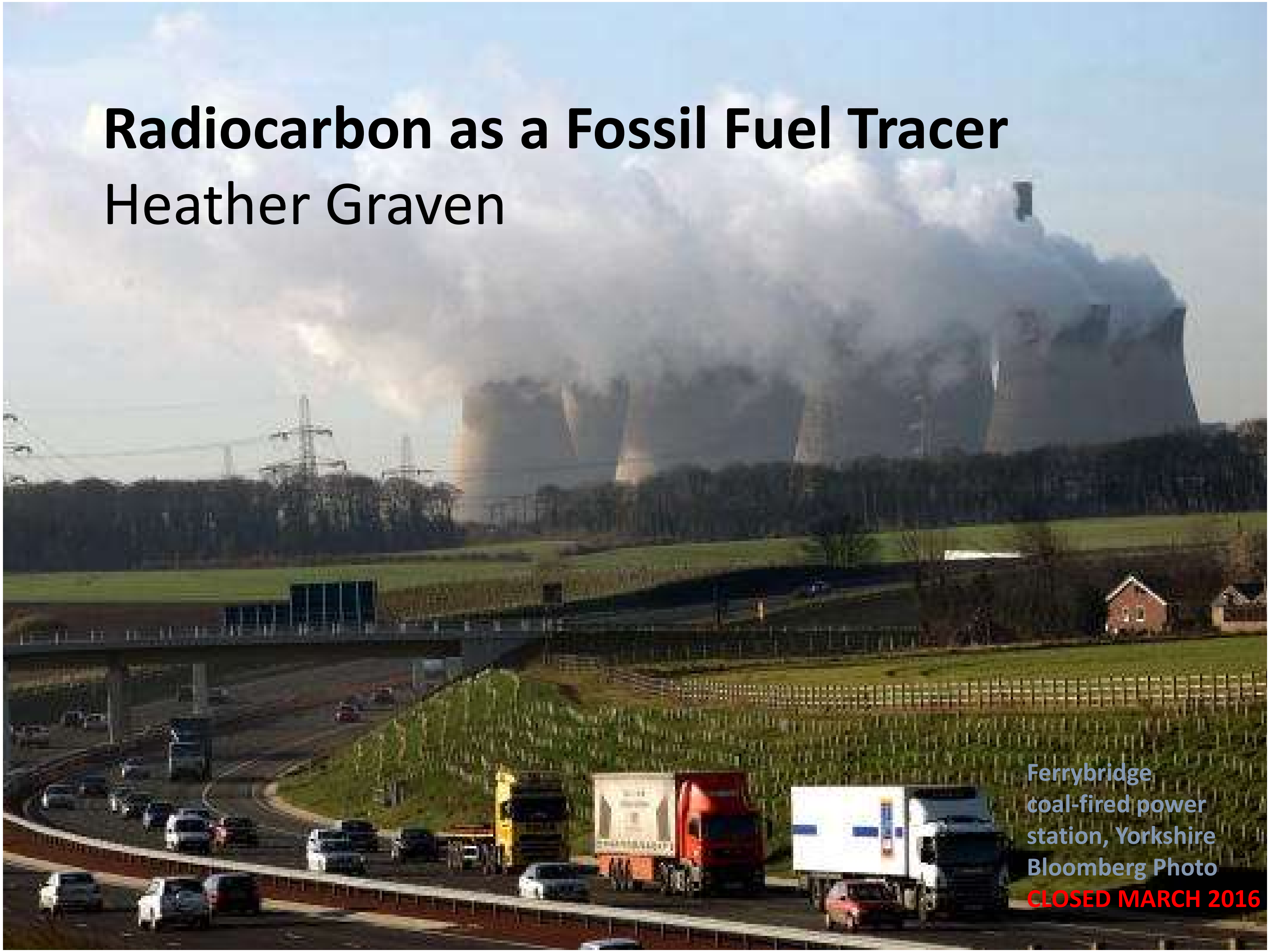
Radiocarbon as a Fossil Fuel Tracer

Heather Graven



Ferrybridge coal-fired power station, Yorkshire
Bloomberg Photo
CLOSED MARCH 2016

Estimates of fossil fuel CO_2 emissions are based on accounting of activities according to standard practices ("bottom-up" estimates)

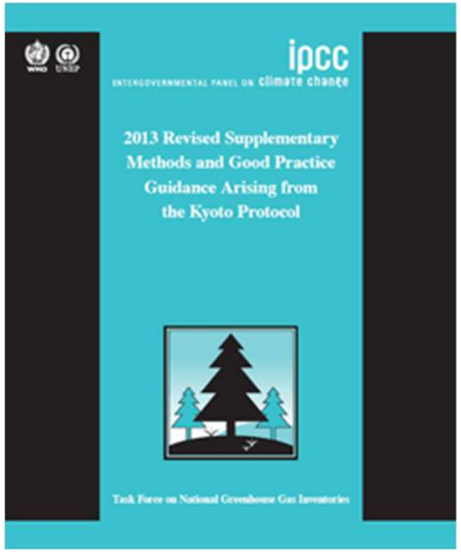
$$\text{Emissions} = \text{Activity Data} \times \text{Emission Factor}$$

Verification done by auditing

Atmospheric observations could provide independent ("top-down") validation

Bottom-up estimates might not include temporal or spatial variations in emissions

Other types of fossil fuel emissions (methane, aerosols) have higher uncertainties



The application of $\Delta^{14}C$ to identify fossil fuel influences has a long history

Radiocarbon Concentration in Modern Wood

HANS E. SUESS

2 SEPTEMBER 1955

Natural atmospheric ^{14}C variation and the Suess effect

P. P. TANS*
A. F. M. DE JONG
W. G. MOOK

1979

[RADIOCARBON, VOL 31, NO. 3, 1989, P 431–440]

THE CONTINENTAL EUROPEAN SUESS EFFECT

INGEBORG LEVIN, JOACHIM SCHUCHARD, BERND KROMER and K O MÜNNICH

Calculating fossil fuel-derived CO_2 using $\Delta^{14}C$

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The mixing model we looked at earlier:

Approximate mass balances for carbon and ^{14}C, considering the addition of CO_2 from a source (s):

$Cm = Cbg + Cs$ $\qquad$ $Cm\, \Delta m = Cbg\, \Delta bg + Cs\, \Delta s$

The change in $\Delta^{14}CO_2$ is the difference between the measured (m) and the background (bg) before the source was added:

$\Delta m - \Delta bg = Cs/Cm\, (\Delta s - \Delta bg)$

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Flipping this around: $Cs = Cm\ (\Delta m - \Delta bg) / (\Delta s - \Delta bg)$

For fossil carbon: $Cff = Cm\ (\Delta m - \Delta bg) / (-1000\ ‰ - \Delta bg)$

$= Cm\ (\Delta bg - \Delta m) / (\Delta bg + 1000\ ‰)$

Alternatively: $Cff = Cbg\ (\Delta bg - \Delta m) / (\Delta m + 1000\ ‰)$

Example

In 2017, what is Cff if a decrease of 5‰ below Δbg is observed?

$$Cff = Cm\,(\Delta bg - \Delta m) / (\Delta bg + 1000\ ‰)$$

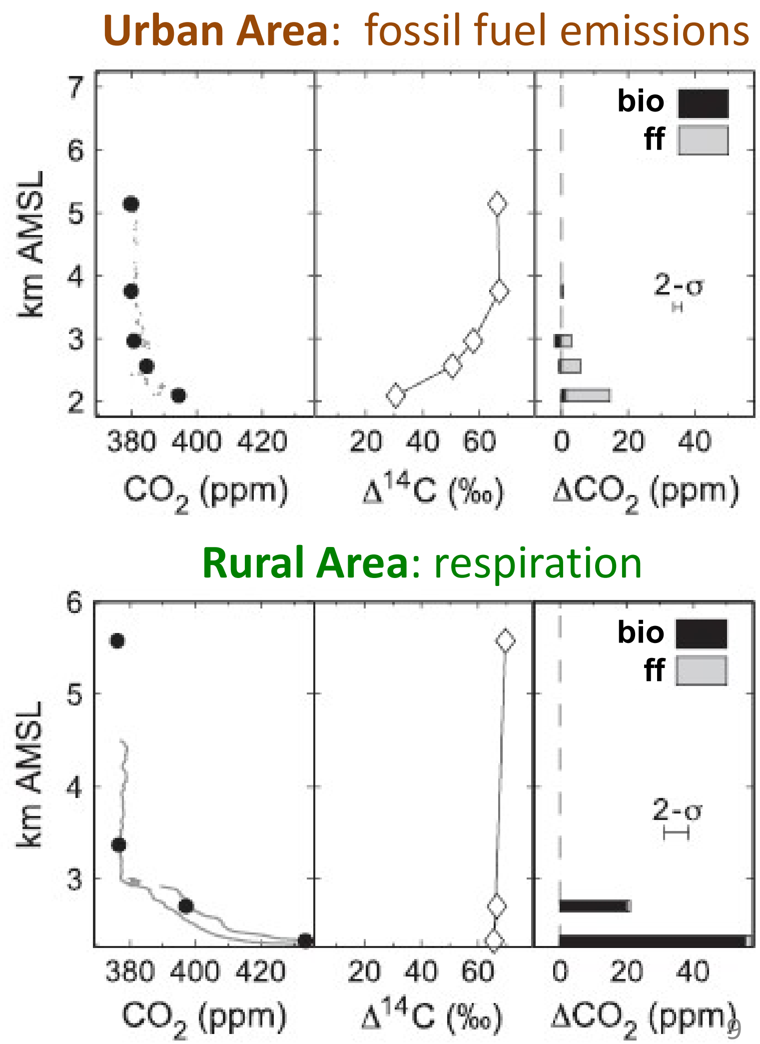
Calculating fossil fuel-derived CO_2 using $\Delta^{14}C$

Aircraft profiles above Colorado, USA

Cm = Cbg + Cff + Cbio

In urban area, CO_2 increase is mirrored by $\Delta^{14}C$ decrease

In rural area, strong CO_2 increase with very little change in $\Delta^{14}C$

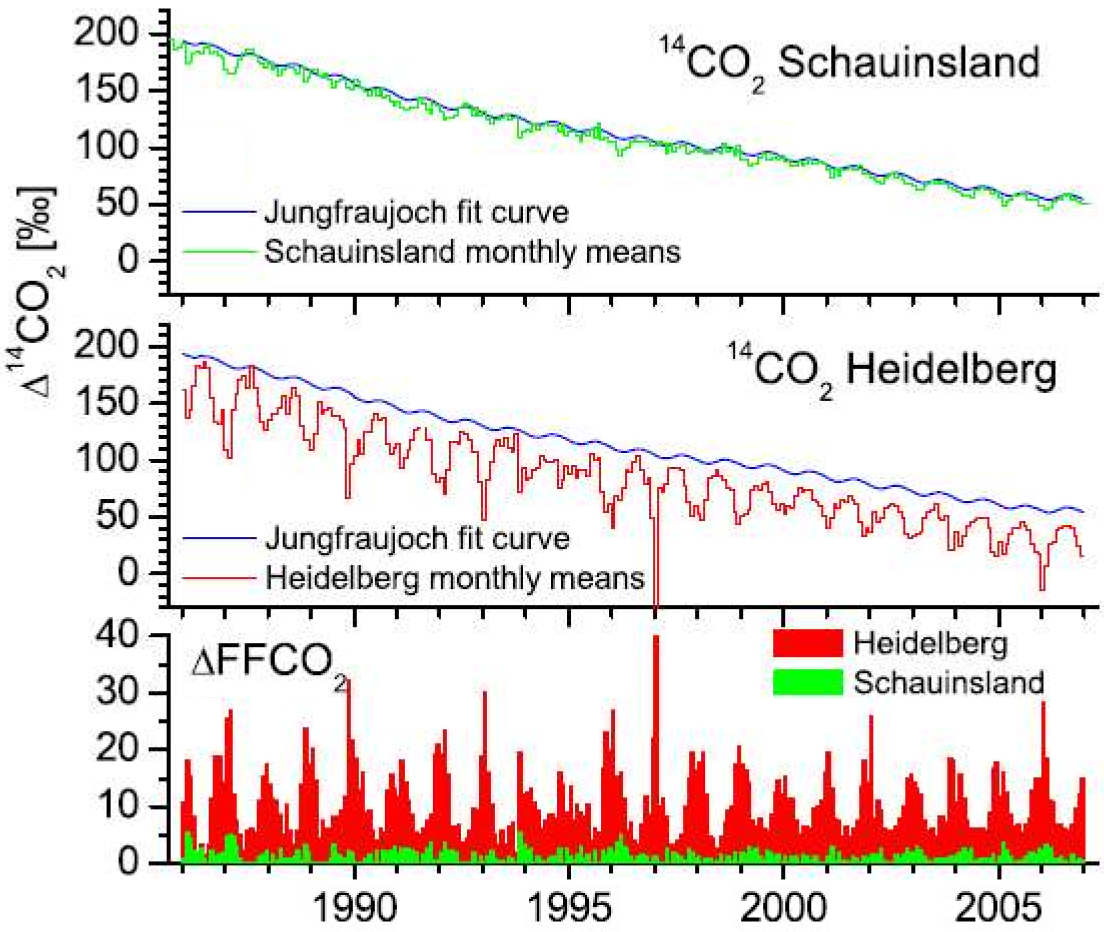


Graven et al. 2009

Long-term observations of Cff in Germany

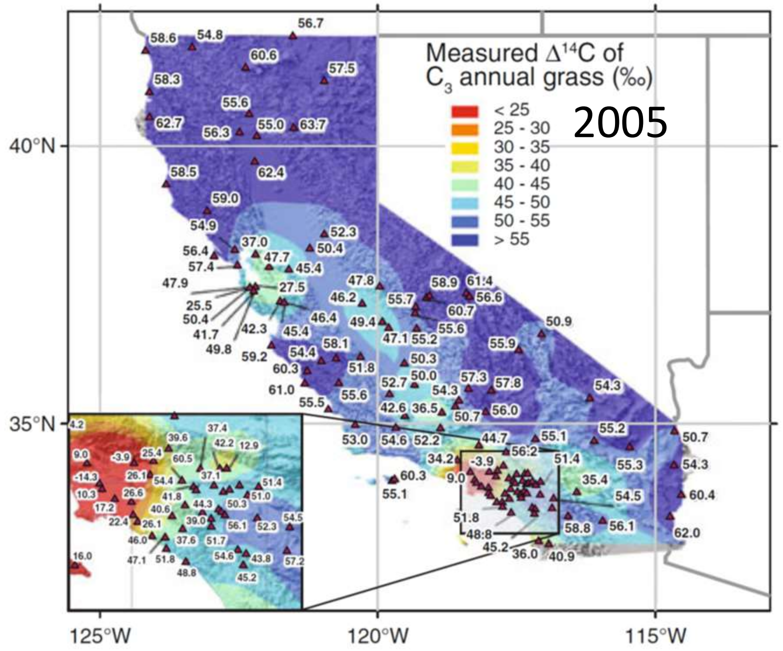
Urban sites show $\Delta^{14}C$ depletion relative to background observations in the Swiss Alps

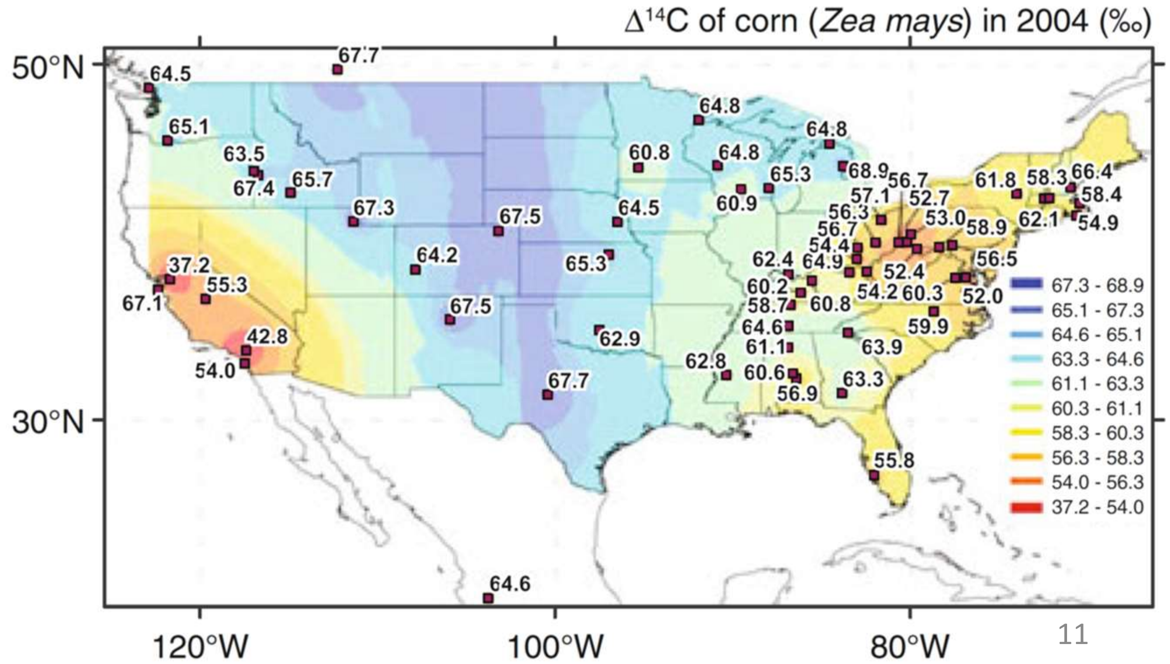
No long-term trend in Cff – consistent with steady emissions inventories in local region



Levin et al. 2008

Not only tree rings but also annual plants have been used to record atmospheric Δ14C variations





Hsueh et al. 2007
Riley et al. 2008

Applications using $\Delta^{14}C$ measurements to trace Cff also often incorporate other tracers

Other tracers can be easier to measure and some can be measured continuously

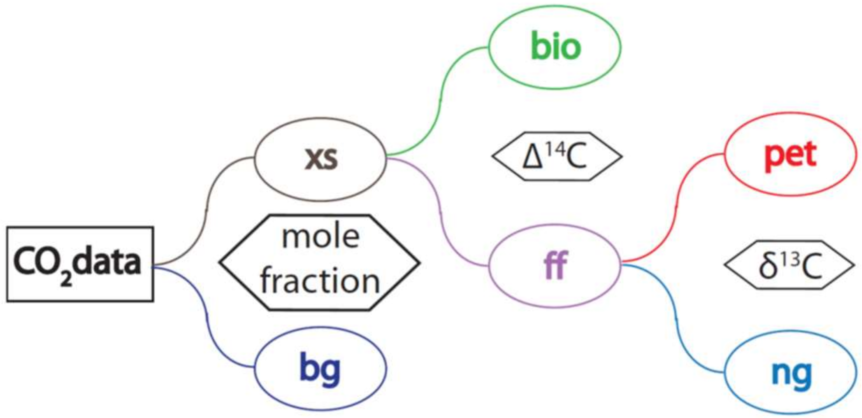
They provide additional information on the sources of Cff

For example, more CO is produced per ppm of Cff by motor vehicles than by power plants, and $\delta^{13}C$ is lower in natural gas than in coal or oil

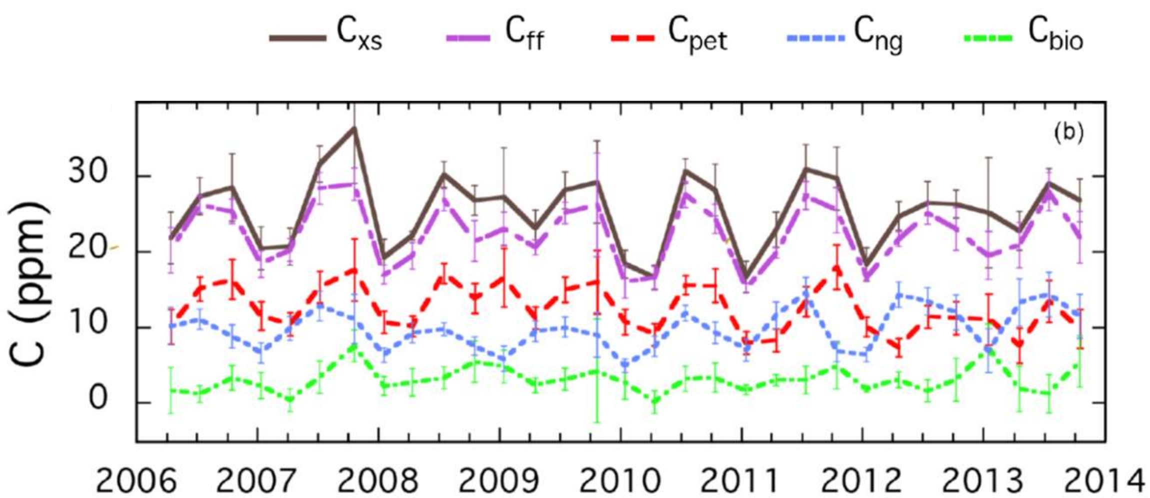
$\Delta^{14}C$ can be used to “calibrate” the CO/Cff emission ratio in a particular region or time period

Atmospheric $\Delta^{14}C$ and $\delta^{13}C$ in Los Angeles

$\Delta^{14}C$ used to estimate Cff and fraction of excess CO_2 observed, $\delta^{13}C$ used to partition Cff into natural gas and petroleum fractions



Observations show average values and seasonal variations caused by changes in emissions and in atmospheric transport



Newman et al. 2016

Calculating fossil fuel-derived CO_2 using $\Delta^{14}C$

For fossil carbon: $Cff = Cm (\Delta bg - \Delta m) / (\Delta bg + 1000 ‰)$

However, there may be other influences on Δm that we need to account for to accurately estimate Cff

Calculating fossil fuel-derived CO_2 using $\Delta^{14}C$

For fossil carbon: Cff = Cm (Δbg – Δm) / (Δbg + 1000 ‰)

However, there may be other influences on Δm that we need to account for to accurately estimate Cff

Cff = Cm (Δbg – Δm) / (Δbg + 1000 ‰) – β

β = Cs (Δbg – Δs) / (Δbg + 1000 ‰)

Respiration of biospheric carbon

Cff = Cm (Δbg – Δm) / (Δbg + 1000 ‰) – β

β = Cs (Δbg – Δs) / (Δbg + 1000 ‰)

Disequilibrium of biospheric carbon depends on turnover time

In the bomb period, most biospheric $\Delta^{14}C$ was lower than atmospheric CO_2

In the post-bomb period, most biospheric $\Delta^{14}C$ is higher than atmospheric CO_2

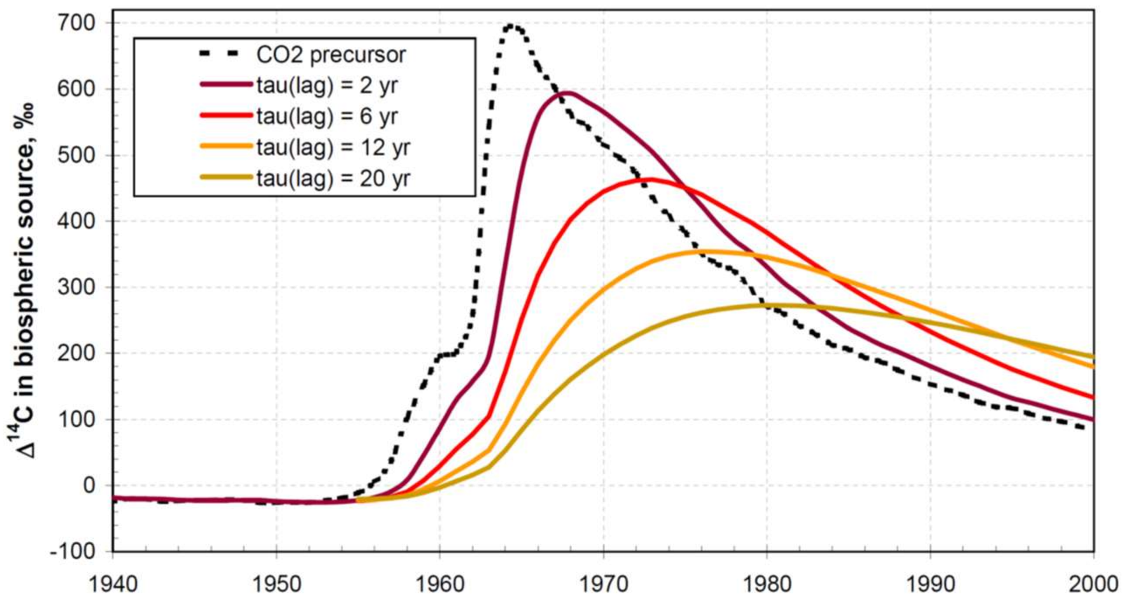


Figure from Lassey et al. 2007

Example

In 2017, what is Cff if a decrease of 5‰ below Δbg is observed?

$$Cff = Cm\ (\Delta bg - \Delta m) / (\Delta bg + 1000\ ‰) - \beta$$

What is β if there is 20 ppm of CO_2 added from respiration of biospheric material that is 20 ‰ higher than Δbg?

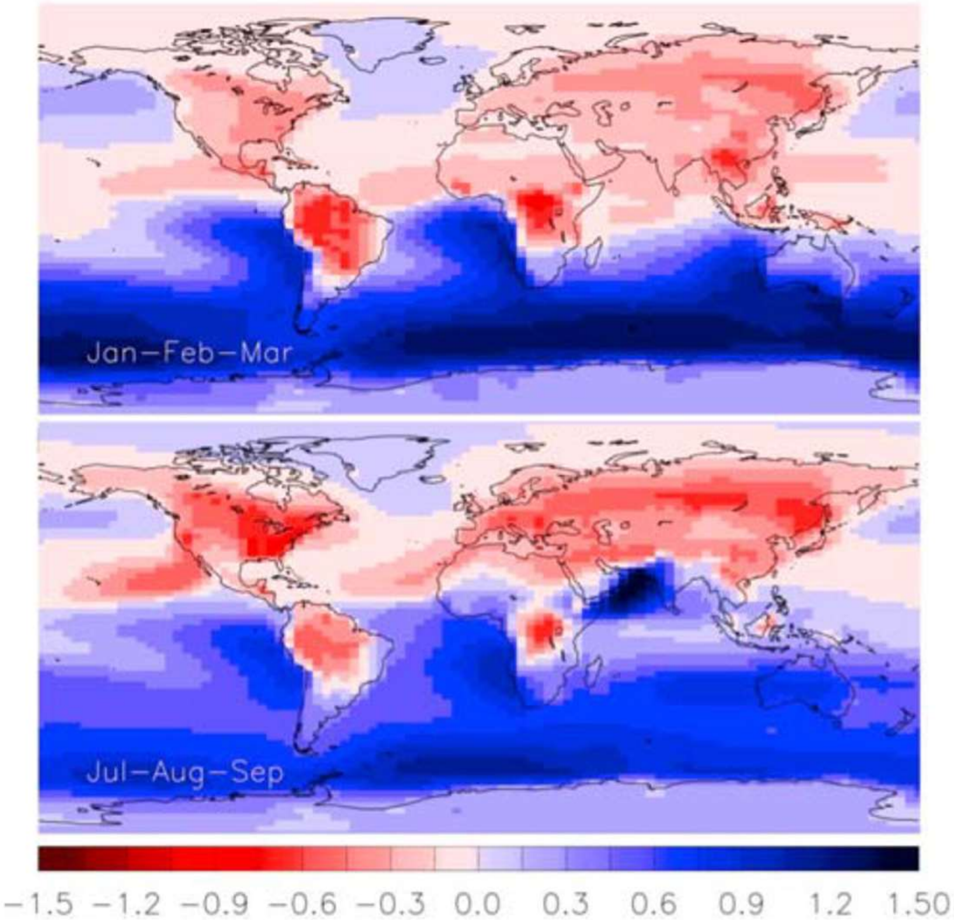
$$\beta = Cs\ (\Delta bg - \Delta s) / (\Delta bg + 1000\ ‰)$$

Simulations from global models suggest β is generally less than 1.5 ppm in magnitude, positive over land and negative over the ocean

Simulations for ~2005

Using air at higher elevation (3.5km) to specify background

Using LMDZ atmospheric model, CASA pulse response functions for respiration, and extrapolating available ocean data

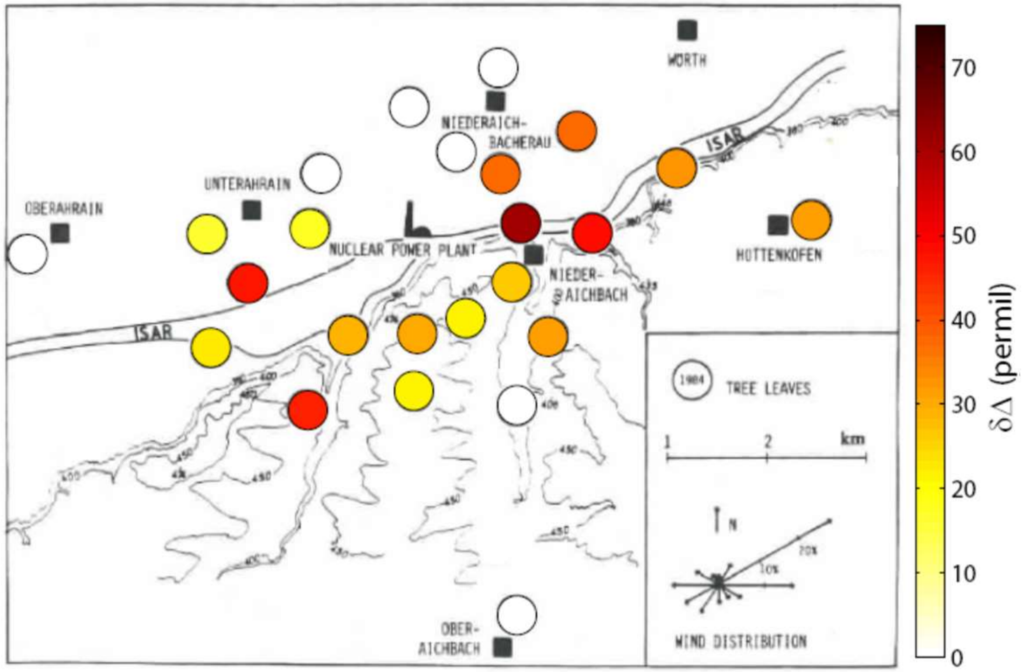


Turnbull et al 2009

^{14}C is produced in nuclear reactors and observations show enhanced $\Delta^{14}C$ in CO_2 near nuclear power plants

^{14}C produced from:

- Nitrogen impurities or oxygen in uranium oxide fuel – can also be released during reprocessing
- Oxygen in coolant water
- Structural material
- Graphite of graphite-moderated reactors
- Cooling gas of gas-cooled reactors

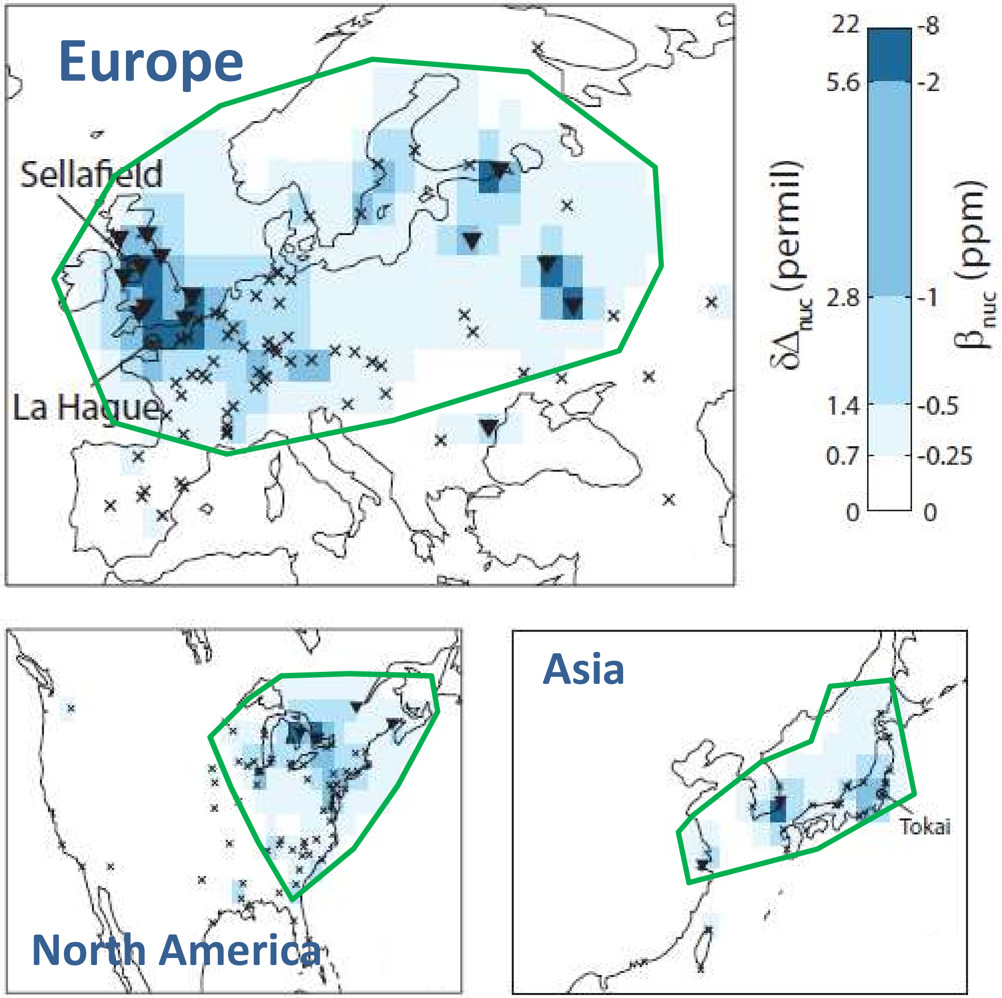


^{14}C emissions are within government limits and occur continually, but can be episodic

Yim and Caron, 2006

Levin et al. Health Physics 1988

Regional $\Delta^{14}C$ gradients from nuclear emissions

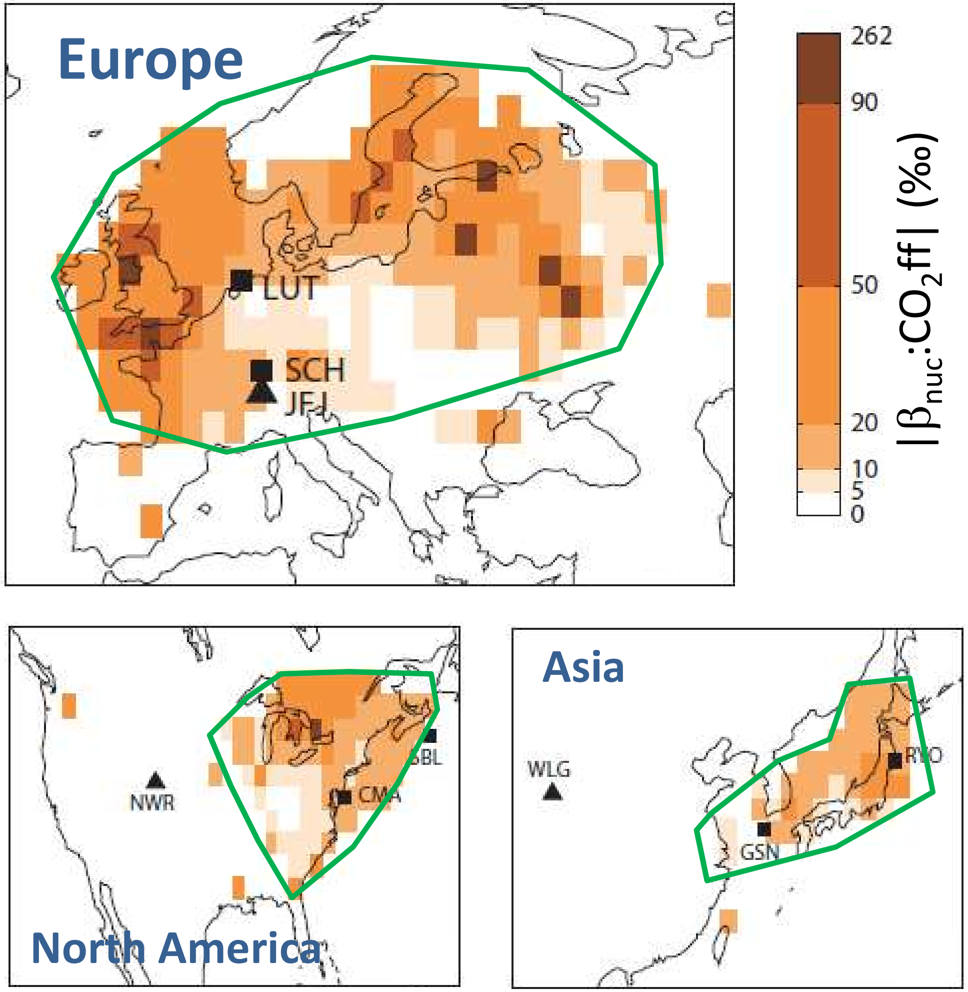


$\Delta^{14}C$ enrichment strongest near fuel reprocessing and high-emission reactor sites in the UK and France

$\Delta^{14}C$ enrichment can extend several hundred kilometers (several model grid cells) away

Simulations for 2005 using the TM3 model at 1.8x1.8° resolution, Graven and Gruber 2011

Counteracting effect of nuclear emissions on Cff



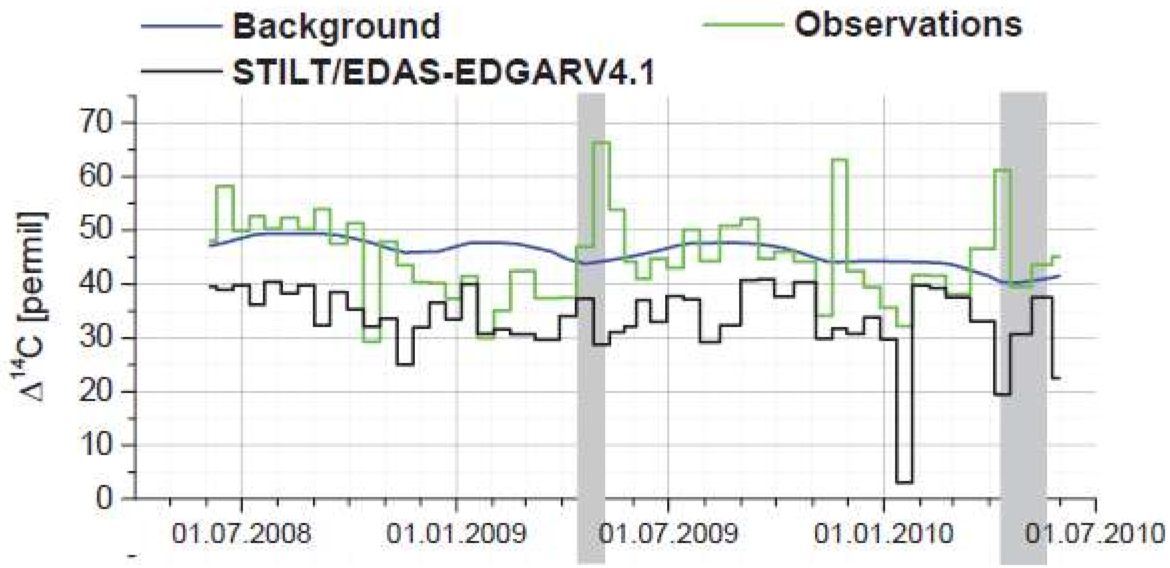
Nuclear $\Delta^{14}C$ enrichment can counteract fossil fuel $\Delta^{14}C$ dilution

Compensates more than 10-20% of fossil influence over large regions

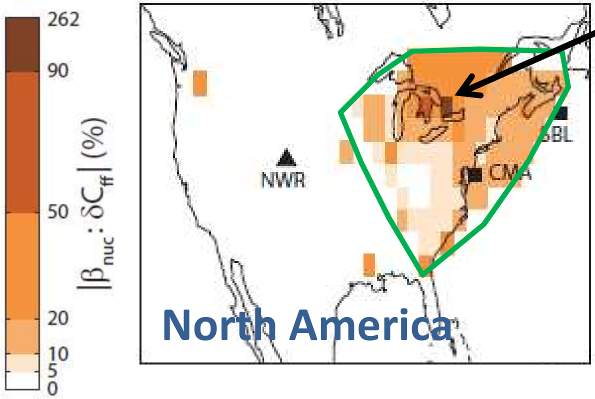
Strongest nuclear $\Delta^{14}C$ enrichment can compensate more than 50% of fossil fuel dilution

Simulations for 2005 using the TM3 model at 1.8x1.8° resolution, Graven and Gruber 2011

Predicted large-scale effect of nuclear power emissions has been observed in Ontario, Canada



Egbert site near Toronto
3 HWR "CANDU" reactors



Vogel et al. 2013

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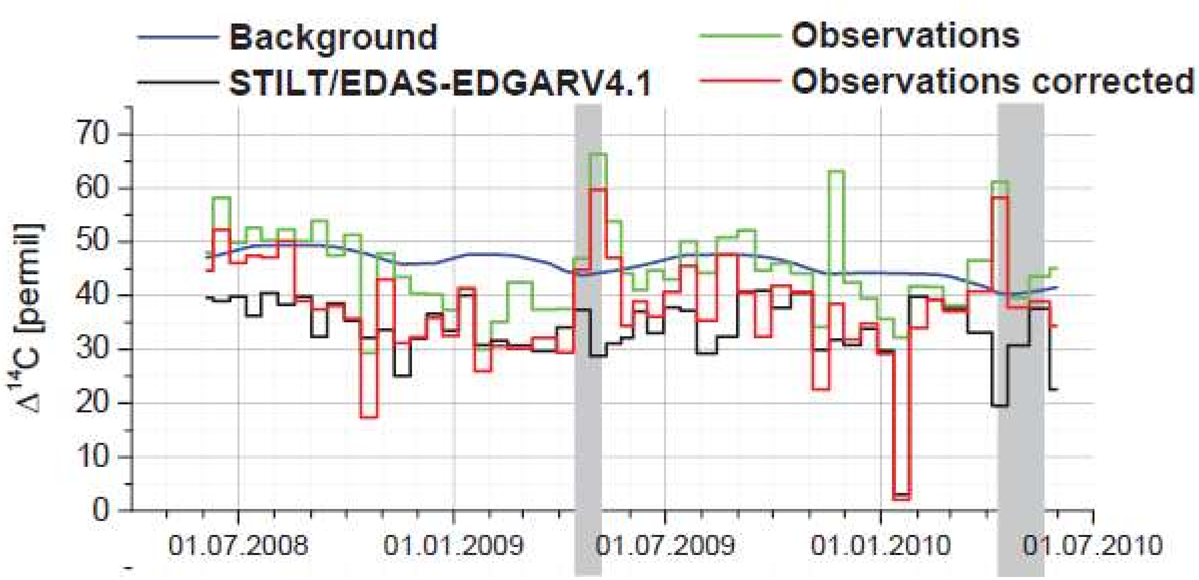
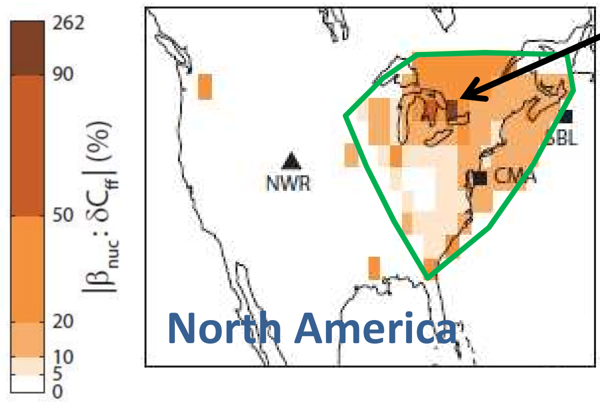


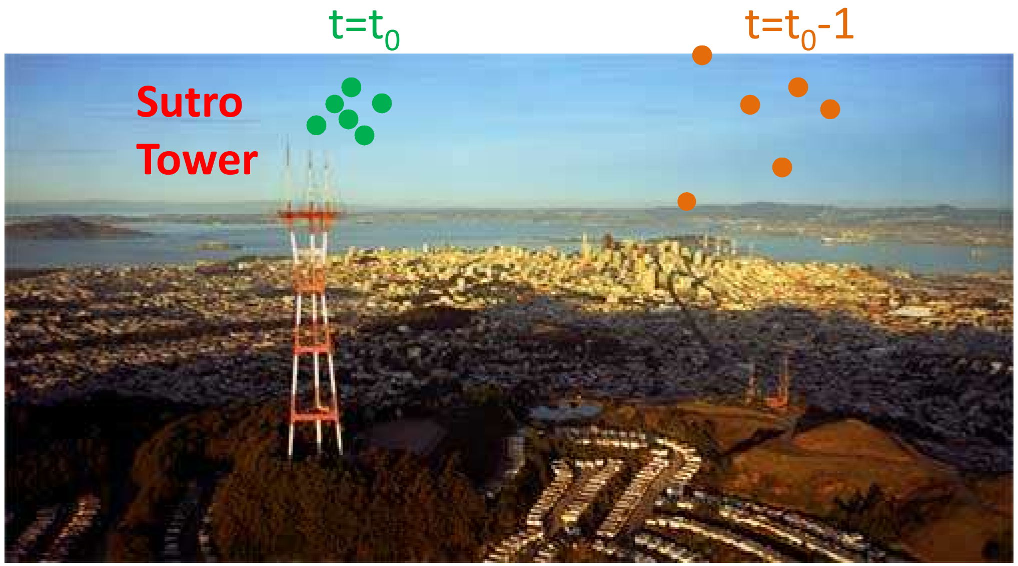
Gray bars:
Maintenance periods

Egbert site near Toronto
3 HWR "CANDU" reactors



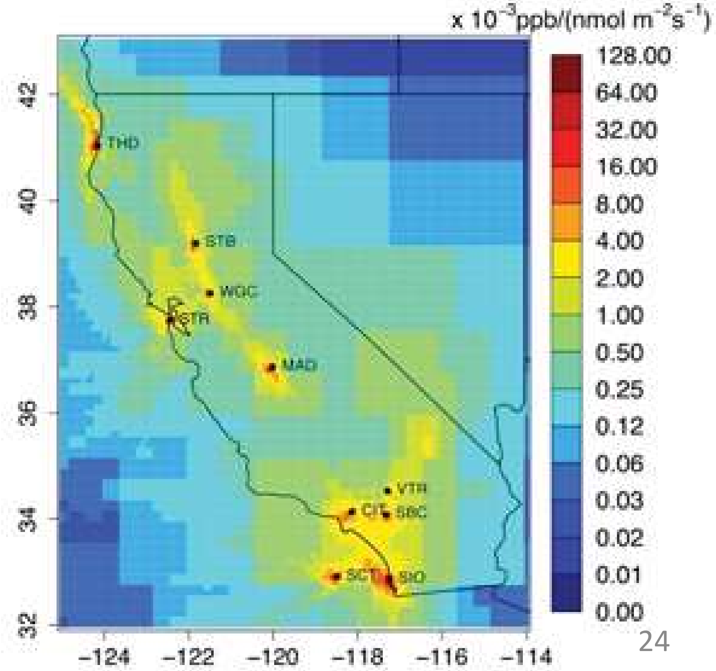
Vogel et al. 2013

Atmospheric transport modelling is needed to connect atmospheric concentrations to emissions



Using meteorological fields from the regional atmospheric model to calculate back trajectories of particles, e.g. Lagrangian particle dispersion modelling with the WRF-STILT model

Concentration/Flux



“Footprints” mapping the influence on observations – composite for California network

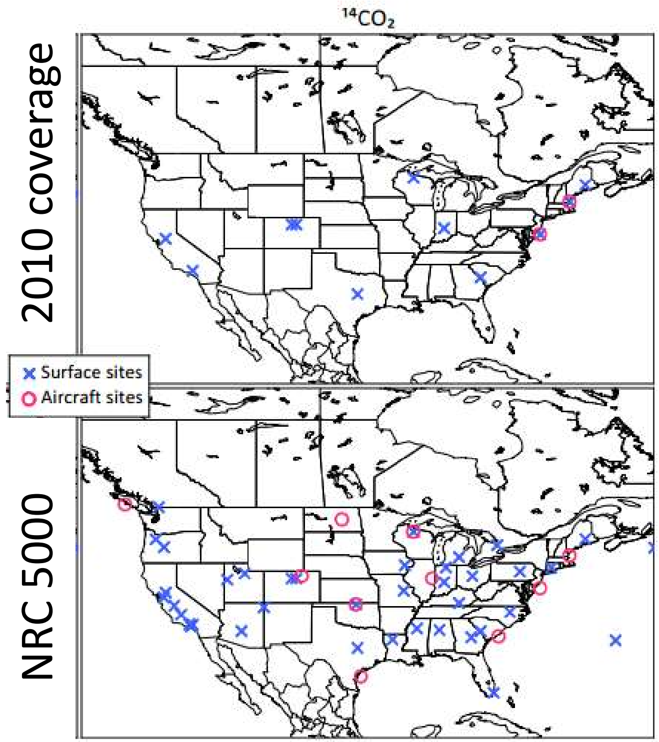
Combine with flux maps in Bayesian inversion to produce “top-down” estimate of emissions

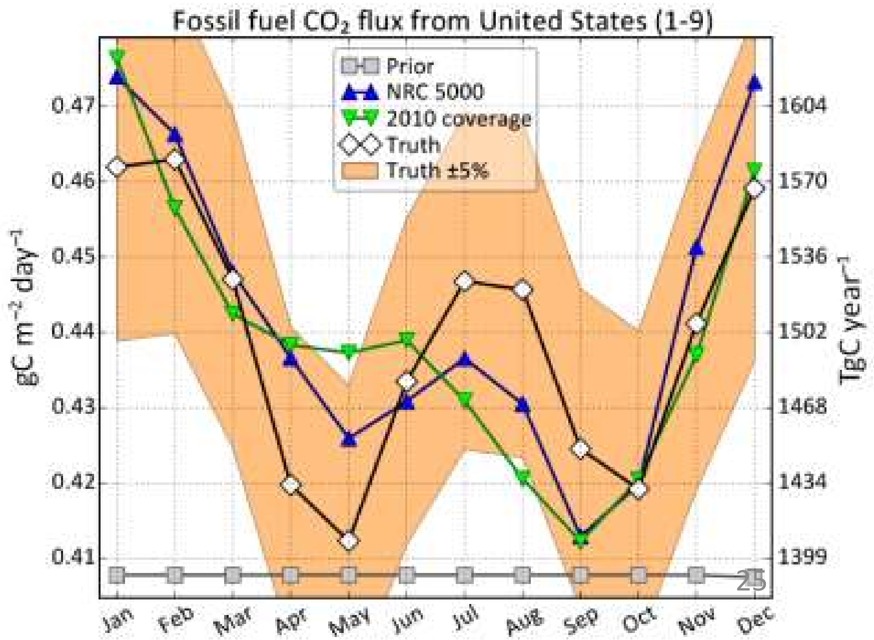
Observing System Simulation Experiments (OSSEs) show promise for validating regional emissions estimates

Basu et al. 2016 incorporated ^{14}C into the NOAA CarbonTracker inversion system

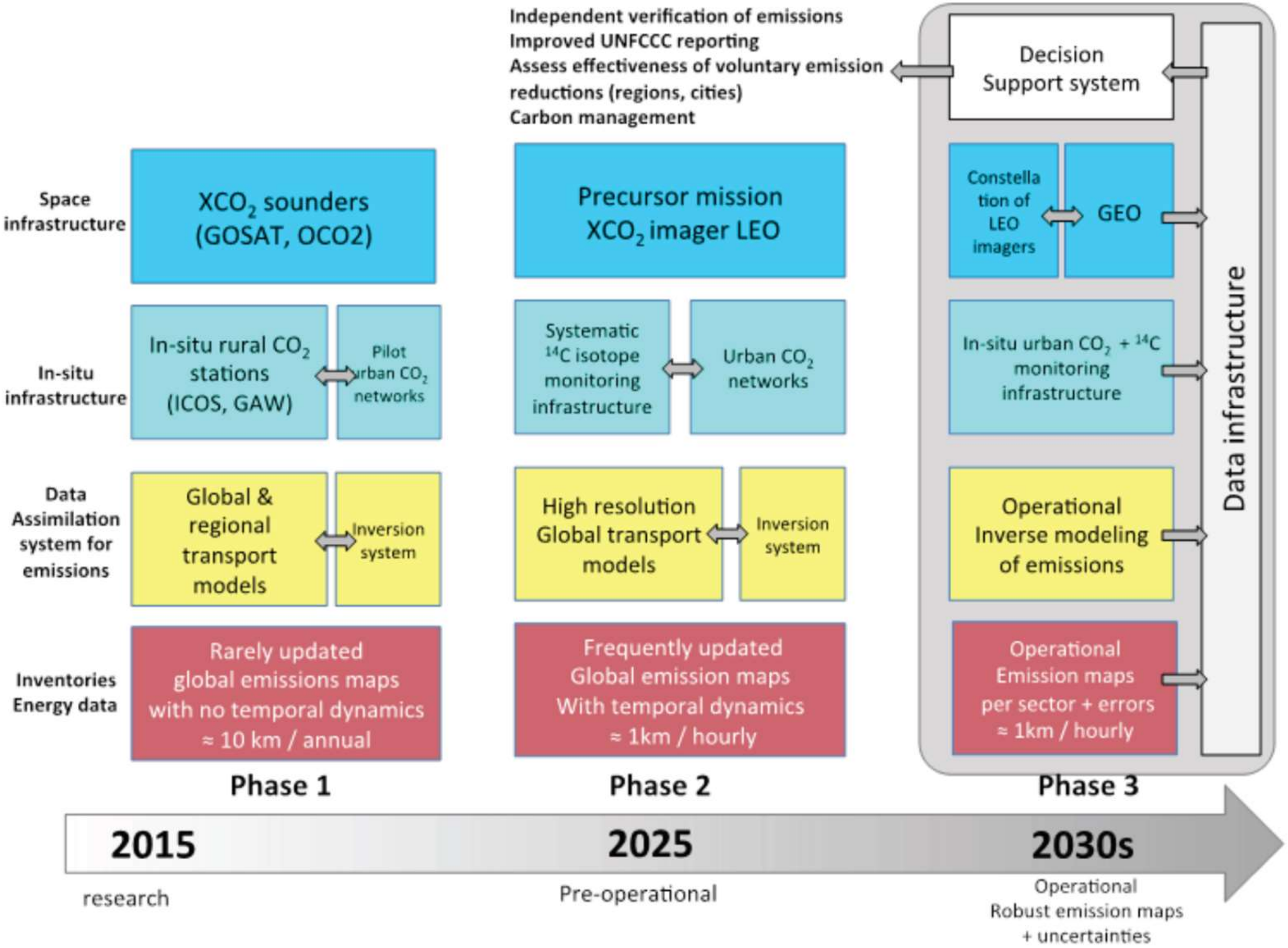
OSSEs indicate that $\Delta^{14}C$ observations can be used to estimate fossil fuel emissions

They also improve estimates of biospheric fluxes by eliminating potential biases from bottom-up fossil fuel emission estimates





Ambitious proposal in Europe to incorporate ^{14}C into a fossil fuel emission monitoring system



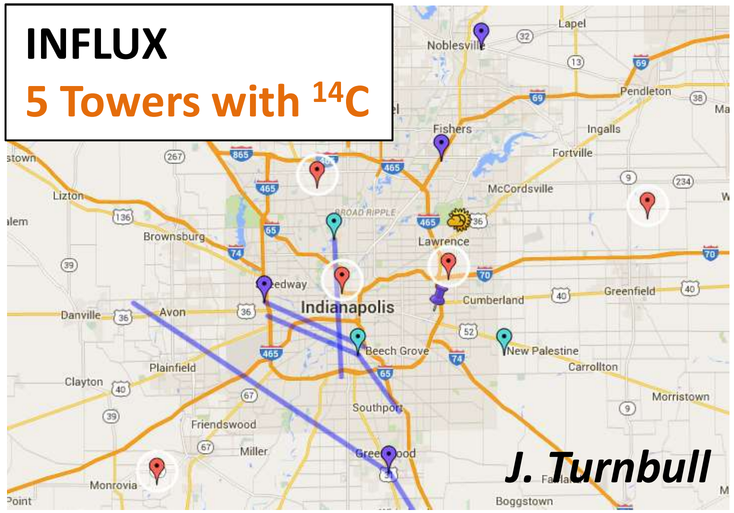
Ciais et al. “Towards a European Operational Observing System to Monitor Fossil CO_2 emissions” 2015

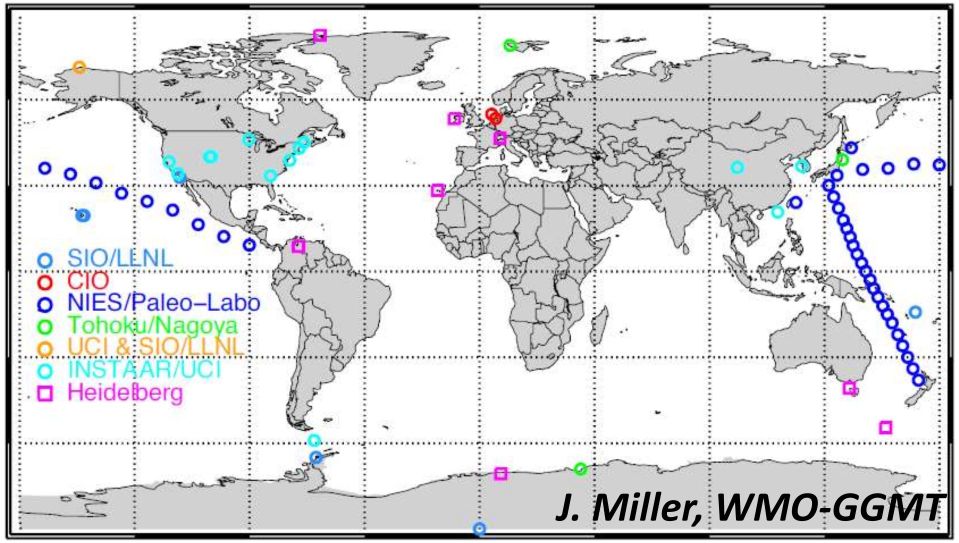
Challenges to using $\Delta^{14}C$ as a fossil fuel tracer

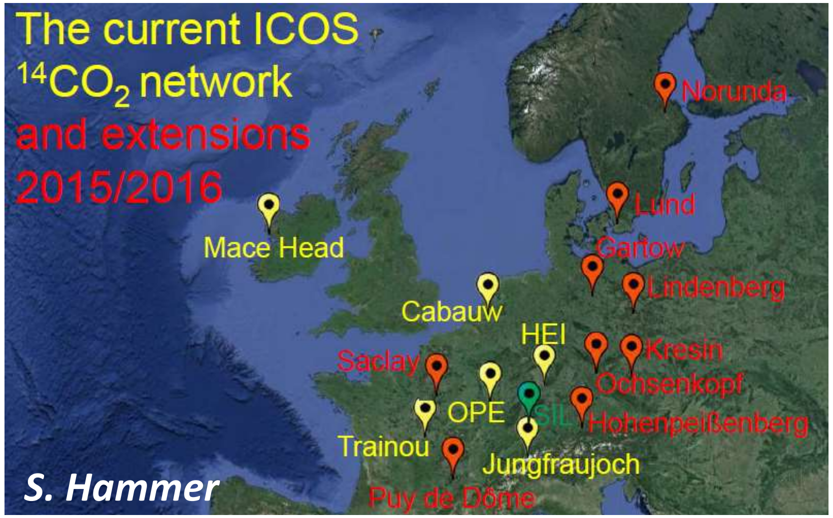
- Lack of atmospheric $\Delta^{14}C$ data
- Measurement uncertainty
- Background uncertainty
- Uncertainty and lack of data on non-fossil influences on $\Delta^{14}C$ (β)
  - Respiration
  - Nuclear power plants
- Atmospheric transport uncertainty

Observational networks for $\Delta^{14}C$ in CO_2

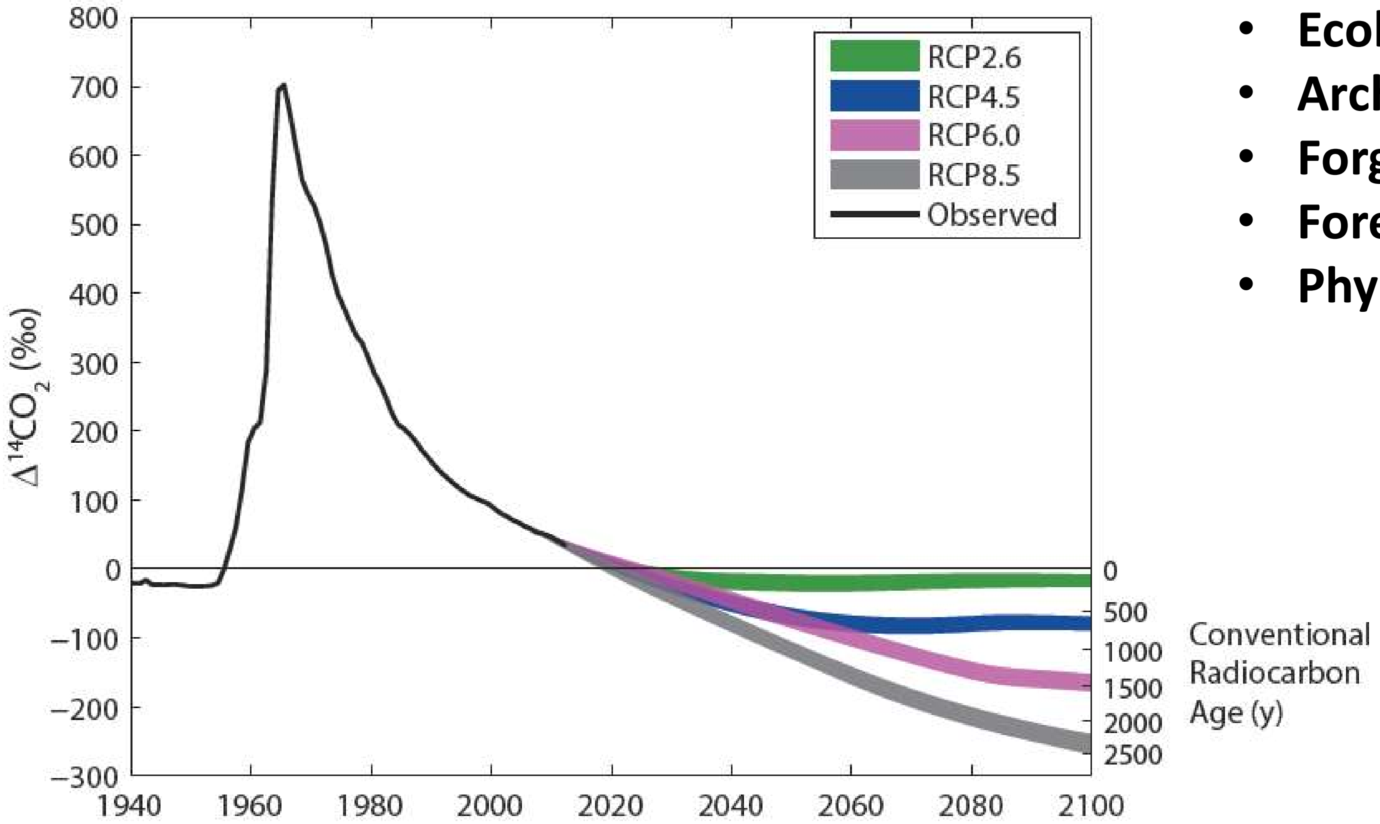
- **Global networks exist, but some sites are discontinued**
- **Recent expansion to urban / polluted sites**
- **More sustained and coordinated observations needed**







Forthcoming changes in $\Delta^{14}CO_2$ have implications for various applications of ^{14}C



- **Ecology**
- **Archaeology**
- **Forgery detection**
- **Forensics**
- **Physiology**

Graven, PNAS, 2015

Sensitivity to fossil fuel CO_2 is decreasing, necessitating higher precision measurements

Sensitivity: (Δm – Δbg)/Cff ≈ - (Δbg + 1000 ‰)/Cm

Currently -2.6 ‰ ppm^{-1}

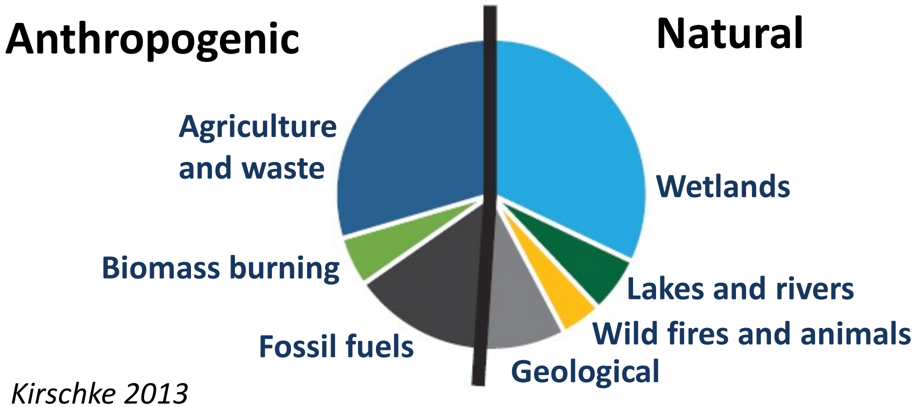
For RCP8.5
in 2050: -1.6 ‰ ppm^{-1}
in 2100: -0.8 ‰ ppm^{-1}

Radiocarbon in atmospheric methane

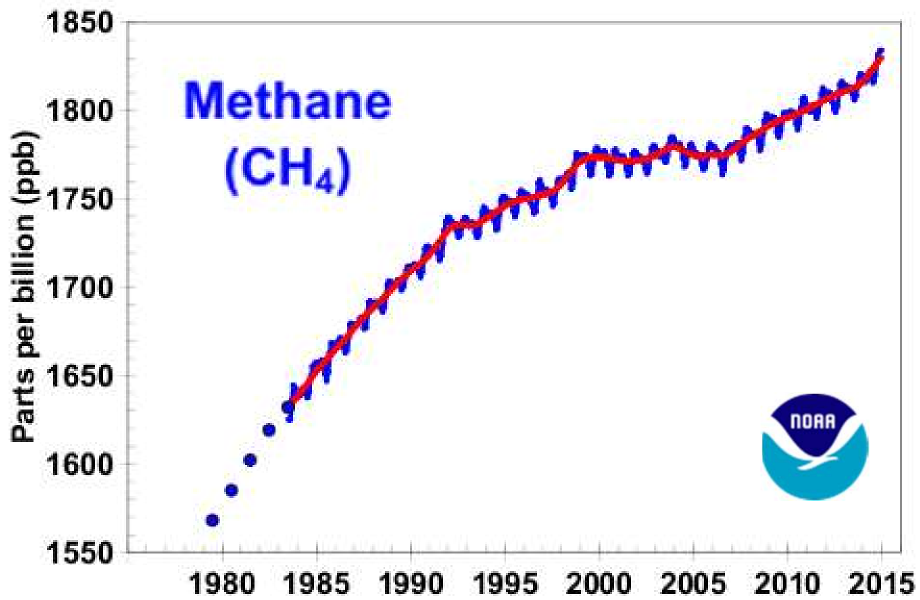
Atmospheric CH_4 concentration has more than doubled since the preindustrial period (~700 ppb)

Global "bottom-up" and "top-down" estimates of emissions have large discrepancies

Recent variations in the CH_4 growth rate are not yet explained



Kirschke 2013

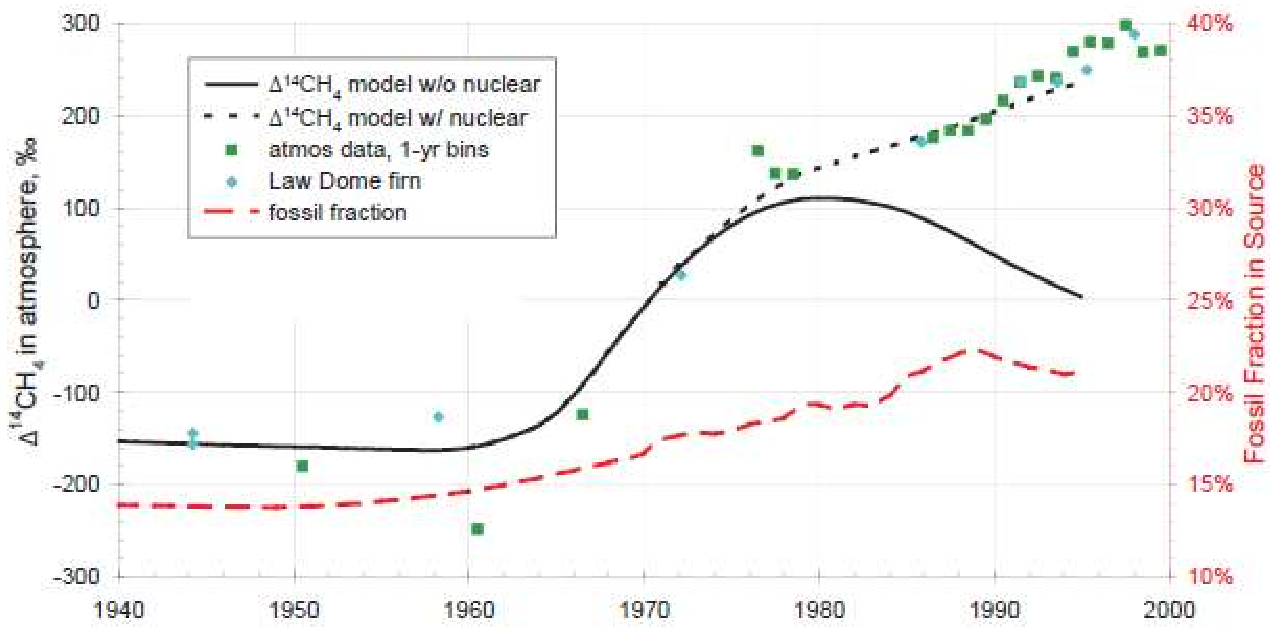


Radiocarbon in atmospheric methane provides a primary constraint on the fossil fraction of emissions

Fossil sources of CH_4 have Δff = -1000 ‰

Biogenic sources of CH_4 track the $\Delta^{14}C$ changes in atmospheric CO_2, incorporating the turnover time of the substrate

However, nuclear power plant emissions of $^{14}CH_4$ are relatively more important for $\Delta^{14}CH_4$ than for $\Delta^{14}CO_2$



Lassey et al. 2007

Summary

$\Delta^{14}C$ is a powerful tracer of fossil carbon for CO_2, also for CH_4 and aerosols

Applications using atmospheric measurements to observe Cff are actively being developed, some combining measurements with atmospheric models to estimate emissions

Challenges include lack of data, measurement uncertainty, uncertainty in background and other influences on $\Delta^{14}C$

Sensitivity to Cff is decreasing as atmospheric $\Delta^{14}CO_2$ decreases and CO_2 concentration increases