Global extrapolations:

- **100 Tg CH_4 yr^{-1} (forced)**
- **<0.2 Tg C[ethane] yr^{-1}**

The ethane yield from **wetlands** is negligible compared to known **ethane** sources of **13-15 Tg C yr^{-1}**

Rice agriculture: CH_4 and ethane

Field measurements of rice paddy emissions: [*Khalil et al*., 1990; *Redeker et al*., 2003]

Median CH_4: 7300 μg CH_4 m^{-2} hr^{-1}
Median ethane: 0.87 μg ethane m^{-2} hr^{-1}

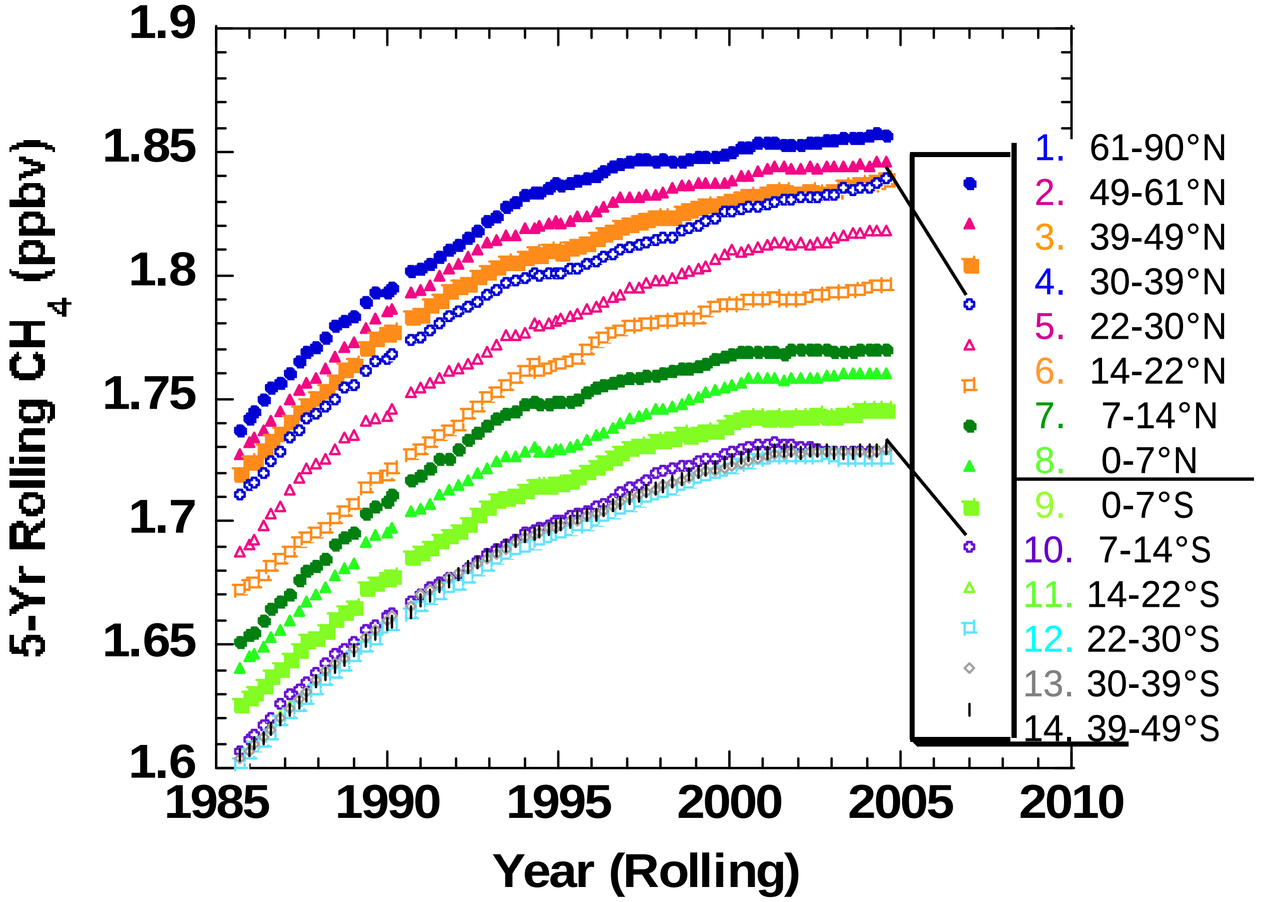
Global rice paddy area: 14 ⑨ 10^7 ha

Global extrapolations:
- **110 Tg CH_4 yr^{-1}**
- **<0.02 Tg C[ethane] yr^{-1}**

The ethane yield from **rice agriculture** is negligible compared to known **ethane** sources of **13-15 Tg C yr^{-1}**

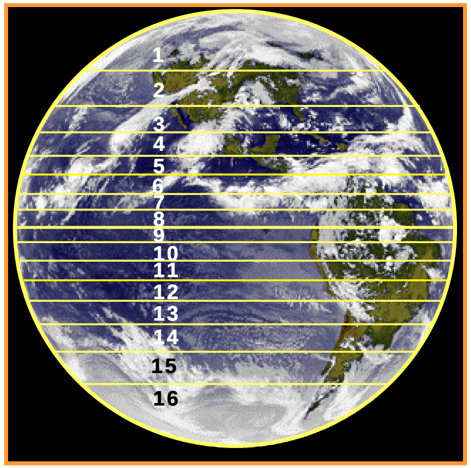
Rice paddy workers, Philippines

Latitudinal Bands of CH_4

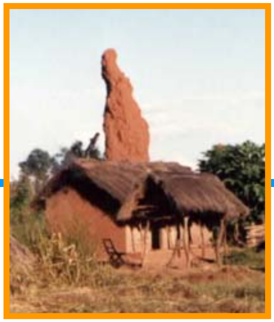


5-Yr Rolling Avg:

- Notable increases:
  - mid-latitude NH
- Notable decreases:
  - tropical SH



Methane growth in some latitudinal bands has been offset by declines in other bands



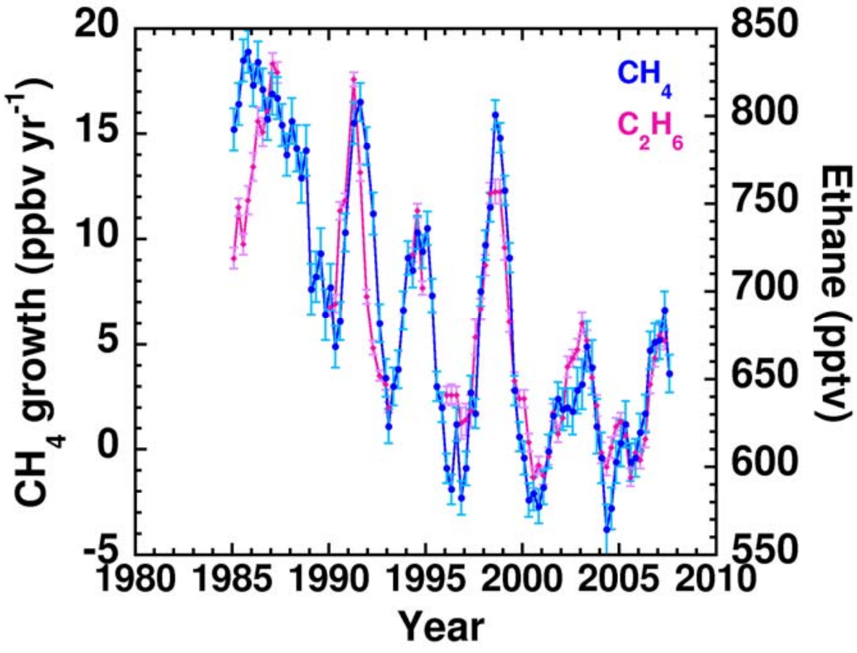
Sources of CH_4 and ethane

	CH_4	Ethane	$\delta^{13}C$
Anthropogenic sources			
• Fossil fuel	100 Tg CH_4 yr^{-1}	4.0 Tg C yr^{-1}	–38‰
• Ruminant animals	80 Tg CH_4 yr^{-1}	-	–62‰
• Rice agriculture	60 Tg CH_4 yr^{-1}	<0.02 Tg C yr^{-1}	–59‰
• Landfills	60 Tg CH_4 yr^{-1}	-	–50‰
• Biomass burning	50 Tg CH_4 yr^{-1}	5.6 Tg C yr^{-1}	–26‰
Natural sources			
• Wetlands	100 Tg CH_4 yr^{-1}	<0.2 Tg C yr^{-1}	–56‰
• Termites	20 Tg CH_4 yr^{-1}	-	–57‰
• Geological	10 Tg CH_4 yr^{-1}	-	-
• Hydrates	5 Tg CH_4 yr^{-1}	-	–52‰
• Oceans	4 Tg CH_4 yr^{-1}	0.8 Tg C yr^{-1}	–40‰
• Wildfires	2 Tg CH_4 yr^{-1}	-	–26‰
• (Vegetation	controversy	4.0 Tg C yr^{-1})	

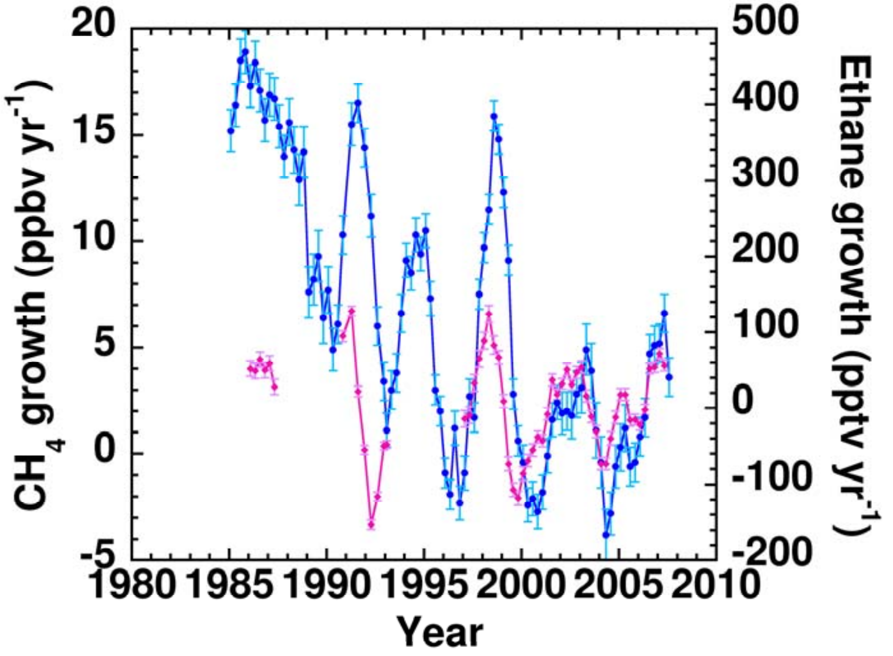
Tyler et al. [2007]

Comparison with ethane growth

CH_4 growth & ethane mixing ratio



CH_4 growth & ethane growth



- 2002-03 peak is fully explained by biomass burning emissions
- 1998 peak is explained by biomass burning + wetlands
- Long-term decline in CH_4 includes factors besides fossil fuel and biomass burning

Latitudinal profiles