Highlights of the UC-Irvine Global Trace Gas Monitoring Program (1978-2010)

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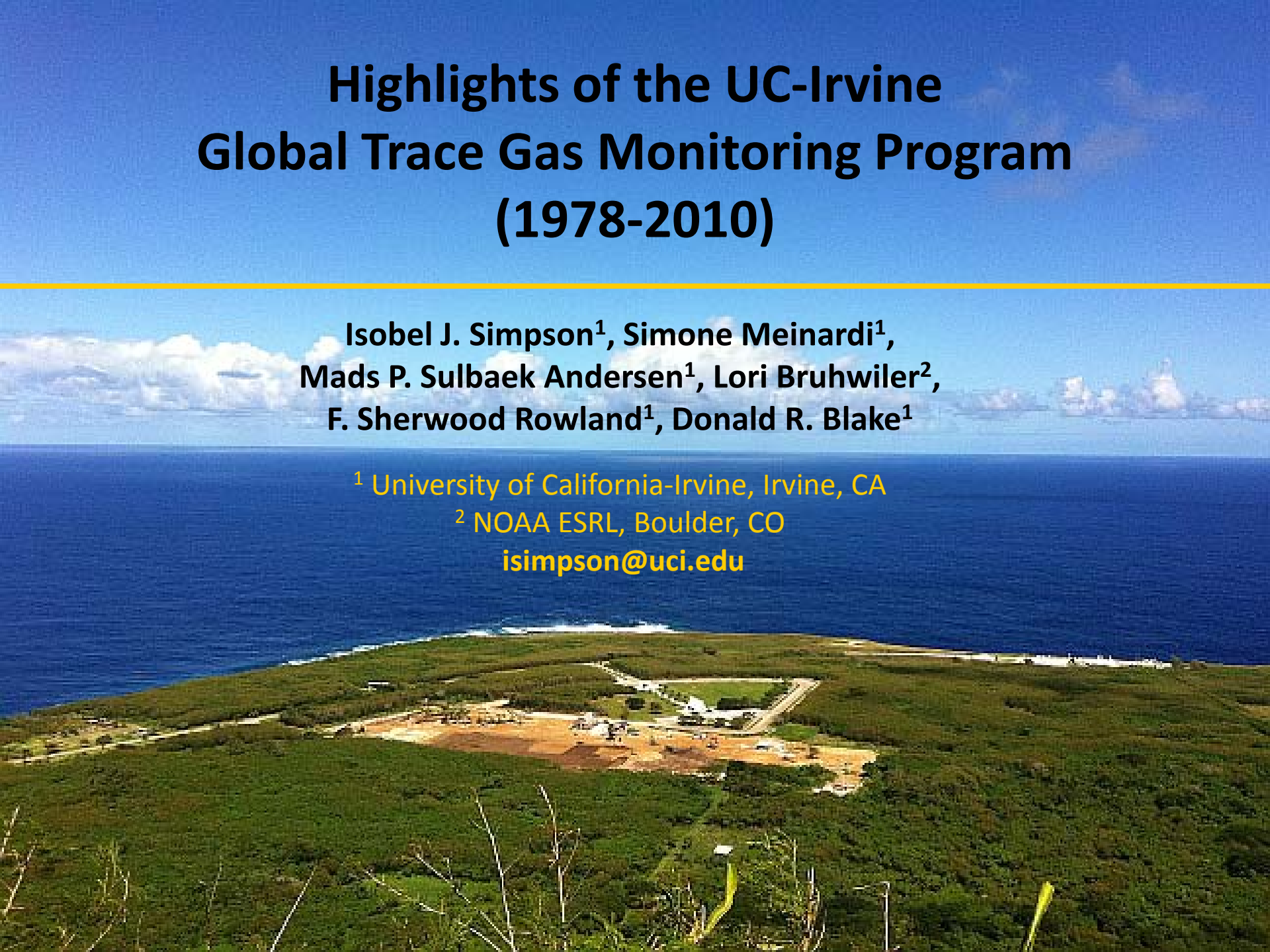

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UC-Irvine whole air sampling (WAS)

Canister sampling in Rarotonga (21°S)

Canister-based global monitoring

- 2-L stainless steel
- Conditioned, evacuated
- Bellows valve
- Sampling period: 1 minute
- Sampling pressure: ambient

Nugget Point, New Zealand (46°S)

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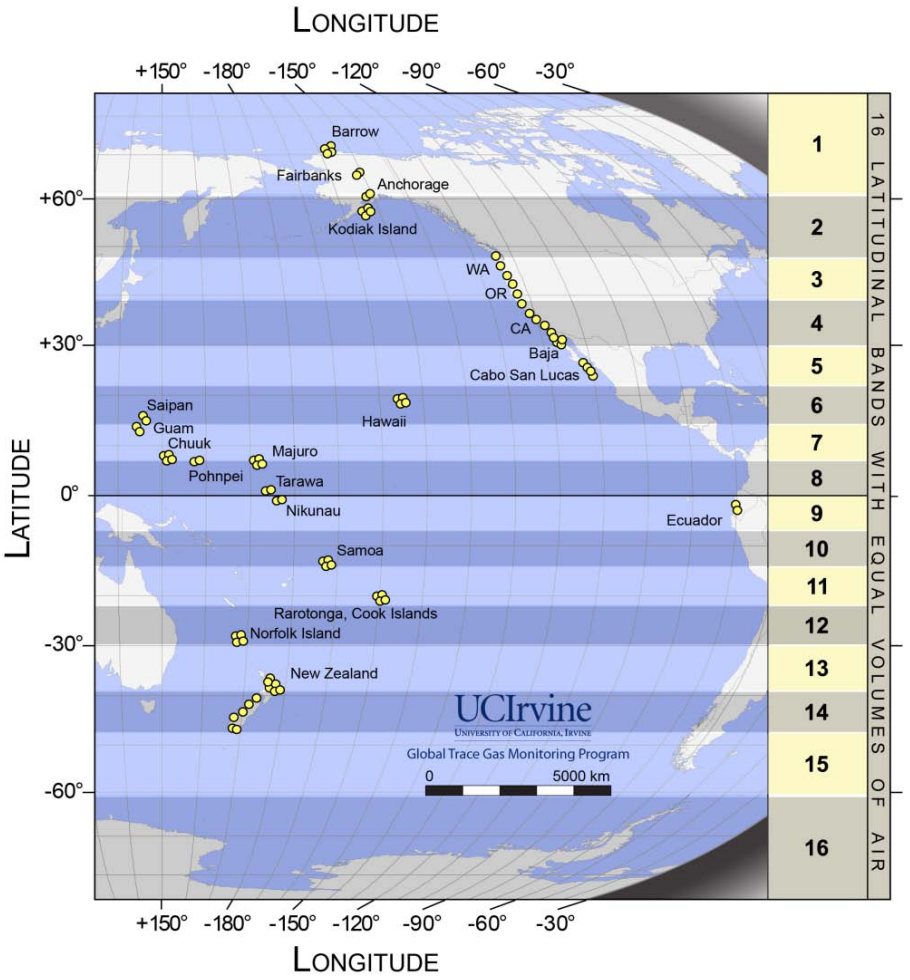
Seasonal sampling in the Pacific Basin

Seasonal sampling

- 80 samples per season
- 40-45 locations
- 3-week period

Global averaging

- 16 latitudinal bands
  - Each with equal volume of air
- Global averaging:
  1. Average within each band
  2. Interpolate box 15 & 16 values
  3. Average 16 band averages



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

Timeline of global trace gases monitored by UC-Irvine

NASA funding began in 1982

Routine seasonal sampling began in 1984

Less frequent sampling in 1991-1992

Biweekly sampling on Norfolk Island began in 2001

1978 — 2011

1978:

CH_4

CFC-11

CFC-12

CFC-113

CH_3CCl_3

CCl_4

1984: Ethane

1988: C_2Cl_4

- March
- June
- September
- December

- April
- August
- December

1996:

$CHCl_3$

H-1211

Propane

i-Butane

n-Butane

Ethyne

$EtONO_2$

i-$PrONO_2$

2001:

$MeONO_2$

Norfolk Island (29°S)

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Laboratory analysis at UC-Irvine

Gas Chromatography (GC)

Flame Ionization Detection (FID)

- Sensitive to hydrocarbons

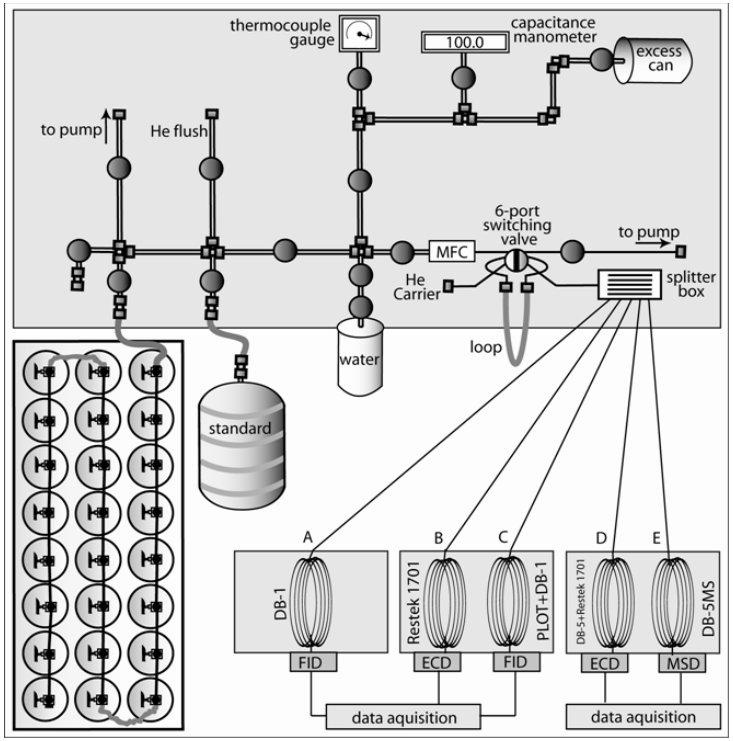
Electron Capture Detection (ECD)

- Sensitive to halocarbons, $RONO_2$

Mass Spectrometer Detection (MSD)

- Unambiguous compound identification

Laboratory analysis performed by Brent Love



Compound	LOD	Precision	Accuracy
Methane		1 ppbv	1%
Ethane	3 pptv	1%	5%
CFC-11	10 pptv	1%	5%
$CHCl_3$	0.1 pptv	5%	5%
C_2Cl_4	0.01 pptv	2%	5%
$MeONO_2$	0.01 pptv	3%	10%

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UC-Irvine C_1-C_{10} 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. α-Pinene
42. β-Pinene

Hydrocarbons

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

Alkyl Nitrates

52. $MeONO_2$
53. $EtONO_2$
54. *i*-$PrONO_2$
55. *n*-$PrONO_2$
56. 2-$BuONO_2$
57. 2-$PeONO_2$
58. 3-$PeONO_2$
59. 3-Me-2-$BuONO_2$

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_4
75. CH_3CCl_3
76. CH_2Cl_2
77. C_2HCl_3
78. $CHCl_3$
79. C_2Cl_4
80. CH_3Cl
81. CH_3Br
82. CH_3I
83. $CHBr_2Cl$
84. $CHBrCl_2$

Halocarbons

85. CH_2Br_2
86. $CHBr_3$
87. Ethylchloride
88. 1,2-DCE

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

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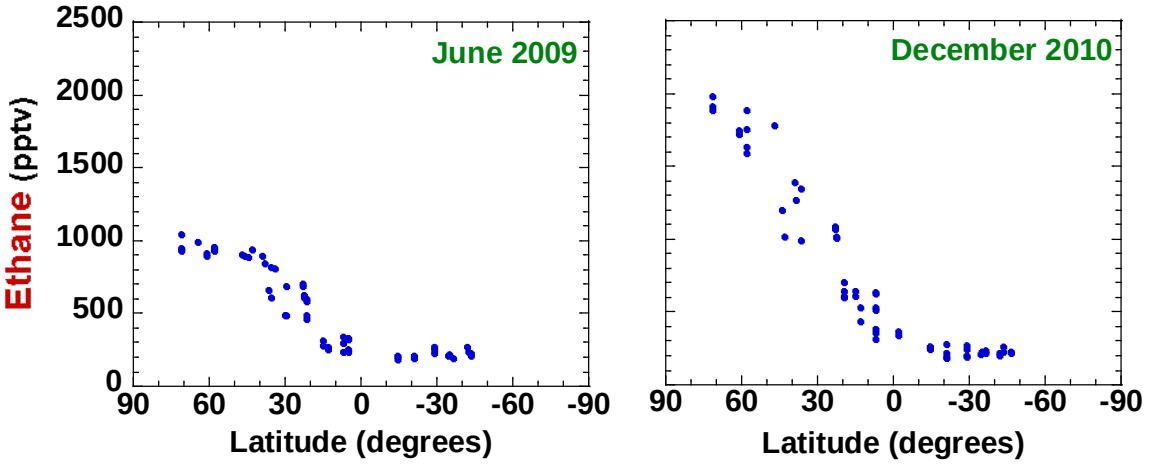
Latitudinal and seasonal trends

Latitudinal trends

- **Anthropogenic sources:**
  - North/South gradient
  - CH_4, C_2Cl_4, CFCs, ethane ...
- **Oceanic sources**:
  - Tropical maximum
  - $MeONO_2$, $EtONO_2$ ...

Ethane: Strong fossil fuel/biomass burning sources



Seasonal trends

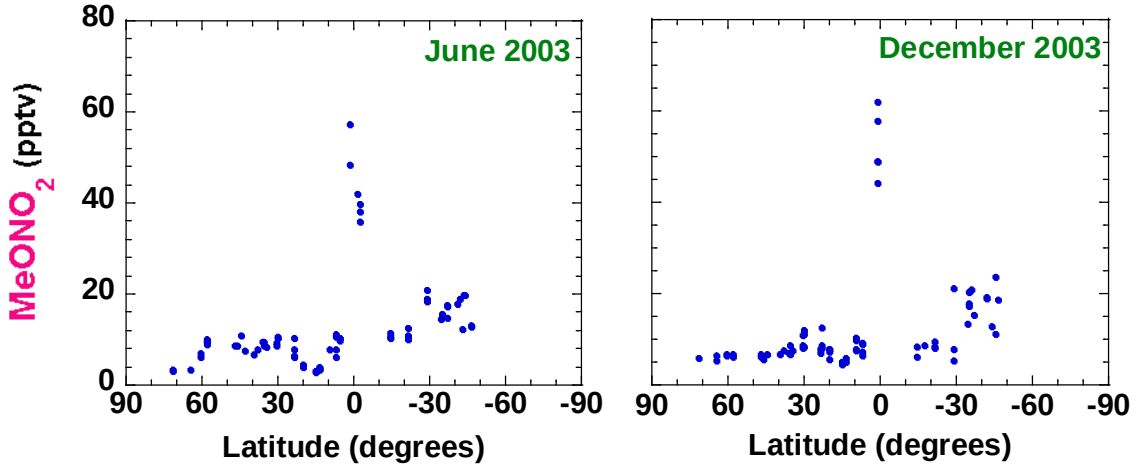
- Many species: major OH sink
- Winter maximum
- Summer minimum

Atmospheric lifetimes:

***Ethane**: 2-3 mo*

***Methyl nitrate**: 1 mo*

$MeONO_2$: Strong equatorial oceanic source



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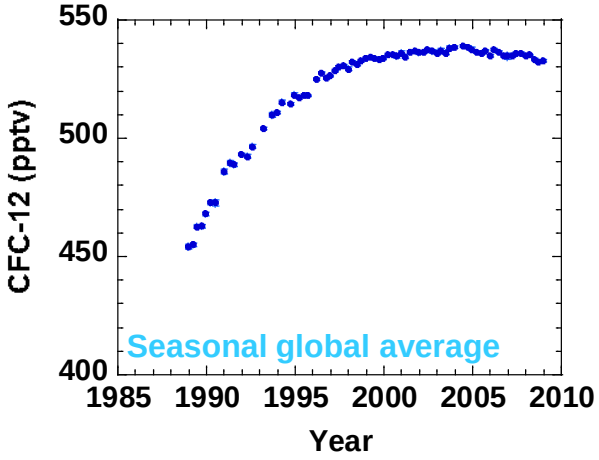
Global trends of long-lived halocarbons

CFC-12 (CCl_2F_2)

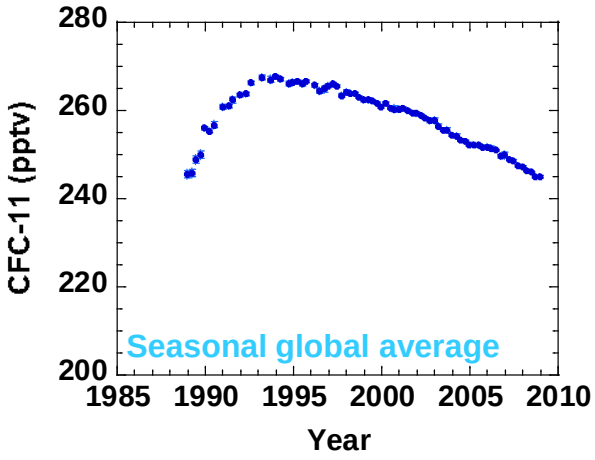
Lifetime: **100 yrs**
Peak: ~2004
Decline: –2.5 pptv yr^{-1} in 2008



Group	CFC-12 (2008)*
UCI	532.6 ppt
NOAA	535.5 ppt
AGAGE	537.4 ppt

CFC-11 (CCl_3F)

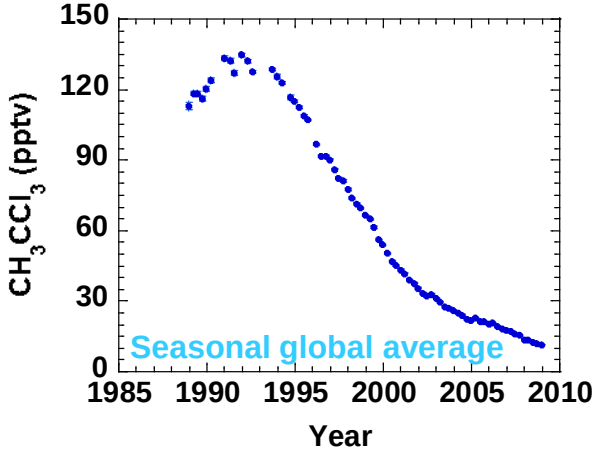
Lifetime: **45 yrs**
Peak: ~1993
Decline: –1.9 pptv yr^{-1} in 2008



Group	CFC-11 (2008)*
UCI	244.2 ppt
NOAA	244.8 ppt
AGAGE	243.4 ppt

CH_3CCl_3

Lifetime: **5 yrs**
Peak: ~1991
Decline: –2.2 pptv yr^{-1} in 2008



Group	CH_3CCl_3 (2008)*
UCI	11.5 ppt
NOAA	11.1 ppt
AGAGE	10.7 ppt

**Montzka, S.A. and S. Reimann (Coordinating Lead Authors), Chapter 1 in Scientific Assessment of Ozone Depletion: 2010*

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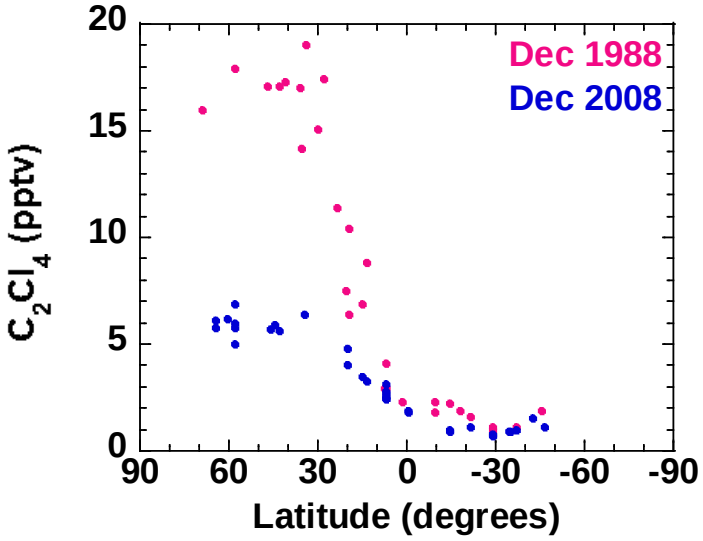
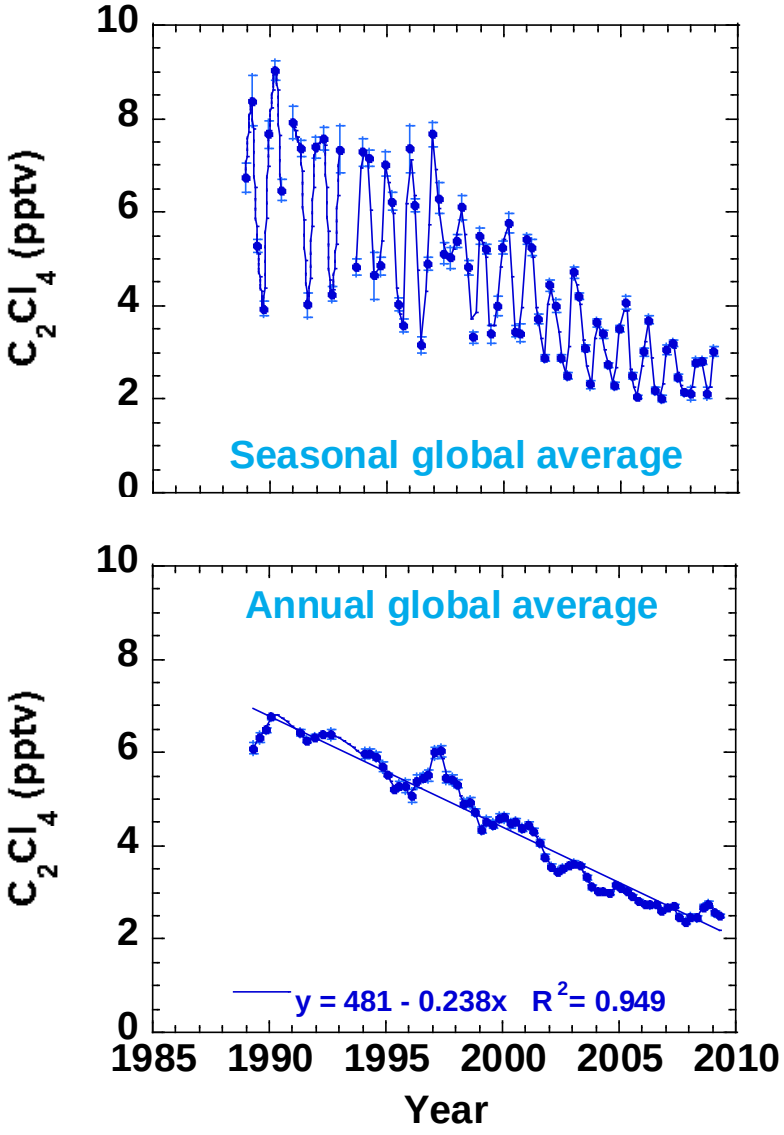
Global C_2Cl_4 trend: Declining

Long-term global C_2Cl_4 decline

- 6.3 ± 0.1 pptv in 1989
- 2.5 ± 0.1 pptv in 2009
- **3.8 pptv (60%) decline in 20 years**





Tetrachloroethene ***(C_2Cl_4)*** *is an industrial solvent (lifetime 3-4 mo). It is carcinogenic and affects the central nervous system.*

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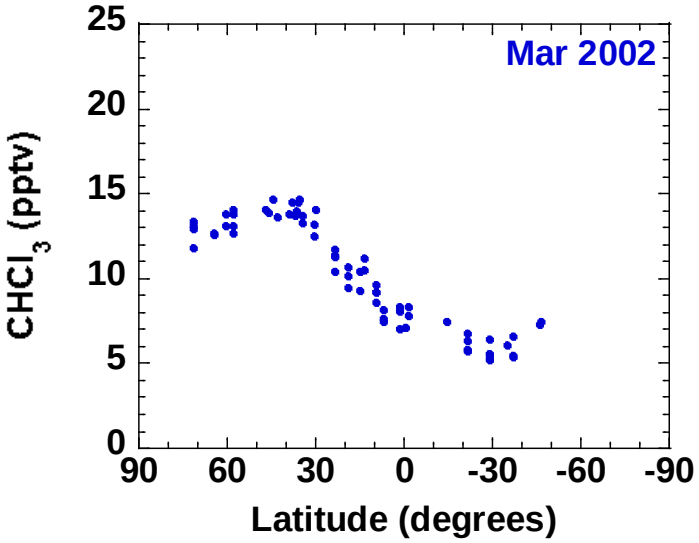
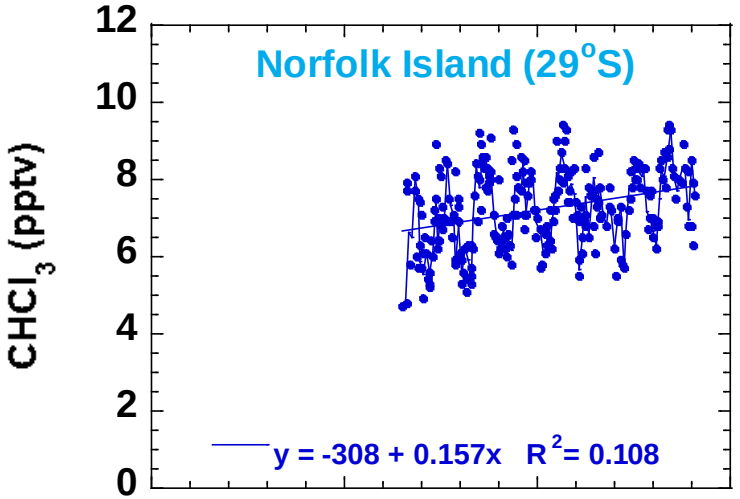
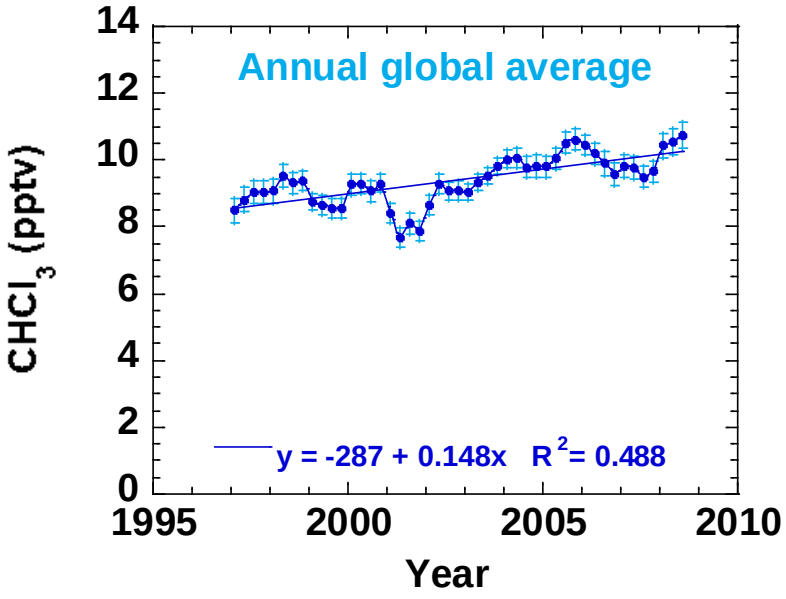
Global $CHCl_3$ trend: Increasing

Long-term global $CHCl_3$ increase

- 9.0 ± 0.3 pptv in 1997
- 10.7 ± 0.4 pptv in 2008
- **~ 20% increase in 11 years**







Chloroform ***($CHCl_3$)*** *is an industrial solvent (lifetime 3-5 mo). It is produced as a precursor to Teflon.*

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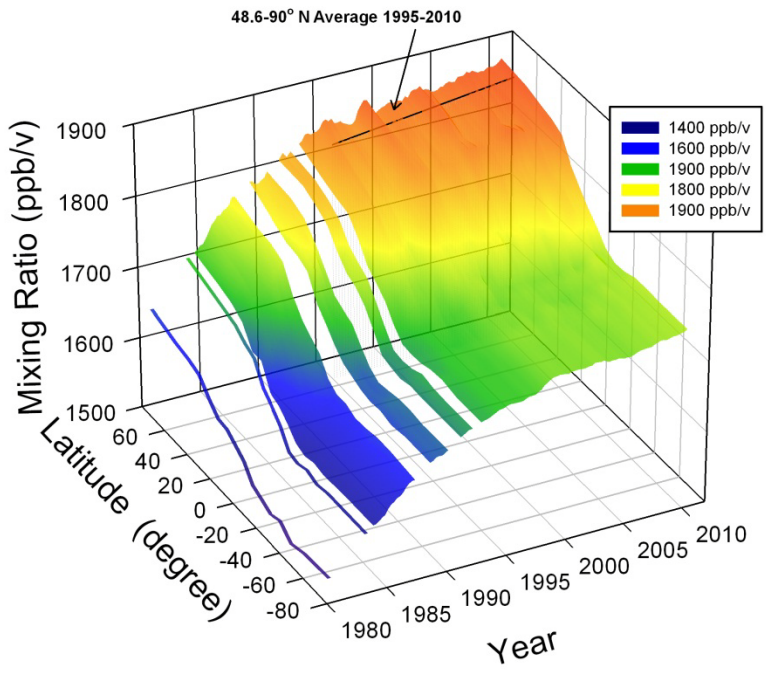
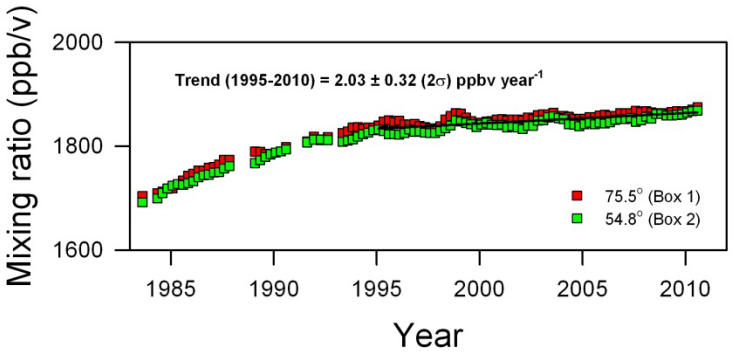
Global CH_4 trend: Increasing, variable

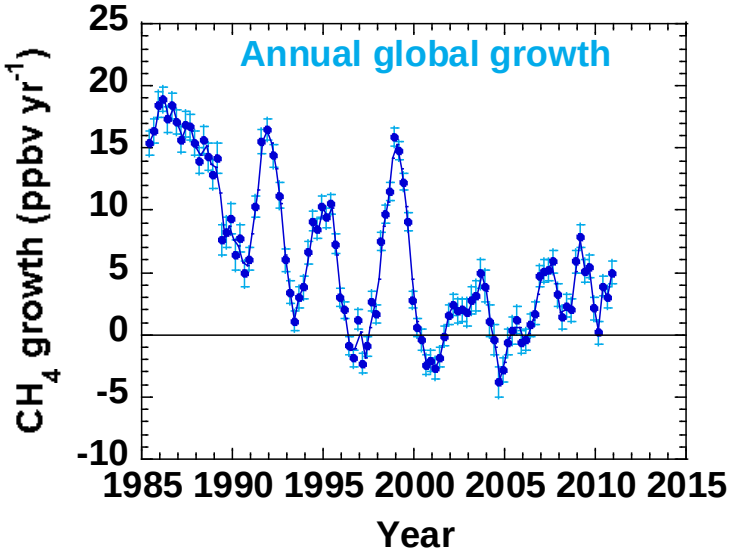
Annual CH_4 Trends





Long-term global CH_4 increase

- 1568 ± 2 ppbv in 1980
- 1792 ± 1 ppbv in 2010
- **225 ppbv (14%) increase in 30 years**
- Growth in 2010: **5.3 ± 0.7 ppbv yr^{-1}**



Methane (CH_4) *is a potent greenhouse gas. Its sources include wetlands, rice paddies, fossil fuel and biomass burning (lifetime 9 years).*

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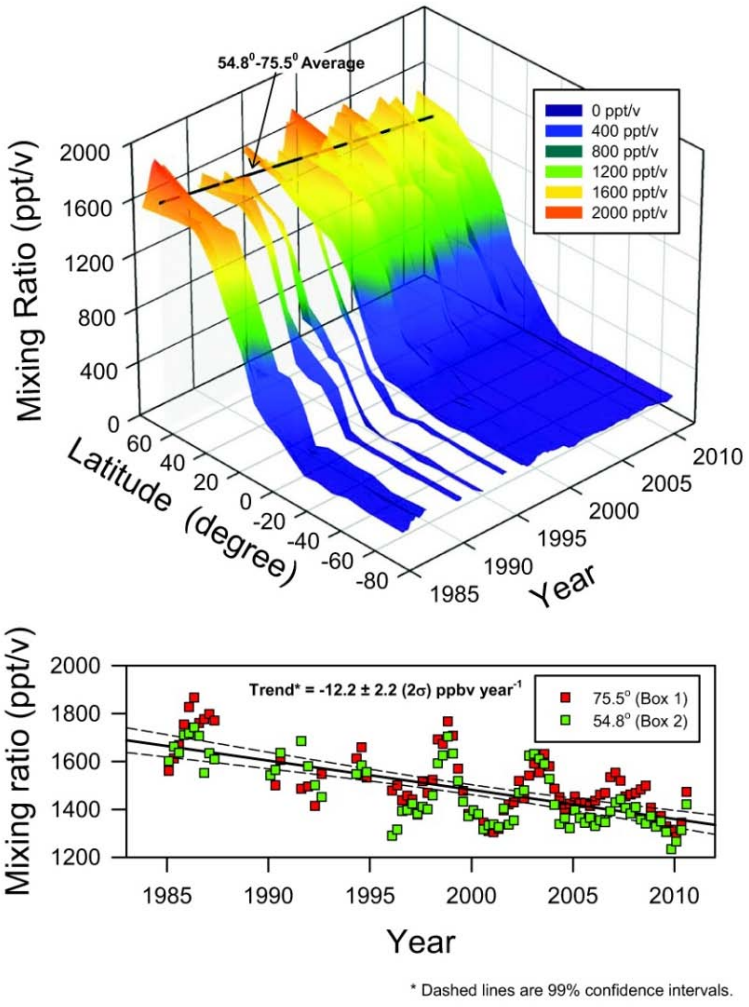
Global ethane trend: Declining

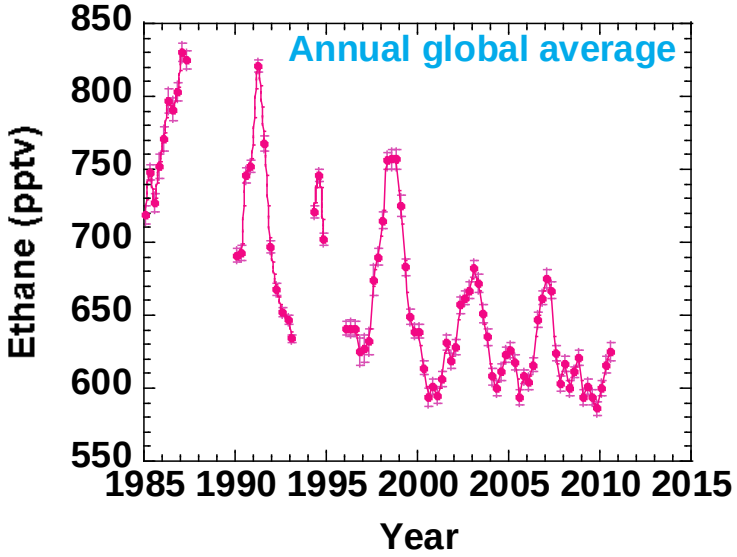
Annual Ethane Trends



* Dashed lines are 99% confidence intervals.

Long-term global ethane decline

- 791 ± 19 pptv in 1986
- 625 ± 10 pptv in 2010
- **170 pptv (21%) decline in 25 years**
- Growth in 2010: **31 ± 11 pptv yr^{-1}**



Ethane ***(C_2H_6)*** *is emitted during fossil fuel production (unburned gas) and by biofuel and biomass burning (lifetime 2-3 months)*

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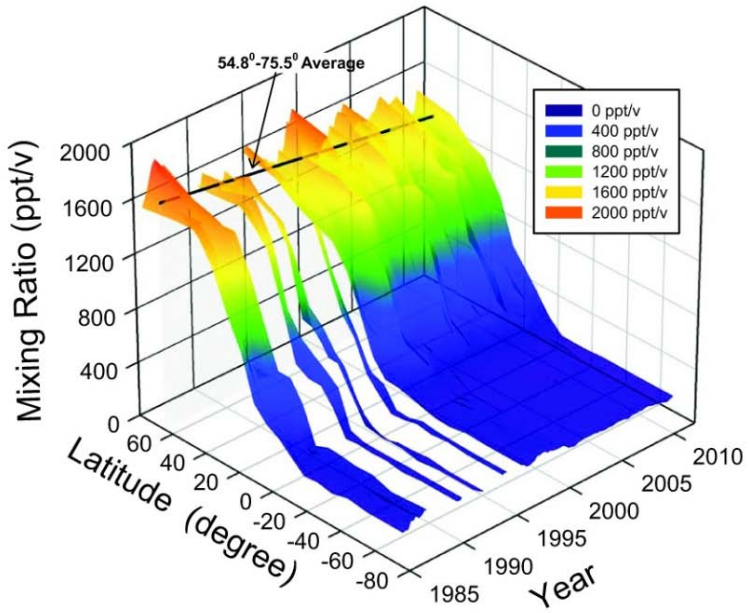
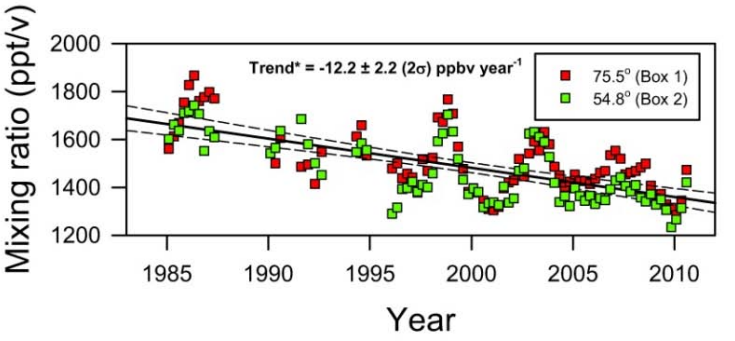
Global ethane trend: Declining

Annual Ethane Trends





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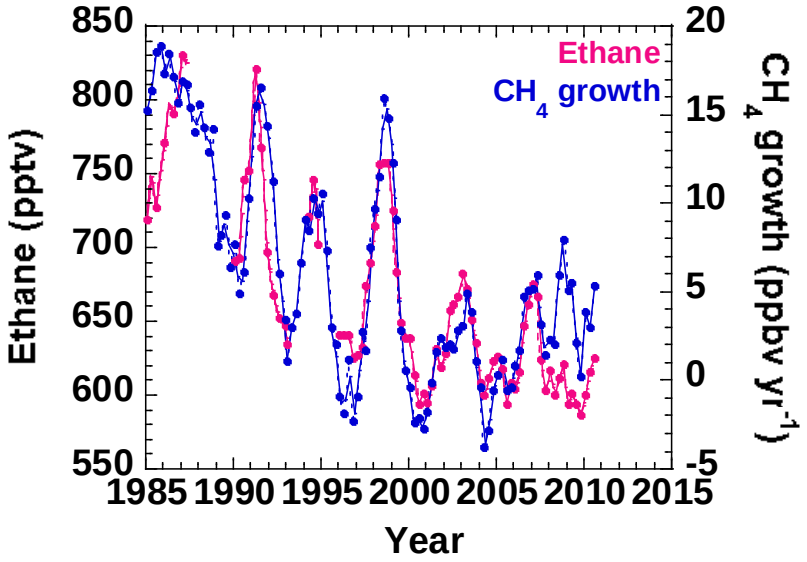

Ethane ***(C_2H_6)*** *is emitted during fossil fuel production (unburned gas) and by biofuel and biomass burning (lifetime 2-3 months)*

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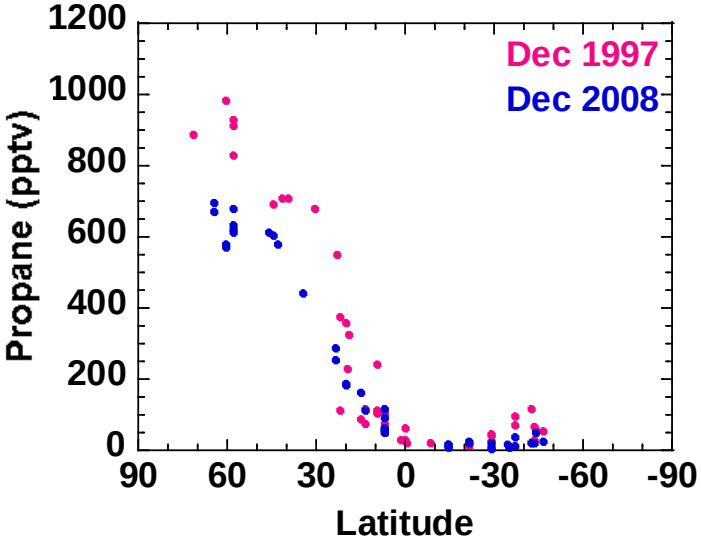
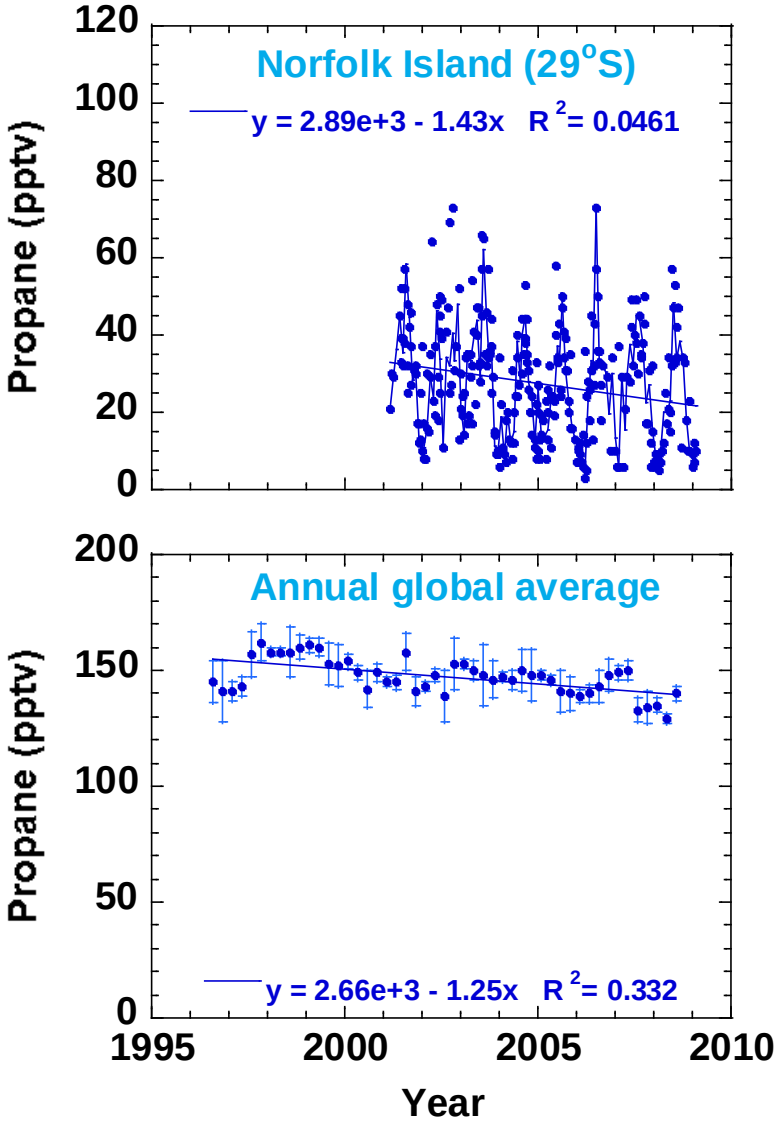
Global propane trend: Decreasing

Long-term global propane decrease

- 158 ± 2 pptv in 1998
- 140 ± 2 pptv in 2008
- **~ 10% decrease in 10 years**



Propane ***(C_3H_8)*** *is emitted by fossil fuel production, biofuel and biomass burning, and gasoline exhaust (lifetime 1-2 weeks)*



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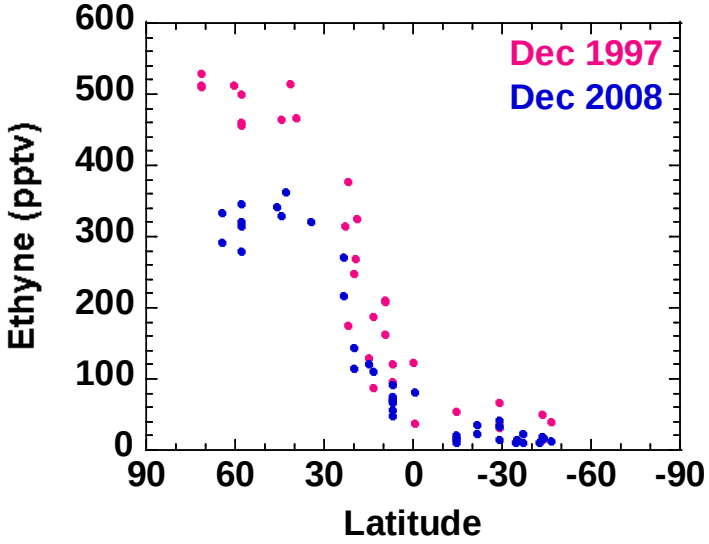
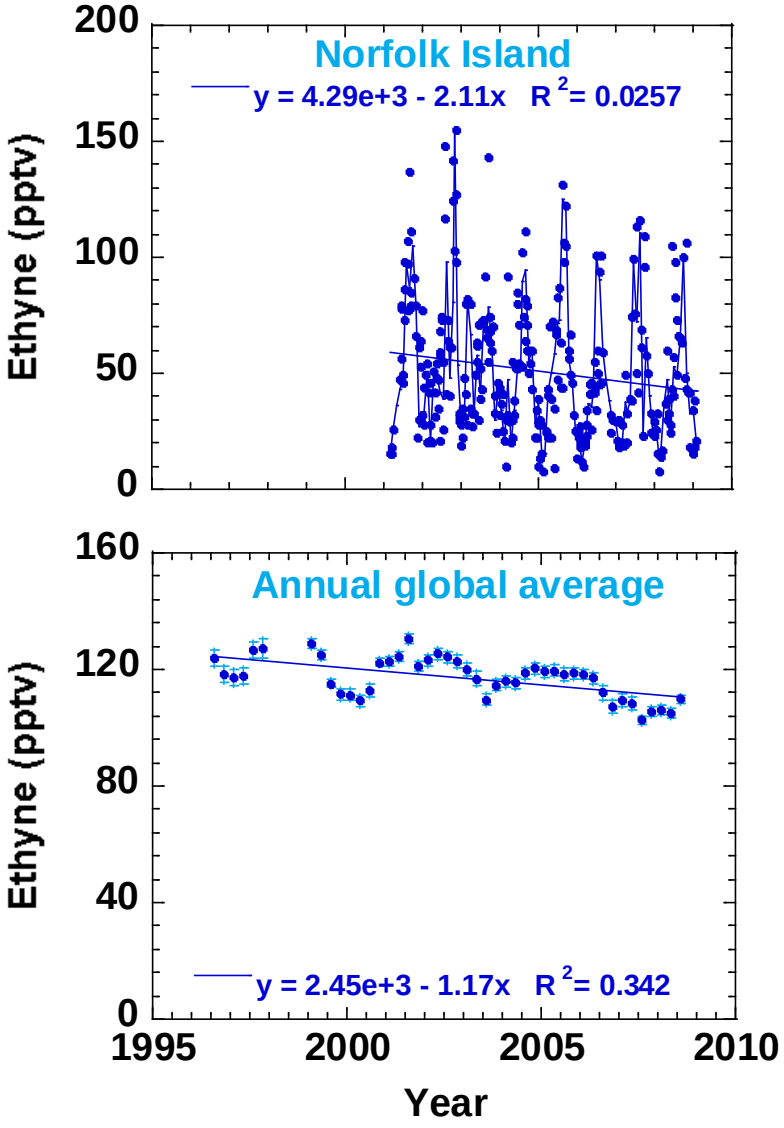
Global ethyne trend: Decreasing

Long-term global ethyne decrease

- 124 ± 3 pptv in 1996
- 110 ± 2 pptv in 2008
- **~ 11% decrease in 12 years**



Ethyne (C_2H_2) is a tracer of incomplete combustion by biomass burning and urban fossil fuel (lifetime 2-3 weeks).



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Conclusions and Acknowledgments

Multi-decade record shows significant trends in global trace gas mixing ratios:

- Global declines of many **halocarbons** in response to banning legislation
- Global declines of many **hydrocarbons** due to less venting/flaring; vehicle emission controls
- Global increases of **$CHCl_3$**, **HCFCs** and **CH_4**

Global declines:

Halocarbons

- CFC-11
- CFC-12
- CFC-113
- H-1211
- CCl_4
- CH_3CCl_3
- CFC-114
- C_2Cl_4

Alkanes

- Ethane
- Propane
- *i*-Butane
- *n*-Butane

Alkynes

- Ethyne

Global increases:

Halocarbons

- HCFC-22
- HCFC-141b
- HCFC-142b
- $CHCl_3$

Alkanes

- Methane

Acknowledgments

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