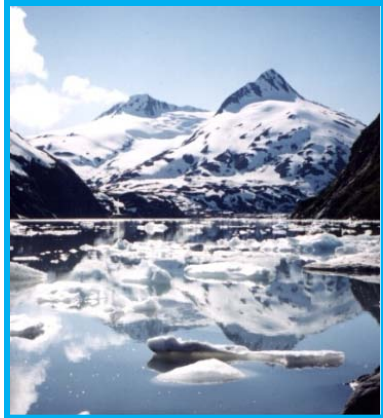


# Global atmospheric methane and ethane: Updated mixing ratios and trends (1983-2009)

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Jens Mühle, Michael Prather,  
James Wang, and many others



# UC-Irvine Global Monitoring Program

## 1978, 1979

- CH<sub>4</sub>, CFCs, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub>
- North and South America
- 2% more CH<sub>4</sub> in Sep'79 than Jan'78

## 1982

- NASA funding begins
- Regular seasonal sampling in Pacific Basin

## Present

- 80 canisters per season
- 45 locations in Pacific Basin
- Sampling period: 1 minute
- Sampling pressure: ambient

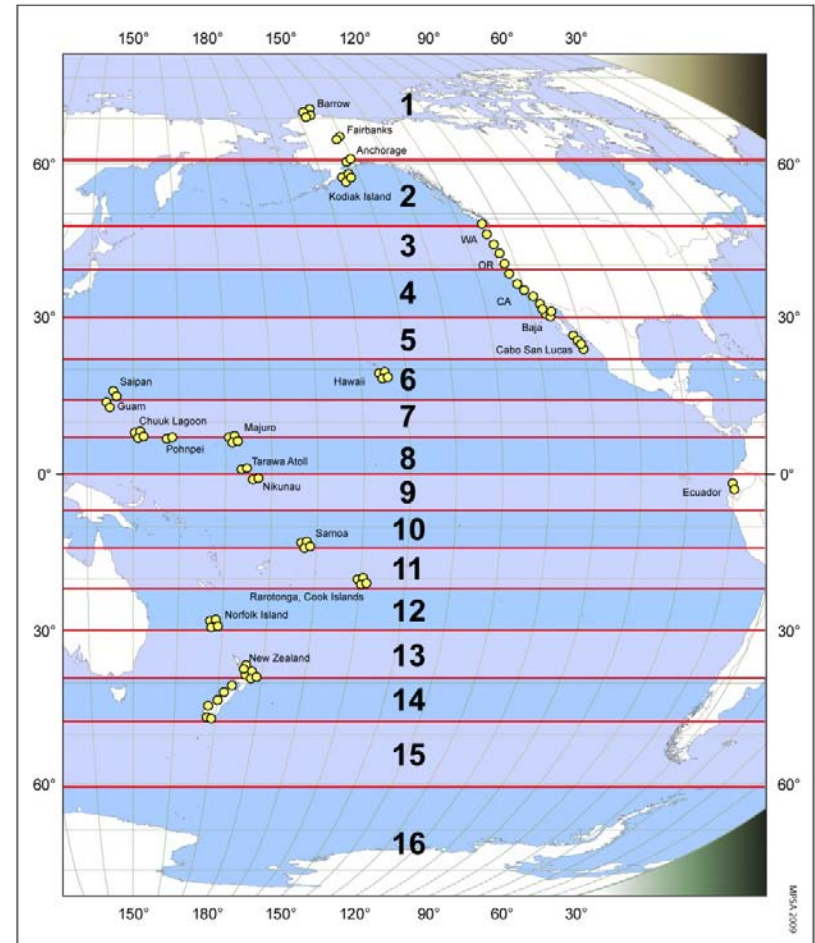
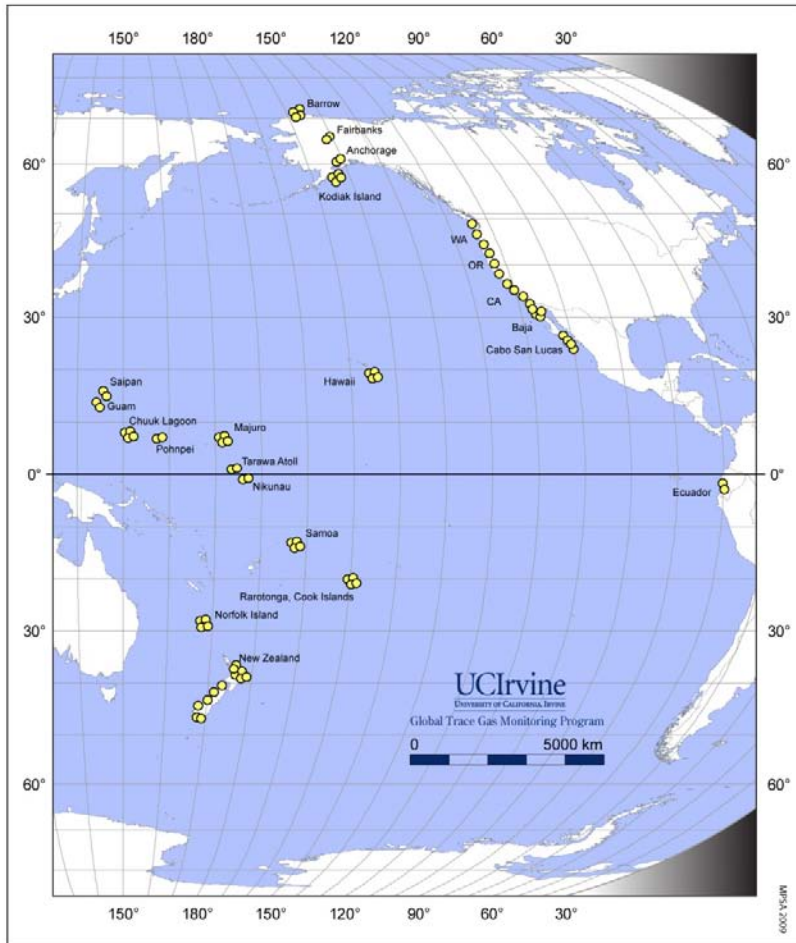
### Canisters

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



*Graduate student Nermine Batniji collecting a sample in New Zealand*

# Seasonal Sampling in the Pacific Basin



**J F M A M J J A S O N D**





# Laboratory analysis at UC-Irvine

## Gas Chromatography (GC)

### Flame Ionization Detection (FID)

- Sensitive to hydrocarbons

### Electron Capture Detection (ECD)

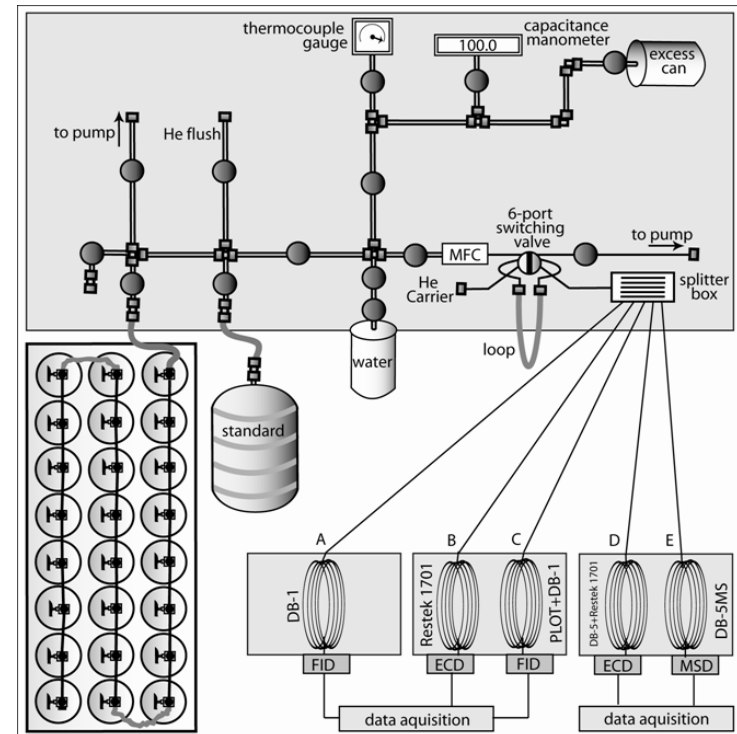
- Sensitive to halocarbons,  $\text{RONO}_2$

### Mass Spectrometer Detection (MSD)

- Unambiguous compound identification



Laboratory analysis performed by Brent Love



<u>Compound</u>	<u>LOD</u>	<u>Precision</u>	<u>Accuracy</u>
<b>Methane</b>		1 ppbv	1%
<b>Ethane</b>	3 pptv	1%	5%
<b>CFC-11</b>	10 pptv	1%	5%
<b><math>\text{CHCl}_3</math></b>	0.1 pptv	5%	5%
<b><math>\text{C}_2\text{Cl}_4</math></b>	0.01 pptv	2%	5%
<b><math>\text{MeONO}_2</math></b>	0.01 pptv	3%	10%

# UC-Irvine C<sub>1</sub>-C<sub>10</sub> VOC measurements

## Hydrocarbons

1. Methane
2. Ethane
3. Ethene
4. Ethyne
5. Propane
6. Propene
7. Propyne
8. *i*-Butane
9. *n*-Butane
10. 1-Butene
11. *i*-Butene
12. *t*-2-Butene
13. *c*-2-Butene
14. 1,3-Butadiene
15. *i*-Pentane
16. *n*-Pentane
17. Isoprene
18. *n*-Hexane
19. *n*-Heptane
20. *n*-Octane
21. *n*-Nonane

## Hydrocarbons

22. 2,3-Dimethylbutane
23. 2+3-Methylpentane
24. Cyclopentane
25. Methylcyclopentane
26. Cyclohexane
27. Methylcyclohexane
28. Benzene
29. Toluene
30. Ethylbenzene
31. *m+p*-Xylene
32. *o*-Xylene
33. Styrene
34. *n*-Propylbenzene
35. 2-Ethyltoluene
36. 3-Ethyltoluene
37. 4-Ethyltoluene
38. 1,3,5-Trimethylbenzene
39. 1,2,4-Trimethylbenzene
40. 1,2,3-Trimethylbenzene
41.  $\alpha$ -Pinene
42.  $\beta$ -Pinene

## Hydrocarbons

43. Furan
44. Methanol
45. Ethanol
46. Acetone
47. Acetaldehyde
48. MEK
49. MAC
50. MVK
51. MTBE

## Alkyl Nitrates

52. MeONO<sub>2</sub>
53. EtONO<sub>2</sub>
54. *i*-PrONO<sub>2</sub>
55. *n*-PrONO<sub>2</sub>
56. 2-BuONO<sub>2</sub>
57. 2-PeONO<sub>2</sub>
58. 3-PeONO<sub>2</sub>
59. 3-Me-2-BuONO<sub>2</sub>

## Sulfur Species

60. OCS
61. DMS

## Halocarbons

62. CFC-11
63. CFC-12
64. CFC-113
65. CFC-114
66. H-1211
67. H-1301
68. H-2402
69. HFC-134a
70. HFC-152a
71. HCFC-22
72. HCFC-141b
73. HCFC-142b
74. CCl<sub>4</sub>
75. CH<sub>3</sub>CCl<sub>3</sub>
76. CH<sub>2</sub>Cl<sub>2</sub>
77. C<sub>2</sub>HCl<sub>3</sub>
78. CHCl<sub>3</sub>
79. C<sub>2</sub>Cl<sub>4</sub>
80. CH<sub>3</sub>Cl
81. CH<sub>3</sub>Br
82. CH<sub>3</sub>I
83. CHBr<sub>2</sub>Cl
84. CHBrCl<sub>2</sub>

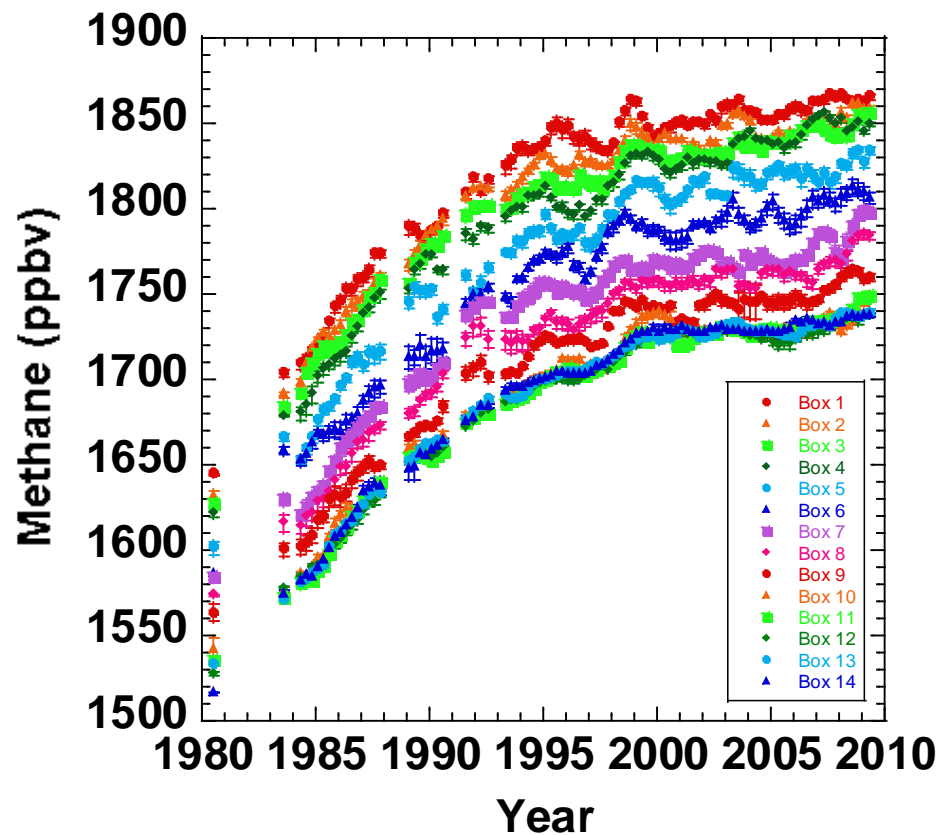
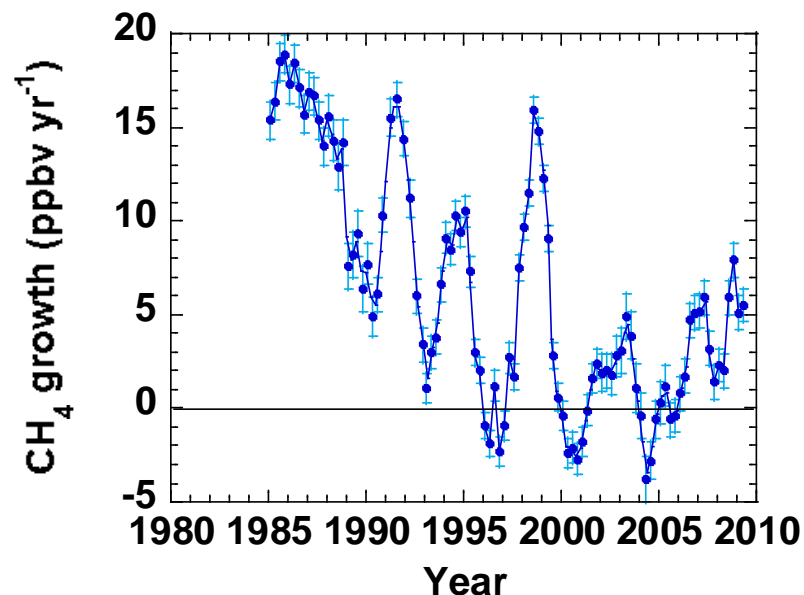
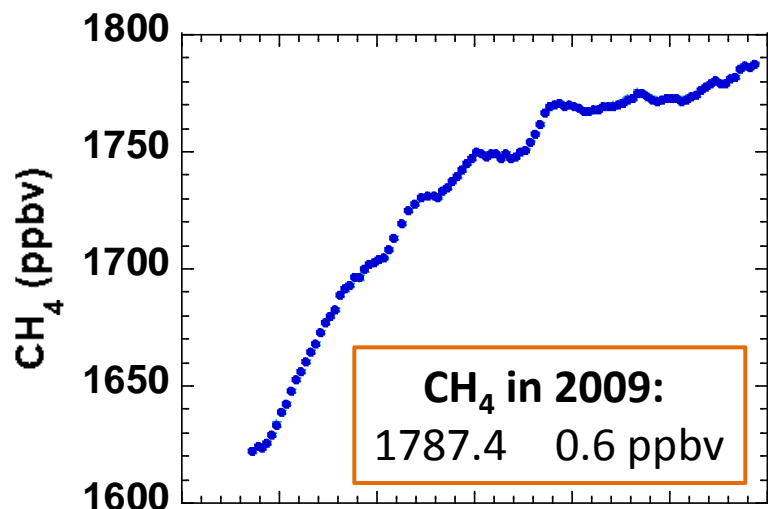
## Halocarbons

85. CH<sub>2</sub>Br<sub>2</sub>
86. CHBr<sub>3</sub>
87. Ethylchloride
88. 1,2-DCE

- Alkanes
- Alkenes
- Alkynes
- Cycloalkanes
- Aromatics
- Monoterpenes
- Oxygenates
- Alkyl nitrates
- Sulfur species
- Halocarbons



# Global CH<sub>4</sub> mixing ratio and growth rate



*Tyler et al. [2007]: Biomass burning and wetlands are the two CH<sub>4</sub> sources most likely to influence short-term CH<sub>4</sub> cycles*

# Ethane latitudinal distribution and seasonality

## Global ethane sources

- Fossil fuel: 8.0 Tg yr<sup>-1</sup>
- Biofuel: 2.6 Tg yr<sup>-1</sup>
- Biomass burning: 2.4 Tg yr<sup>-1</sup>

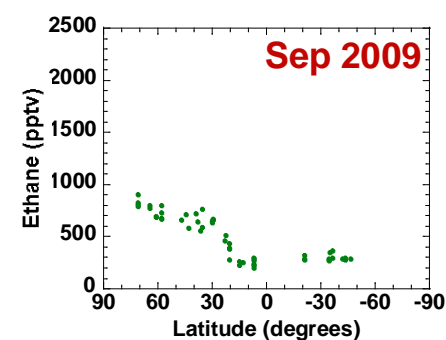
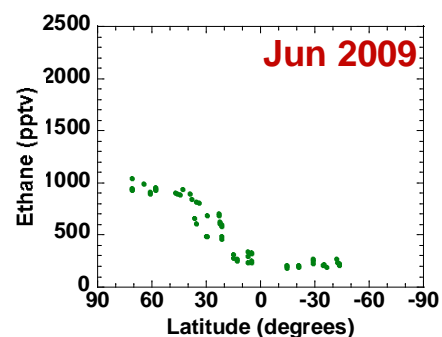
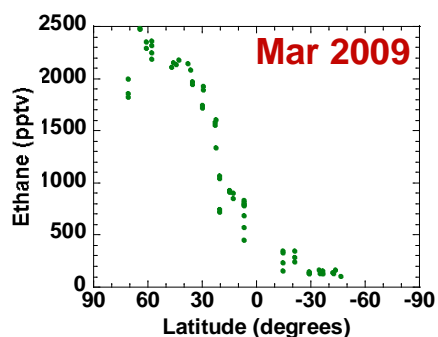
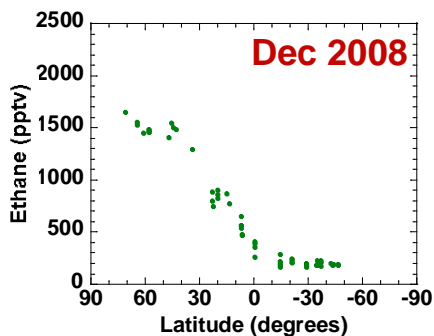
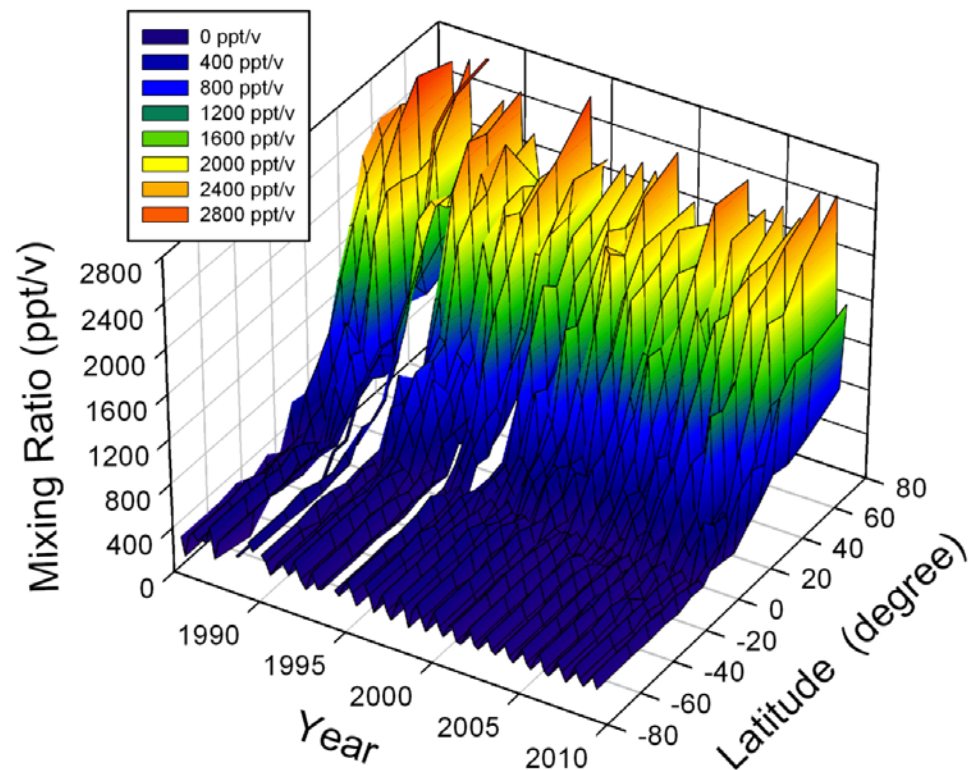
## Global ethane sink

- Hydroxyl radical (OH)
- Ethane lifetime: 2-3 months

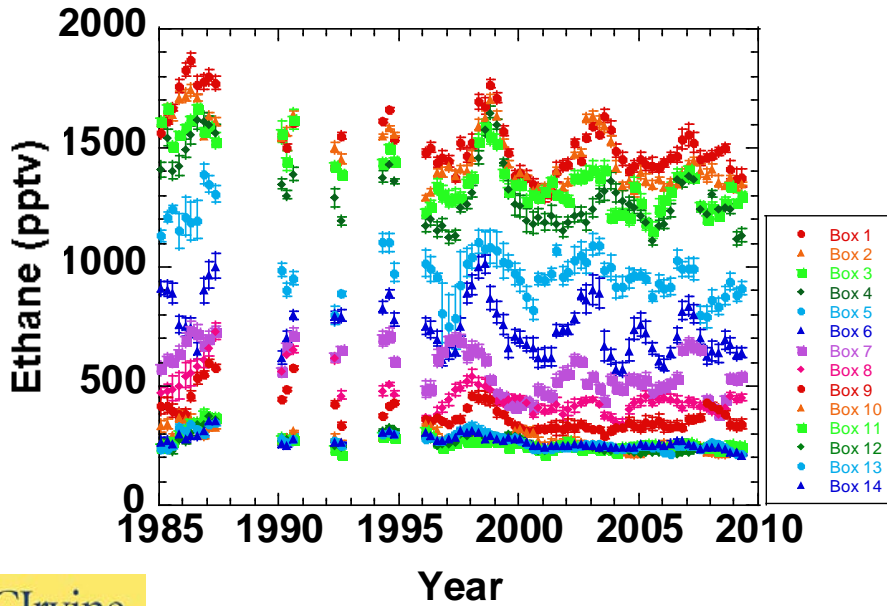
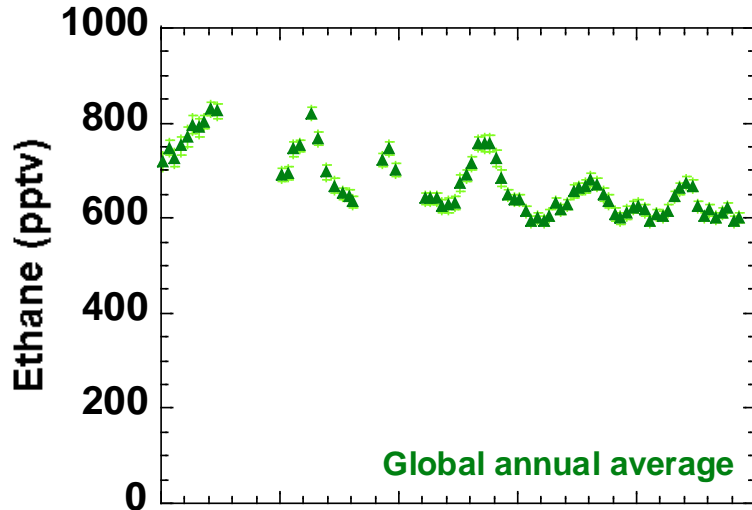
## Global ethane distribution

- 80% emitted in NH

*Y. Xiao et al., JGR, 113, 2008*



# Global annual ethane mixing ratio

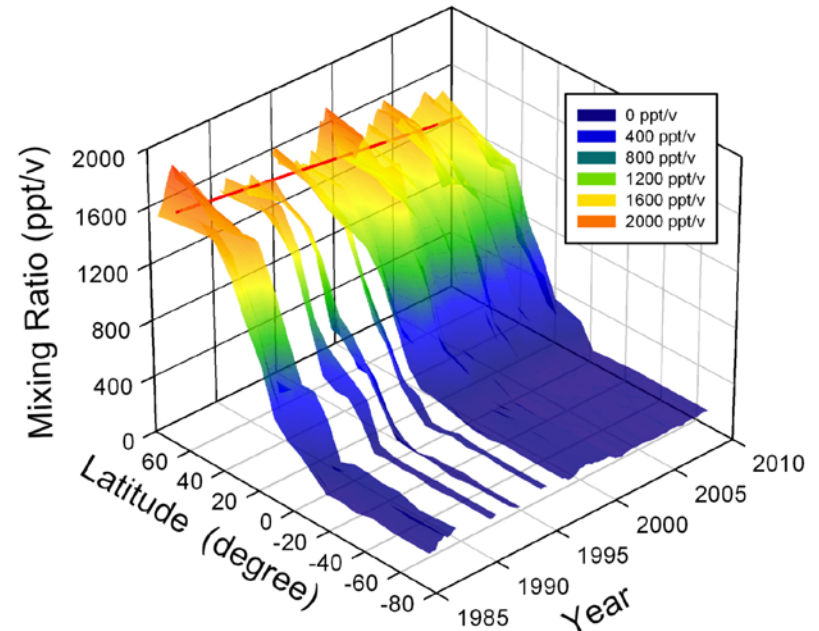


## Global ethane mixing ratio

- 1986: 791 19 pptv
- 2009: 601 10 pptv

## Global ethane trend

- 190 pptv (24%) decline in 23 yrs
- Average decline:  $-8 \text{ pptv yr}^{-1}$

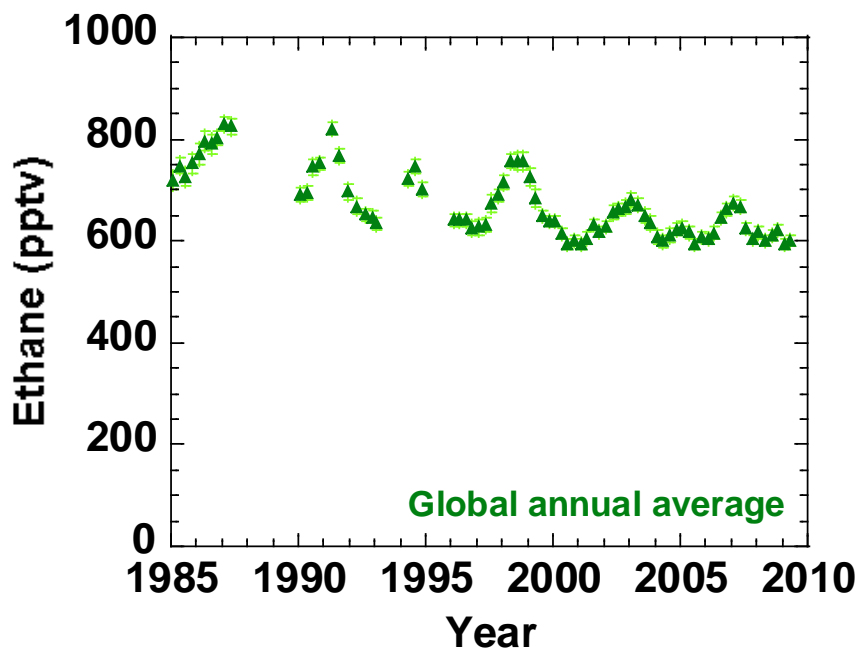




# Global ethane mixing ratio: Long-term decline

## Modeling long-term ethane decline

- NOAA/ESRL CarbonTracker model
- Optimized for global ethane emissions:
  1. **Global observations:** UC-Irvine
  2. **Global atmospheric transport:** TM-5 model
  3. **Ethane sources:** POET global emissions



### Global ethane levels:

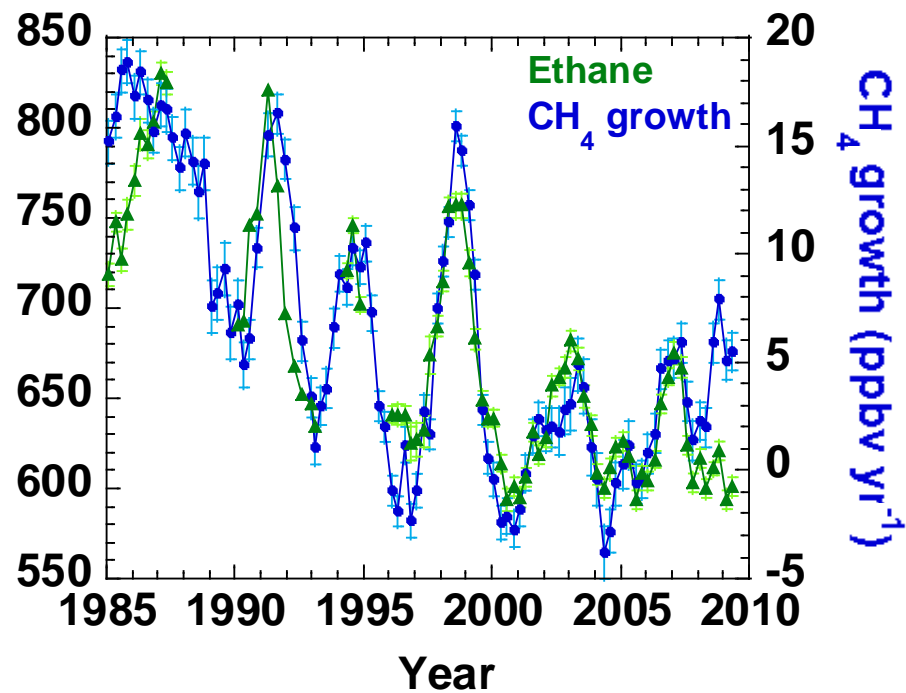
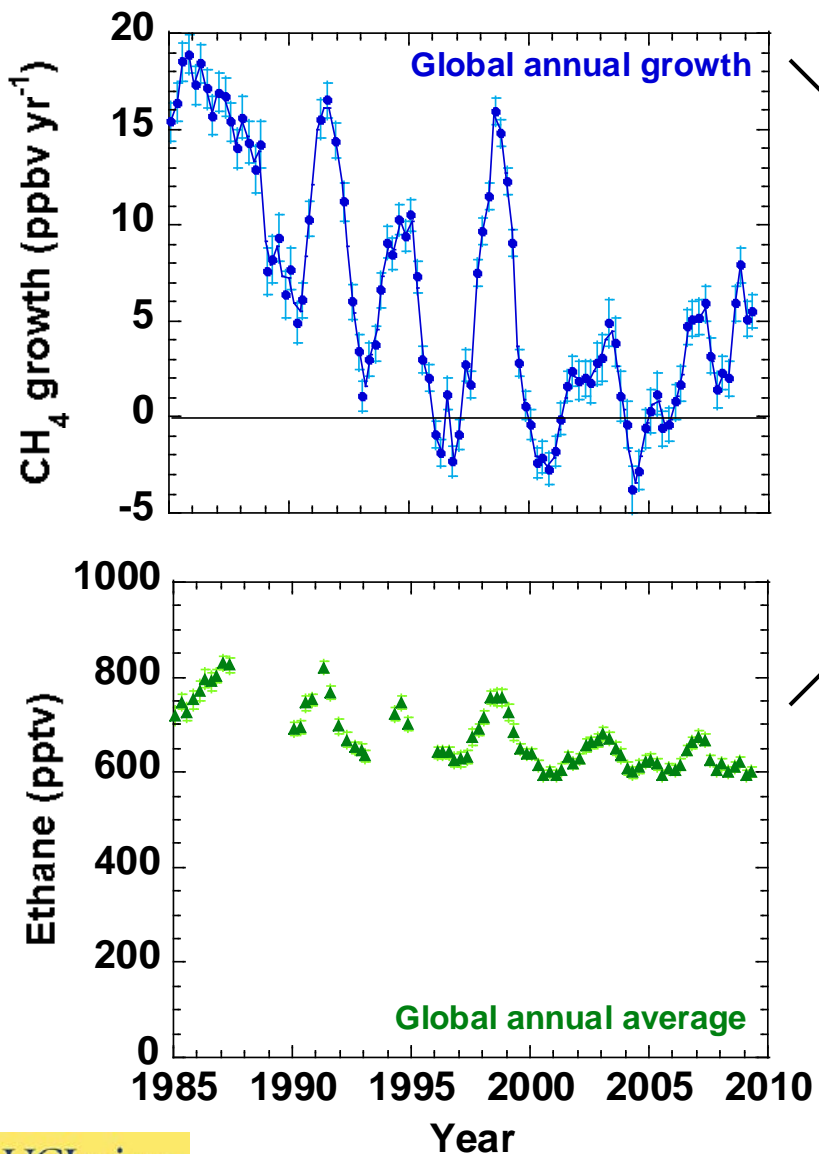
800 pptv in 1986  $\sim 17 \text{ Tg yr}^{-1}$

600 pptv in 2009  $\sim 12 \text{ Tg yr}^{-1}$

$\sim 5 \text{ Tg yr}^{-1}$  decrease

- Declining fossil fuel emissions?
  - Less venting & flaring?
- Consistent with declining  $\text{CH}_4$  growth?
  - Natural gas ethane: $\text{CH}_4 \sim 1:20$
- Effects of OH?

# Global CH<sub>4</sub> and ethane: Similar trends



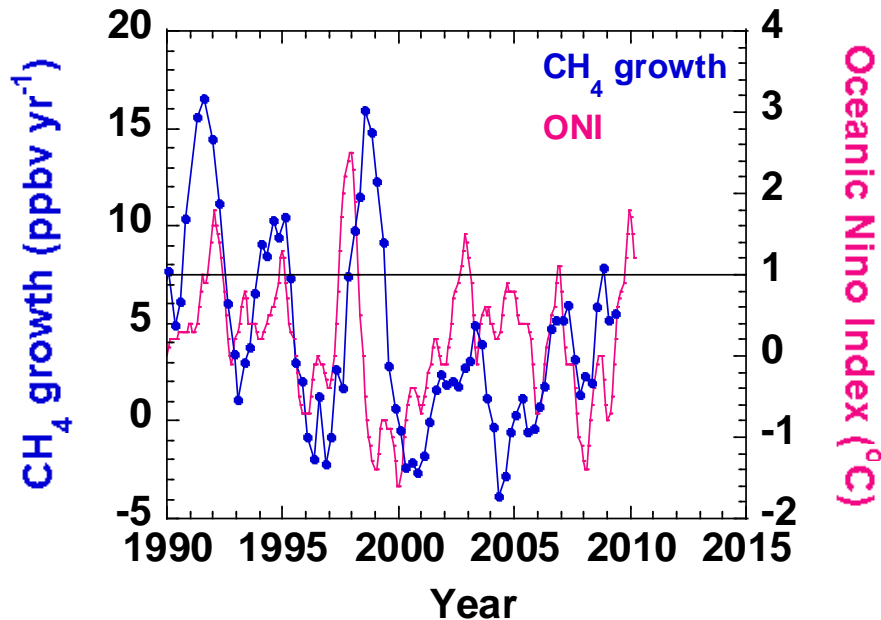
## CH<sub>4</sub> fluctuations

- 1998: Wetlands + biomass burning
- 2003: Biomass burning (Siberia)
- 2007: Wetlands + biomass burning
- 2008: Wetlands (tropics)

# Best guesses for CH<sub>4</sub> and ethane behaviour in 2010

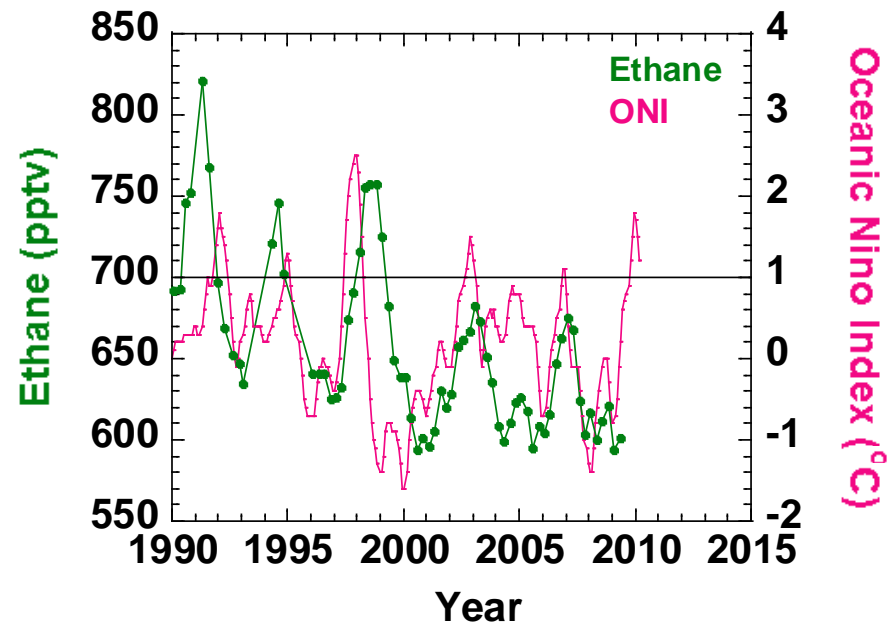
## CH<sub>4</sub>:

- Continued growth of 5-10 ppbv yr<sup>-1</sup>?
- Boreal wetlands, biomass burning?



## Ethane:

- Growth from 600 to 650 pptv?
- Boreal biomass burning?



The Oceanic Niño Index (ONI) is a 3 month running mean of sea surface temperature anomalies in the Niño 3.4 region (5°N-5°S, 120°-170°W), based on the 1971-2000 base period.  
[http://www.cpc.noaa.gov/products/analysis\\_monitoring/ensostuff/ensoyears.shtml](http://www.cpc.noaa.gov/products/analysis_monitoring/ensostuff/ensoyears.shtml)

# Conclusions

**Global CH<sub>4</sub> mixing ratio:** 1787.4 0.6 ppbv  
**Global C<sub>2</sub>H<sub>6</sub> mixing ratio:** 601 10 pptv

## Global CH<sub>4</sub> growth + ethane mixing ratio

- Long-term decline
  - Fossil fuel?
- Short-term anomalies
  - CH<sub>4</sub>: Wetlands + biomass burning
  - Ethane: Biomass burning

## CH<sub>4</sub> peak in 2008/2009

- Growth in the tropics
- Weak ethane peak
  - Minimal biomass burning influence
- Still no evidence of CH<sub>4</sub> release from Arctic permafrost in our record

## Expect CH<sub>4</sub> and ethane growth in 2010

- Following El Niño in 2009/2010

