A 20th century atmospheric history of ethane and implications for the methane budget

Kristal R. Verhulst[1], M. Aydin[1], E. S. Saltzman[1], P. Lang[2], S. A. Montzka[2], K. Sorg[3], D. A. Plotkin[3] M.Battle[3], Q. Tang[1], and M. J. Prather[1]

[1]UC Irvine, Department of Earth System Science
[2]NOAA/ESRL/GMD, Boulder, CO
[3]Bowdoin College, Department of Physics and Astronomy

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Overview

- Ethane atmospheric histories developed using firn diffusion model
- CTM and box model used to explain changes in atmospheric ethane levels throughout 20th century
- Implications of derived fossil fuel emissions

Ethane budget

Sources:
- Fossil fuels
- Biomass burning
- Biofuel use

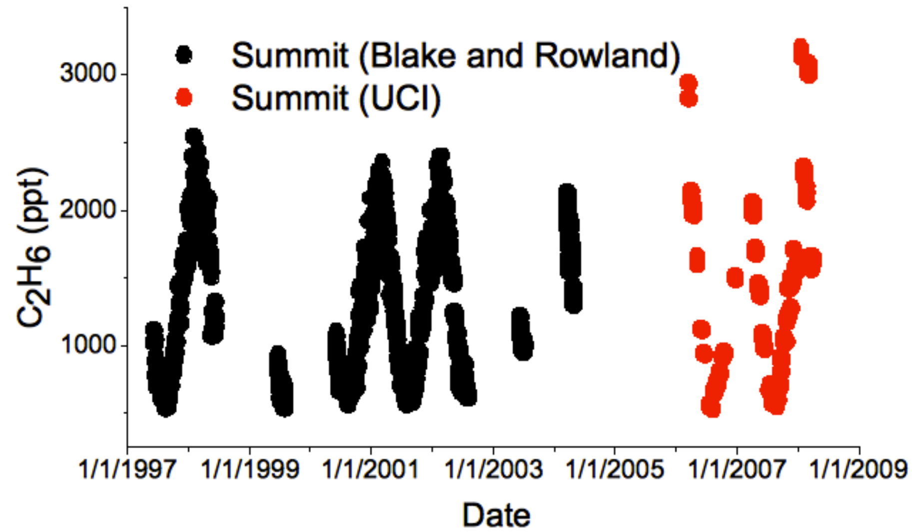
Sink:
- OH
(summer lifetime ~1-2 mo.)

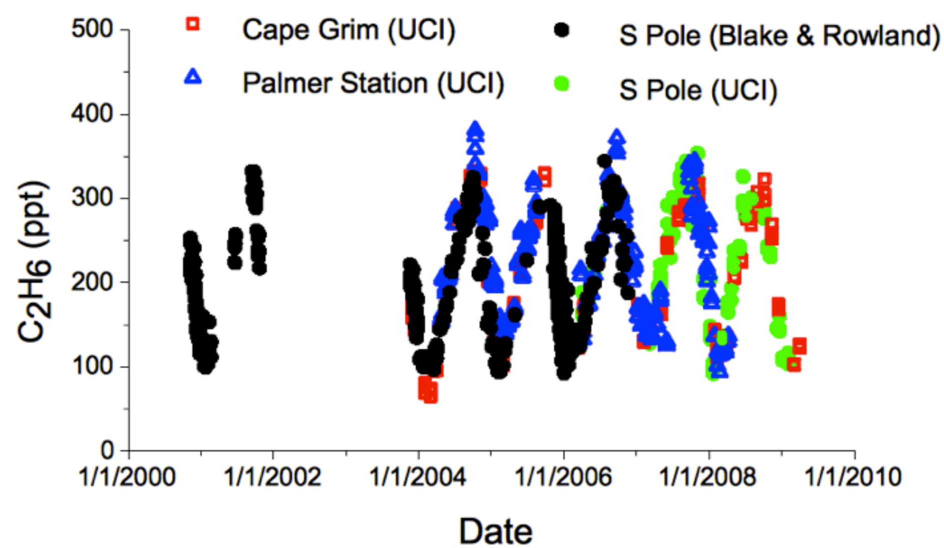
	Ethane (Tg)
Fossil fuels	4.8 - 8
Biomass burning	2.4 - 5.6
Oceans	0.2 - 0.5
Vegetative/Soils	0.4 - 2.5
Wetlands	< 0.2
Rice	<0.2
Total	~8-17

(Xiao et al., 2008)

Surface air observations
(NOAA/HATS flasks)

- Seasonal drawdown due to OH (winter maxima)
- Summit mean: ~1.4 ppb
- S Pole mean: ~210 ppt
- Summit = high latitude NH levels
  S Pole = high latitude SH levels,
  (based in Simpson et al., 2006)
- UCI measurements show agreement with Blake & Rowland measurements (2004-2007)





(D. Blake, A. Beyersdorf)

Firn diffusion model: tuning and validation

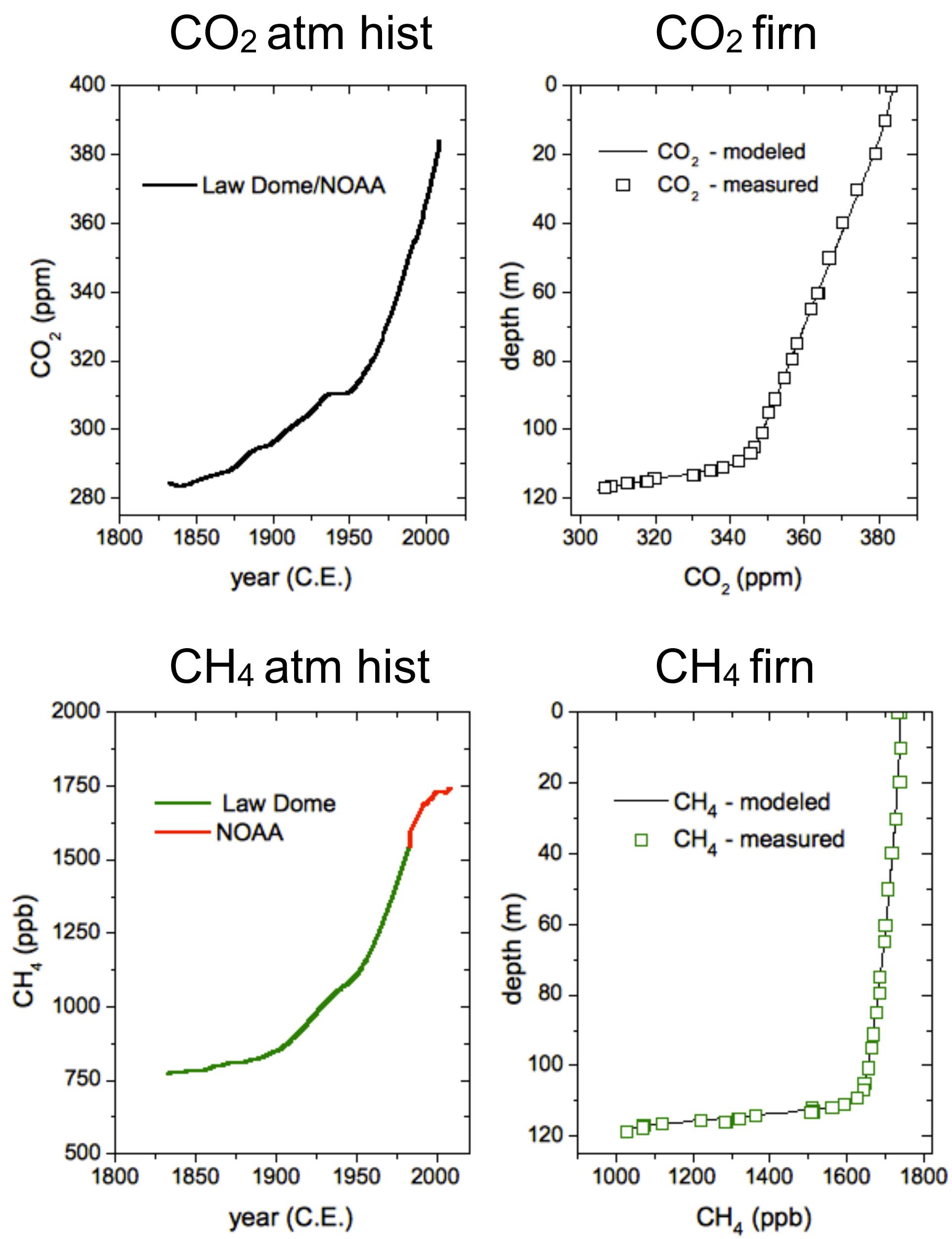
- 1-D firn diffusion model used to simulate gas diffusion in firn columns at S Pole, WAIS-D and Summit.

- Model generates a set of functions describing age distribution of air as a function of depth

- The diffusivity profile is tuned to reproduce the measured CO_2 profile (WAIS, S Pole) or CFC-12 and CH_3CCl_3 (Summit) using known atmospheric histories

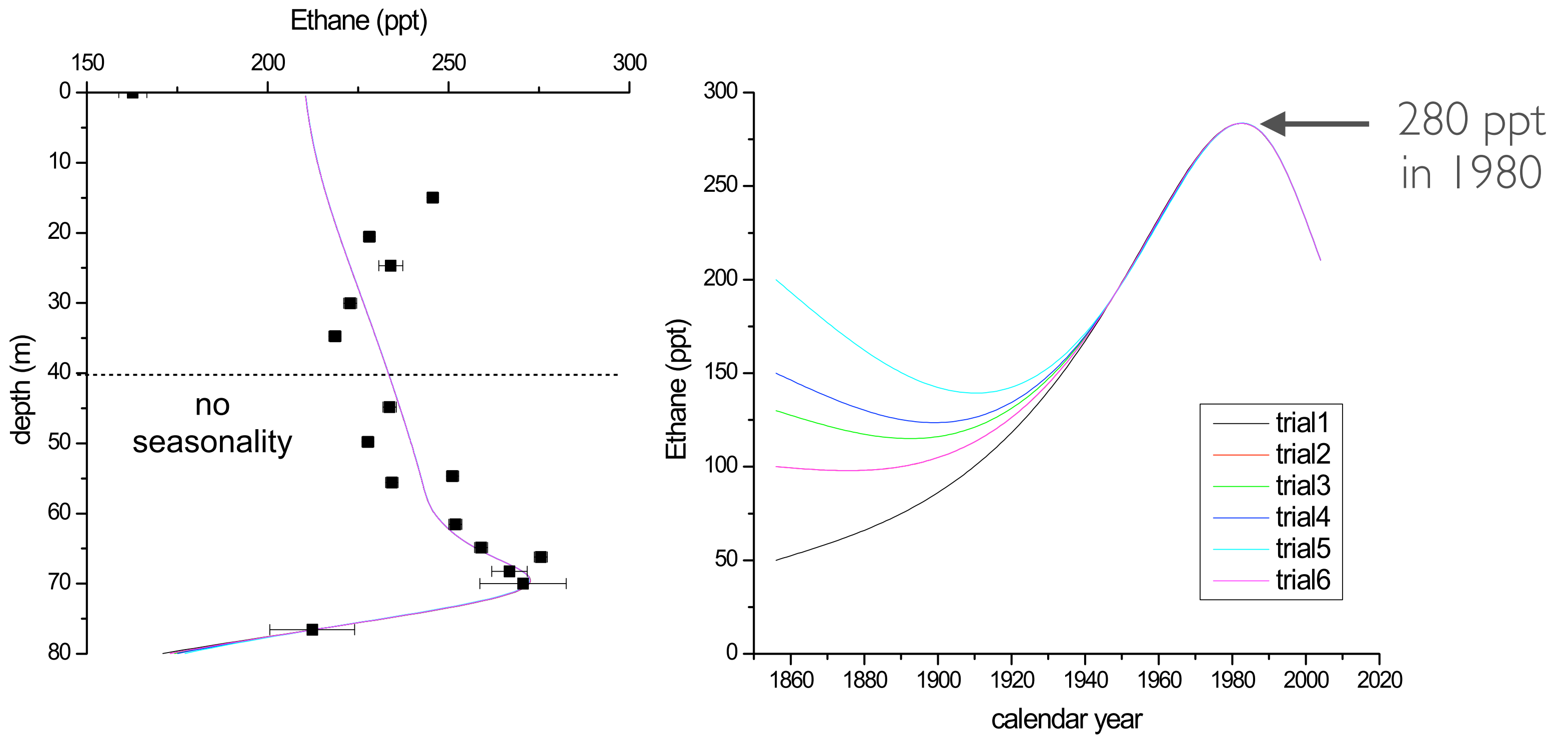
- Validation using other gases with well known atmospheric histories (e.g. halocarbons, CH_4).

South Pole



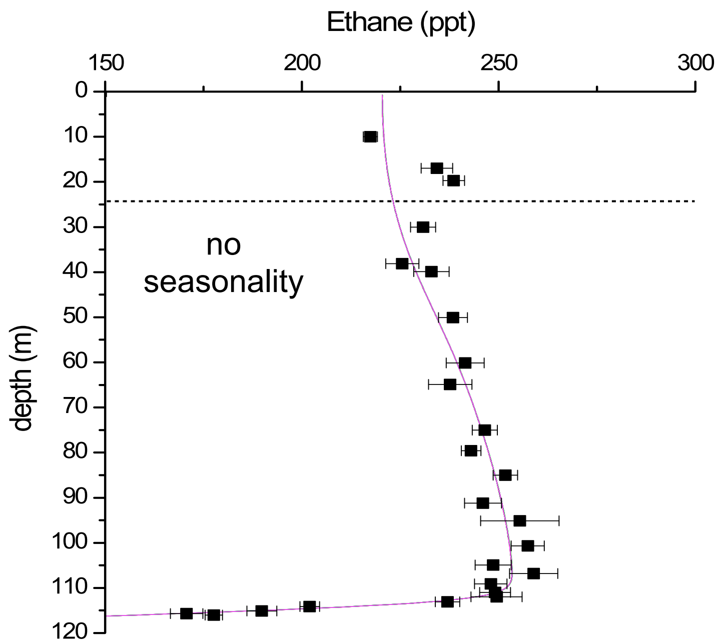
(Etheridge et al., 1996,1998; Dlugokencky, 2009)

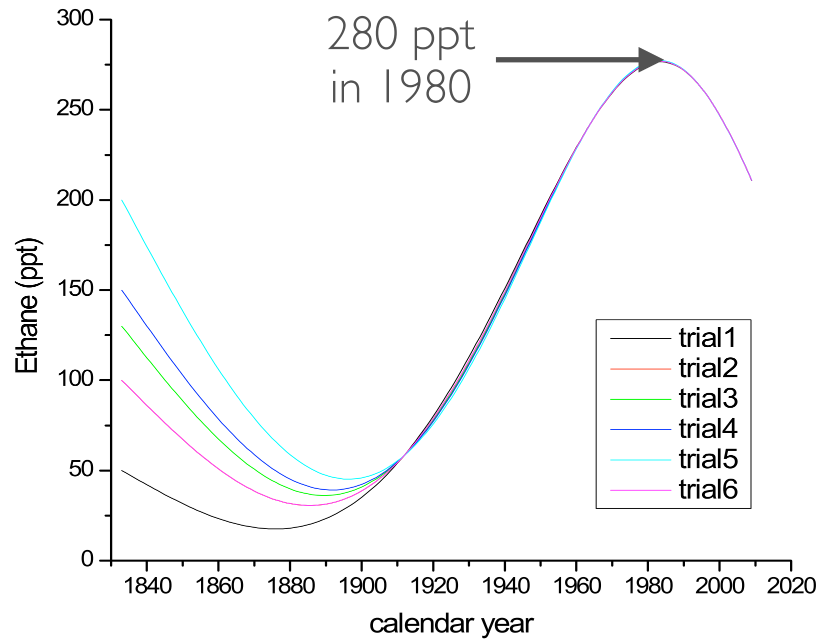
WAIS-Divide '05-06



- Objective minimization algorithm minimizes a cost function based on:
  - chi-square term (statistical fit to firn data)
  - smoothness parameter
- Present day mean atmospheric ethane level ~210 ppt)

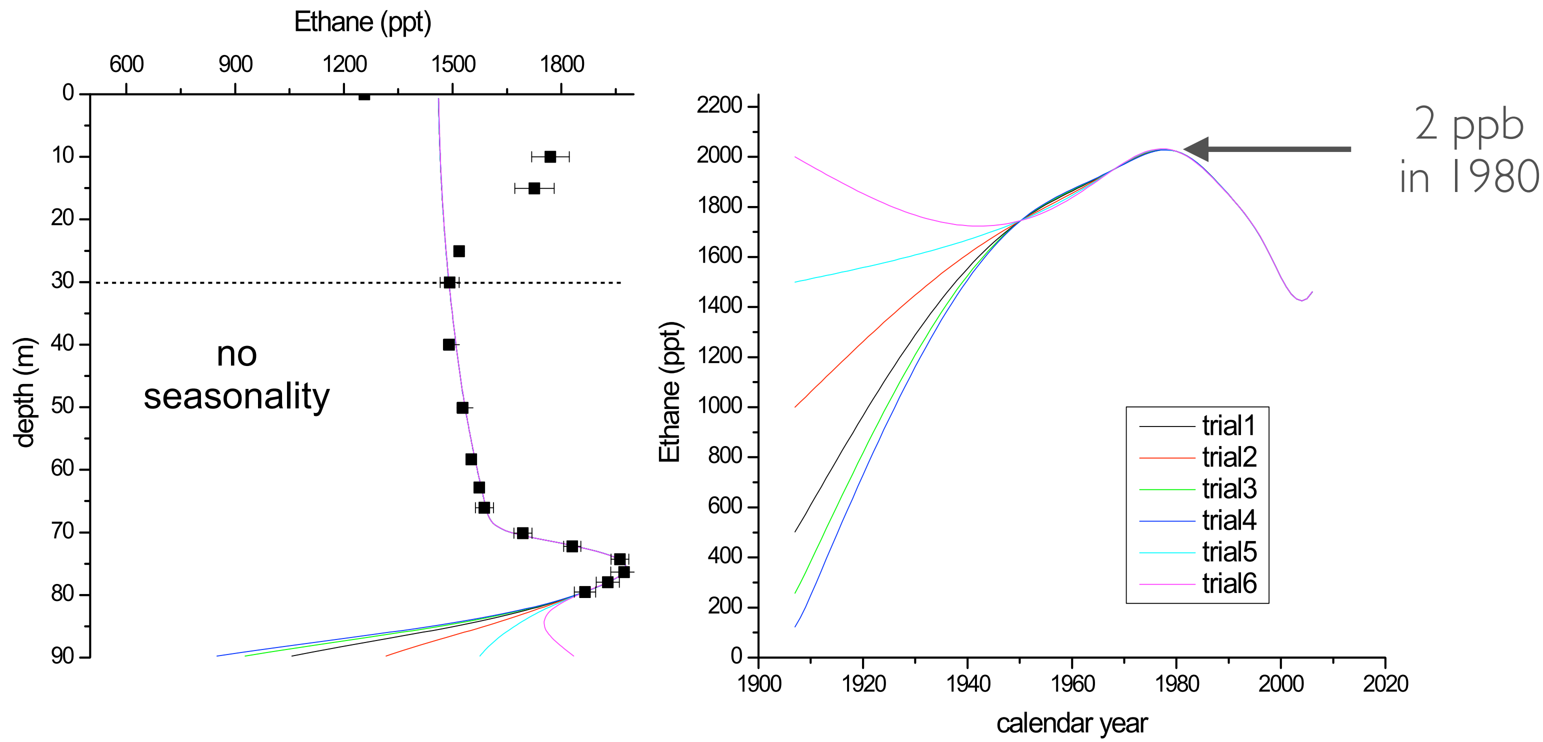
South Pole '08-09





- S Pole atmospheric histories for ethane better constrained after 1920s
- Ethane levels over Antarctica roughly doubled between 1930-1980, stabilized during 1980's, and declined to modern mean level

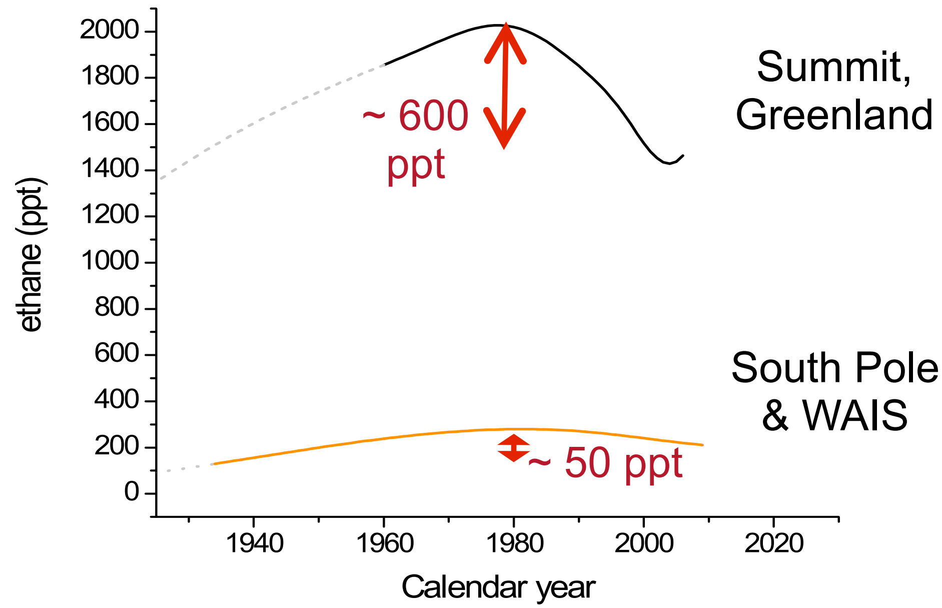
Summit 2006



- Atmospheric history for Summit better constrained after 1950s
- Ice core ethane measurements needed to constrain older part of histories at Summit

NH versus SH ethane histories

- Similar trends in both hemispheres:
  - Increasing levels through 1970s
  - Decline since 1980s
- Decline ~12x larger in NH
- Ratio of change Greenland/Antarctica implies variability is driven by changes in NH source



Ramp up

	Rate	% change
Summit (1950-1980)	+10 ppt/yr	+15%
S Pole (1920-1980)	+3.3 ppt/yr	+71%

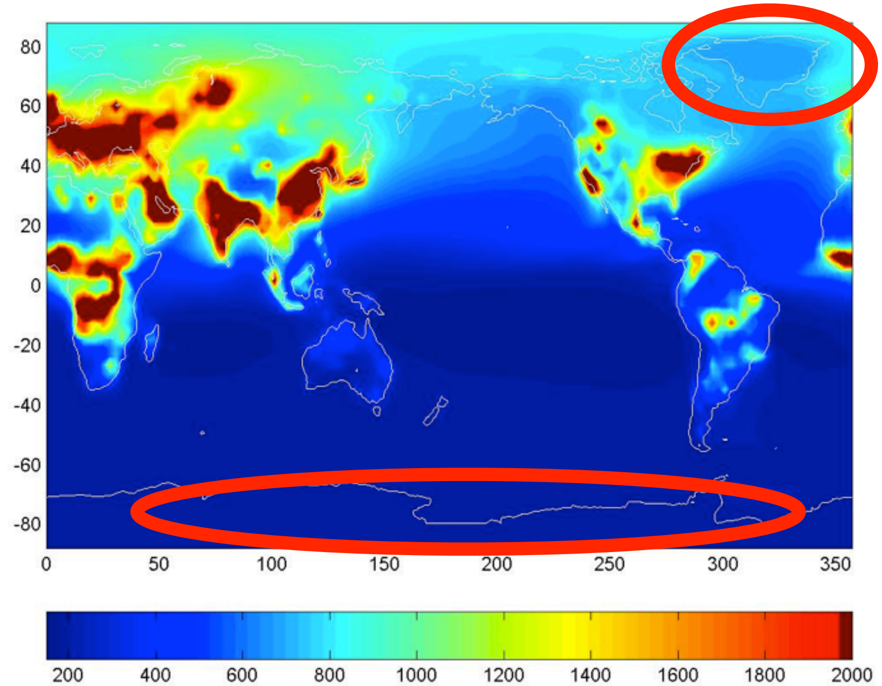
Decline

	Rate	% change
Summit (1980-2006)	-23 ppt/yr	-30%
S Pole (1980-2009)	-2.4 ppt/yr	-25%

Ethane source distribution

- Sources affect S Pole mixing ratios equally (UCI-CTM)
- UCI-CTM underestimates observed mixing ratios at Summit
- Summit mean levels ~50% higher than NH mean (based on HNH levels from Simpson et al., 2006)
- S Pole mean ~70% of the SH mean (based on HSH levels from Simpson et al., 2006)

Global ethane levels (ppt) (UCI-CTM)



Ethane 2-box model

- Variable OH (based on CH_4 concentrations)
- Developed FF source histories based on statistical fit to ethane atmospheric histories for Summit/S Pole

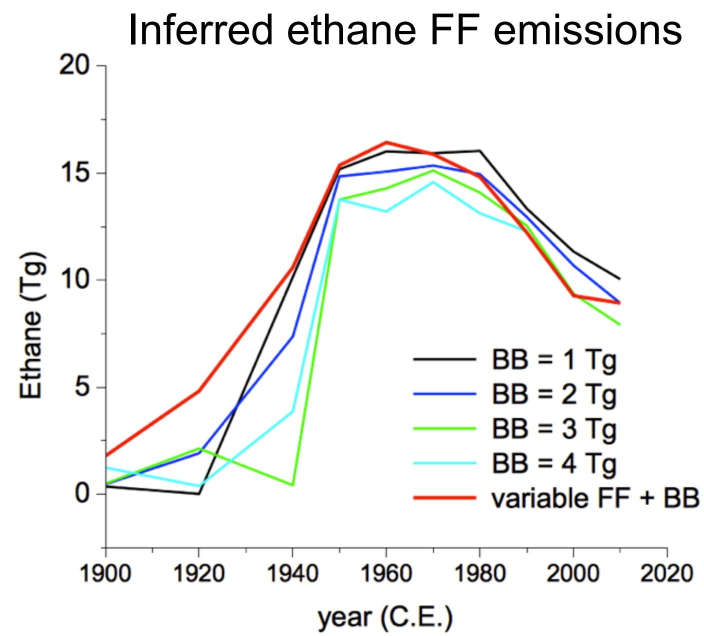
Ethane box model inversions:

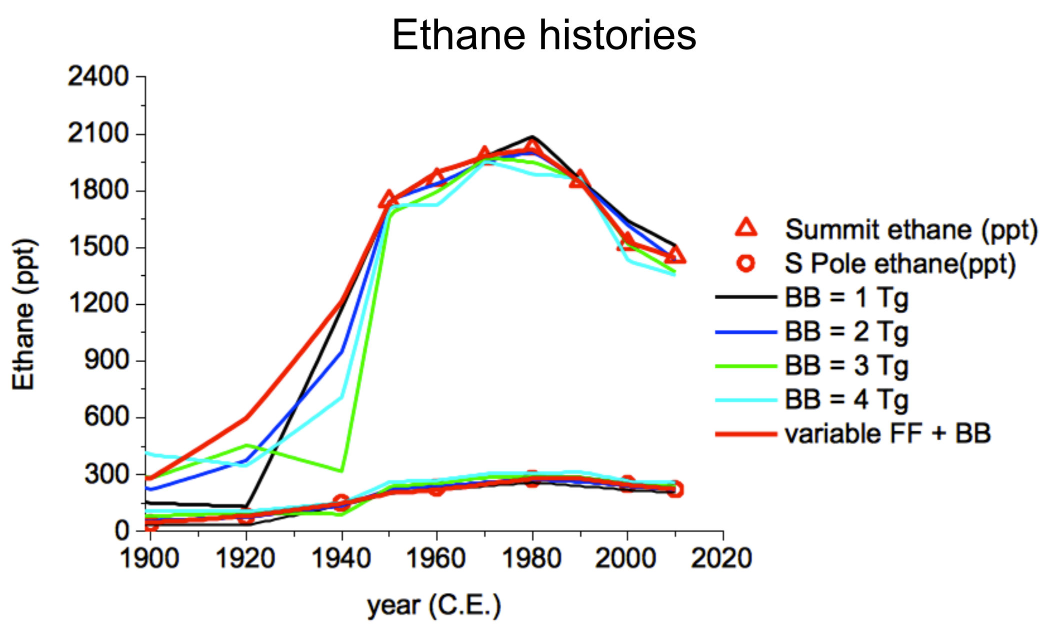
1. BB fixed at 1, 2, 3, and 4 Tg

2. BB vary (solid red line)

   - Fixed biofuel source (EDGARv.1.4) used for all inversions

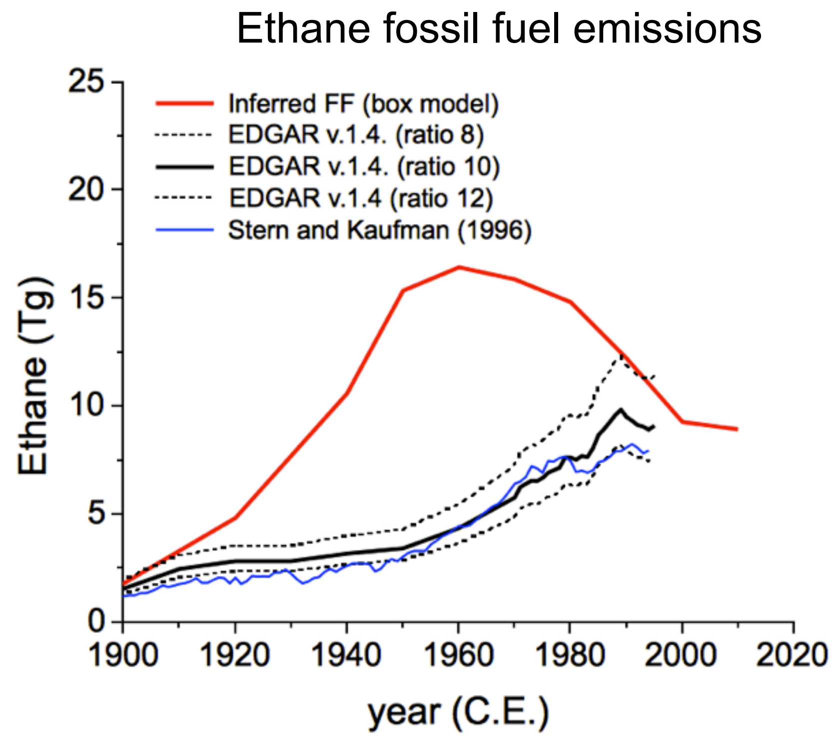
• Model reproduces rollover in the FF ethane source independent of a changes in BB source





Implications: ethane fossil fuel source

- Assuming a constant methane/ ethane ratio from fossil fuels:
  - ~40 yr difference in timing of ramp-up
  - Rollover occurs when growth of methane and ethane FF source thought to be most rapid
  - Reduction in FF ethane source is not in agreement with existing emissions inventories

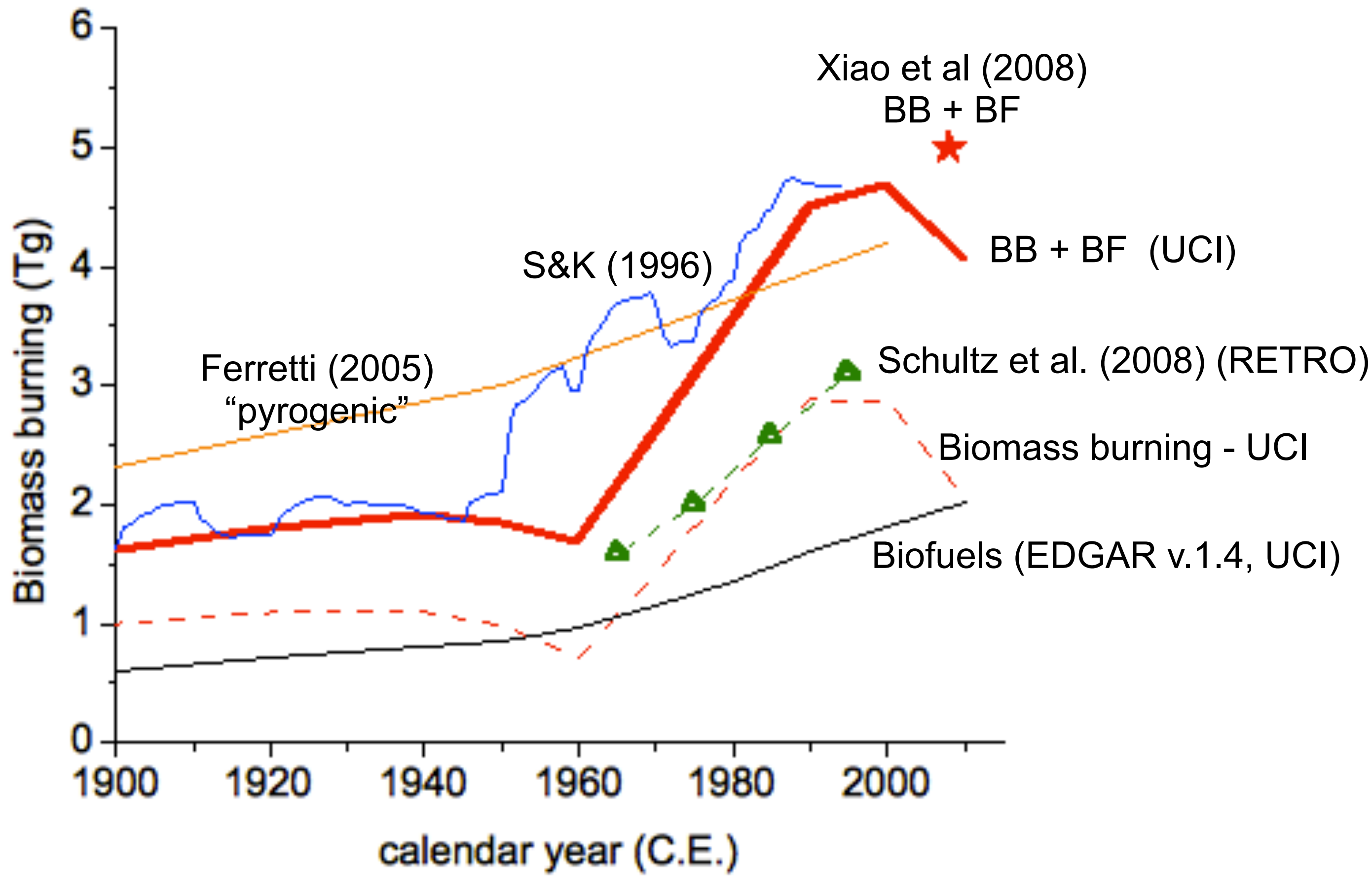


- Alternative hypotheses:
  - Ratio of methane/ethane emitted from fossil fuels may have changed dramatically
  - Sink with Cl atom
    - Rollover in ethane levels may also be reproduced with a small Cl sink, on the order of ~3% of the total methane sink

Conclusions

- Ethane levels increased at polar latitudes until 1970s, decreased since 1980s
- Reduction in hydrocarbon emissions during the production, transport, storage, and/or use of fossil fuels is still a possibility, however this is not in agreement with existing emissions inventories
- Alternative explanations include a changing ratio of methane/ethane emitted from fossil fuels, and/or an increasing in the atmospheric ethane sink

Biomass burning/biofuels estimates

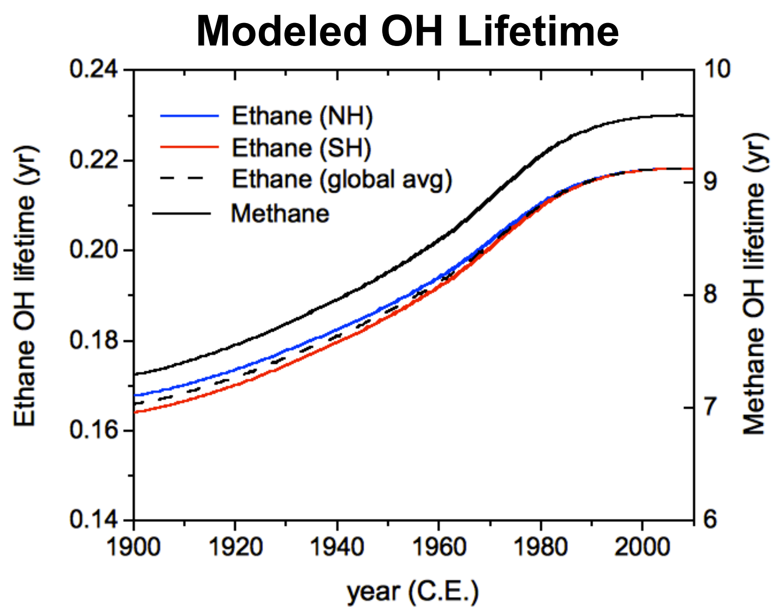


Variable FF + BB simulation:

- Biomass burning trend similar to estimate from Schultz et al (2008)
- Estimate for Biomass burning + Biofuel use is comparable to estimate from Xiao et al (2008) and scaled estimate from Stern and Kaufman (1996)

Ethane 2-box model: OH Lifetime

- OH controlled by CH_4
- Methane and ethane lifetimes due to OH getting longer (more CH_4 = less OH)
- Modern CH_4 lifetime: 9.6 (IPCC TAR)
- Modern ethane lifetime: ~2 months
- Difference in ethane lifetime between hemispheres, getting smaller over time

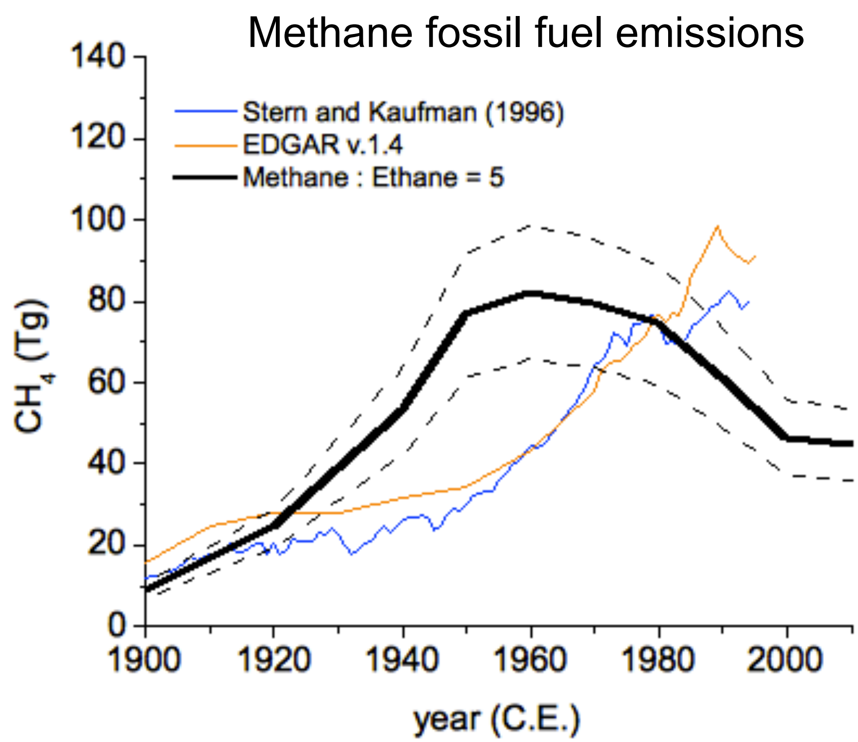


- CH_4 lifetime

year	1/k(OH) (yr)	1/k(Total) (yr)
1900	7.30	5.94
1950	8.21	6.04
2000	9.59	6.23
IPCC (TAR)	9.6	8.4

Implications for the CH_4 budget

- Ethane decline coincides with decrease in atmospheric growth rate of methane, suggesting related change
- Constant methane/ethane ratio from FF:
  - Ramp-up in FF source ~40 yr early
  - Rollover in FF occurs during time when growth thought to be most rapid



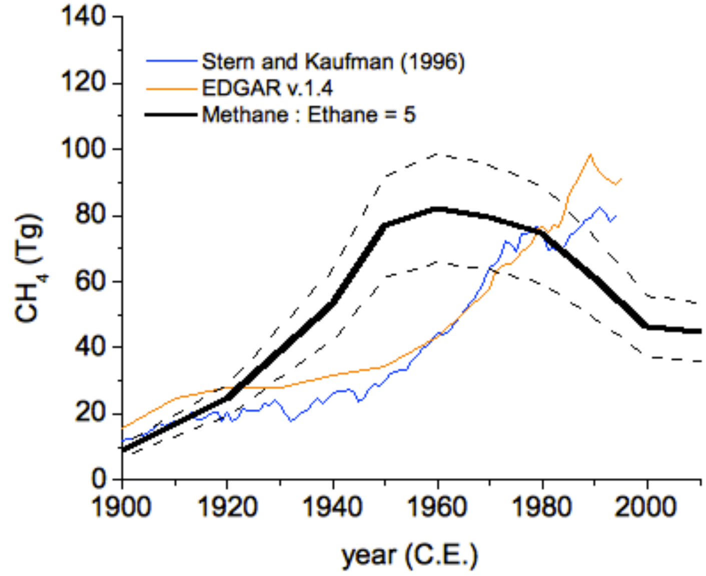
- Alternative explanations:
  - Changing ratio of methane/ethane emitted from fossil fuels.
    - Did hydrocarbon fuel use efficiency improve dramatically throughout the last half of the 20th century?
  - Sink with chlorine atom
    - Cl atoms preferentially oxidize ethane relative to methane (~1000x) compared to their respective reaction rates with OH.

Implications for the CH_4 budget

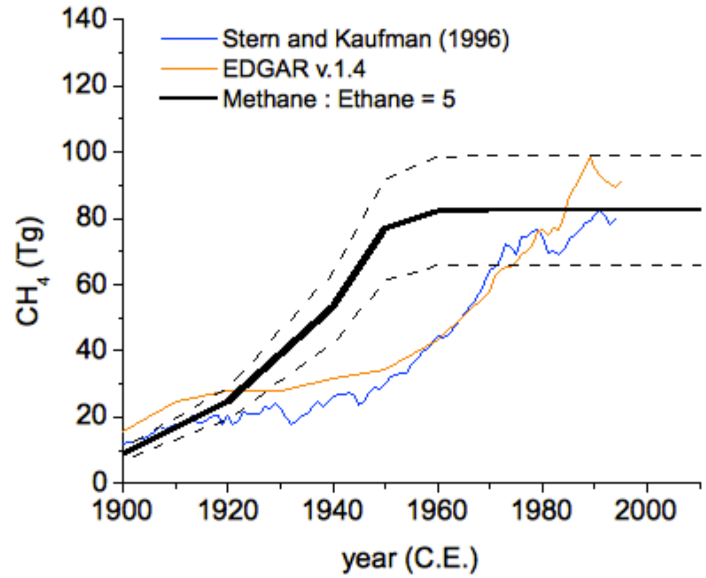
- Ethane decline coincides with decrease in atmospheric growth rate of methane, suggesting related change
- Constant methane/ethane ratio from FF:
  - 1900-1960 ramp up in FF methane source earlier than prior analyses
  - Predicted rollover in FF source occurs during time when FF CH_4 growth thought to be most rapid

- Alternative explanations:
  - Changing ratio of methane/ethane emitted from fossil fuels.
    - Did hydrocarbon fuel use efficiency improve dramatically throughout the last half of the 20th century?
  - Sink with chlorine atom
    - Cl atoms preferentially oxidize ethane relative to methane (~1000x) compared to their respective reaction rates with OH.

Methane fossil fuel source



Methane fossil fuel source



Ethane 2-box model: Source distribution

- Fraction of source contributing to ethane levels at high latitudes based on:

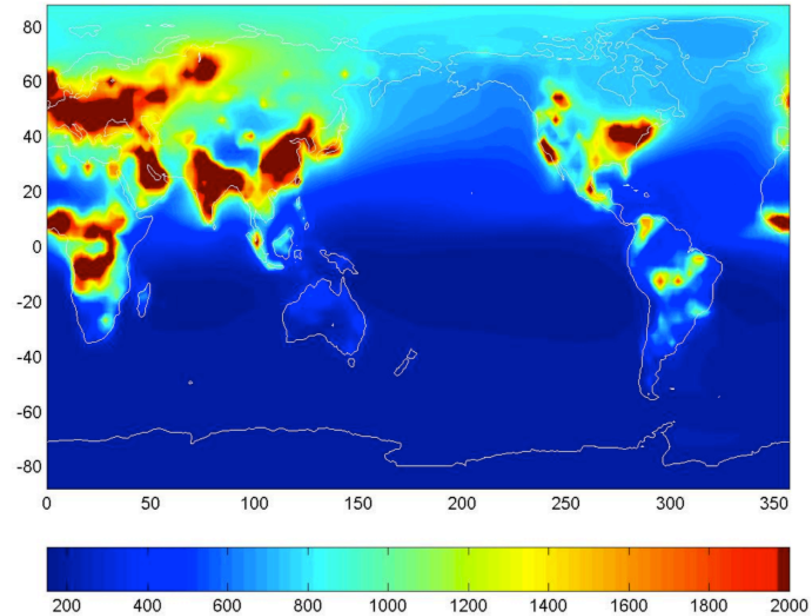
  - surface air observations (Simpson et al., 2006)

  - literature estimates (Xiao et al., 2008)

  - UCI CTM perturbation experiments

- Summit mean levels ~50% higher than NH mean
- S Pole mean ~70% of the SH mean
- Sources affect S Pole mixing ratios equally (remote location, approx equal time for transport)
- Large NH sources close to Summit, difficult to determine directly
- UCI CTM underestimates observed mixing ratios at Summit

Global ethane levels (ppt) (UCI-CTM)



Fraction of sources reaching Summit and SPole

	FF	BB	Biofuels
NH mean	0.9	0.6	0.8
Summit	1.6	1.0	1.4
S Pole	0.7	0.7	0.7

(Simpson et al., 2006; Xiao et al., 2008)