Methane and other trace gases: NIWA measurements

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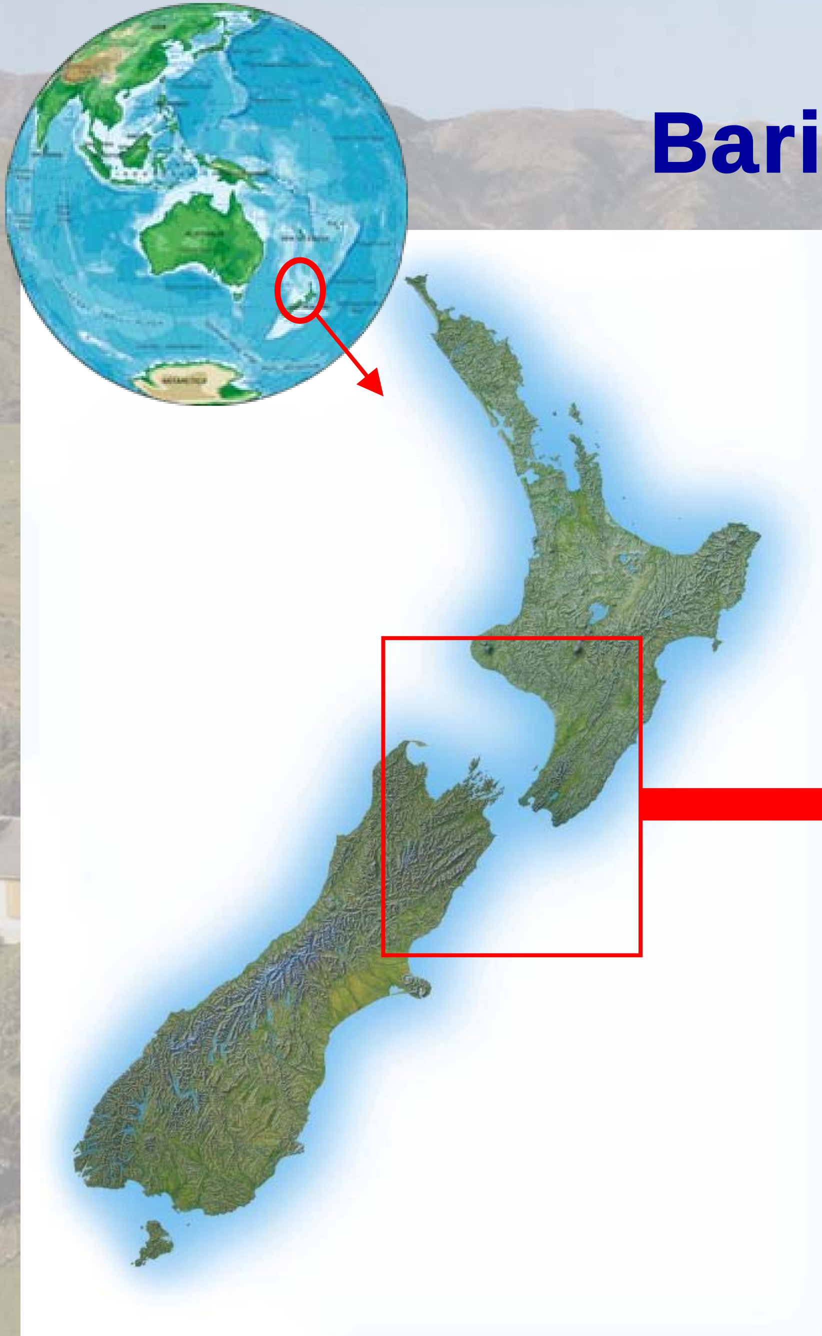
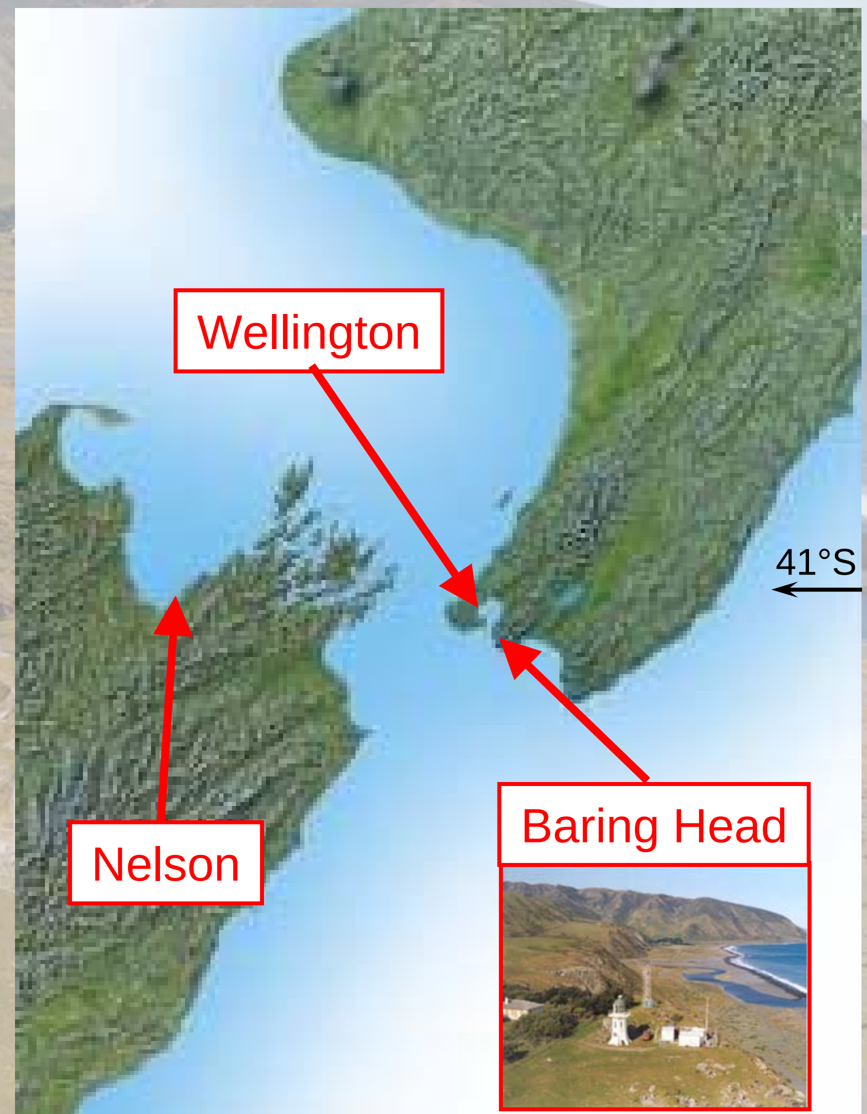
Trace gas sampling programme

- **Baseline levels of trace gases at Baring Head, Wellington:**
  - **CO_2 (since 1972), CH_4 (since 1989), CO (since 1989), N_2O (since 1996), O_2/N_2 (since 1999)**
  - **^{13}C, ^{14}C in above, and ^{18}O in some of above**
- **Baseline levels of some gases/isotopes at Scott Base, Antarctica**
- **Trace gases/isotopes in shipboard air samples (NZ to Japan), since May 2004**
- **pCO_2, etc, in sub-Antarctic surface water**

Baring Head

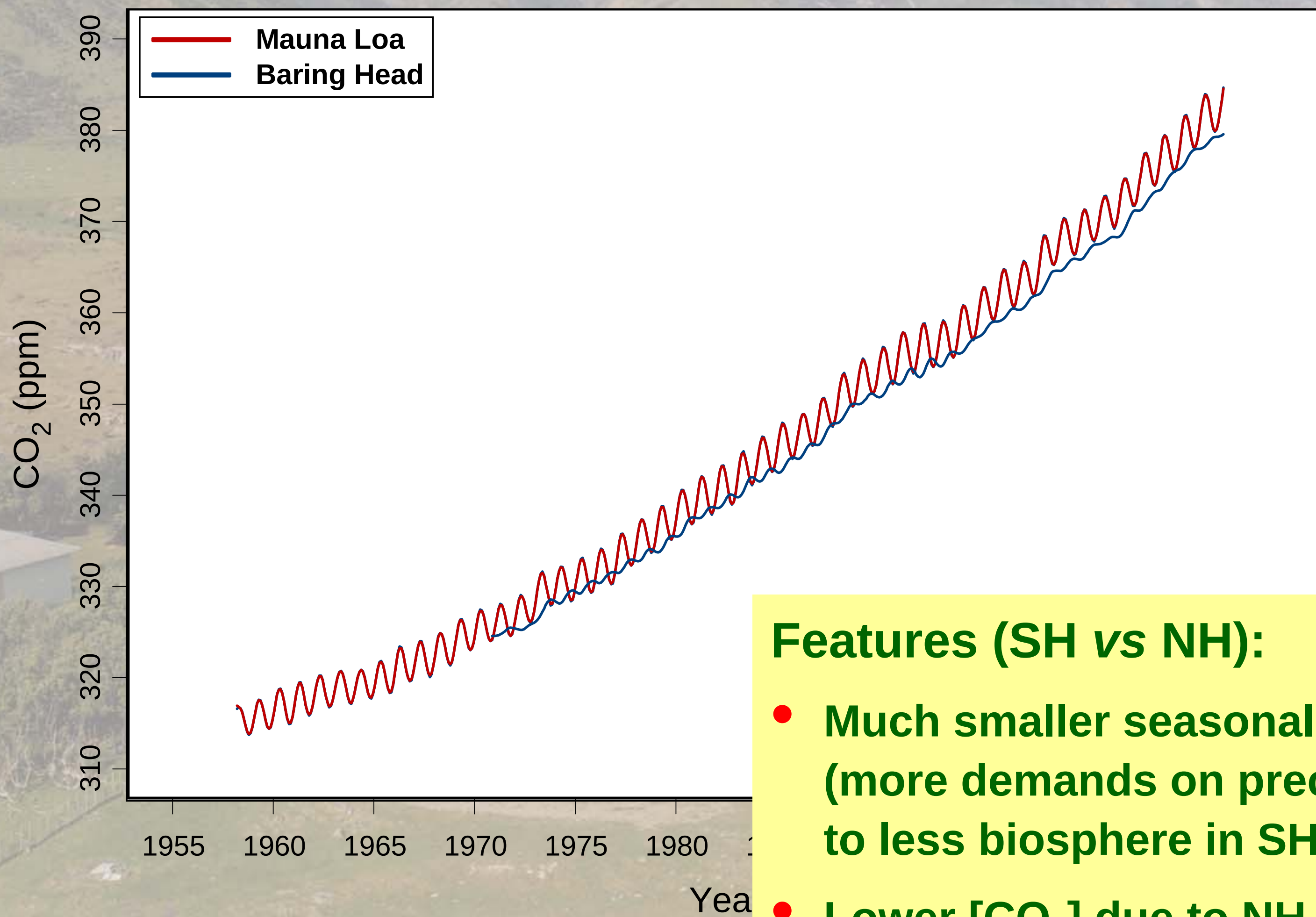




Baring Head CO_2

- monitoring commenced in Dec 1972 in cooperation with C.D. Keeling, Scripps
- measured continuously in situ by NDIR
- longest-running continuous station in SH, next longest in world after Mauna Loa
- inter-calibrated with Scripps & NOAA
- complemented in 1998 by $\delta^{13}C$ measurements (continuous flow: D. F. Ferretti)
- complemented in 1999 by O_2 measurements (paramagnetic analyser: A. C. Manning)

Baring Head & Mauna Loa CO_2



Features (SH *vs* NH):

- Much smaller seasonal amplitude (more demands on precision) due to less biosphere in SH
- Lower [CO_2] due to NH-dominated anthropogenic sources

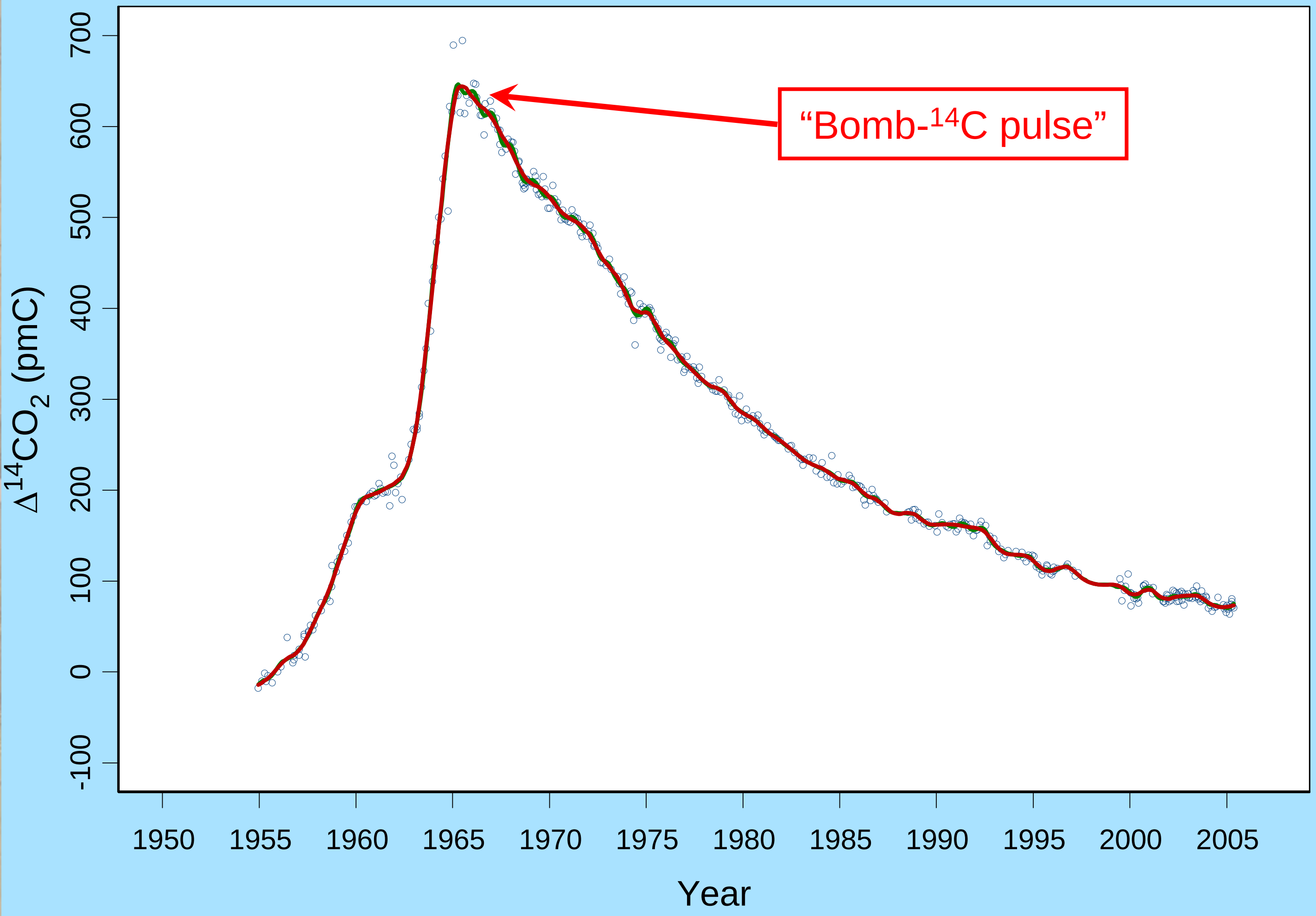
Acknowledgement: Scripps I

Baring Head CO_2

- **Dataset largely under-utilised in global carbon-cycle studies**
- **Data (not just CO_2) submitted to World Data Centre for Greenhouse Gases (Tokyo)**
- **Reported strongly in IPCC 4th Assessment Report (Dave Lowe, Lead Author, Chapter 2)**
- **Data used in recent study of the Southern Ocean as a CO_2 sink [Le Quéré et al., 2007]**

Le Quéré, C. et al. (2007). *Science 316*: 1735–1738.

Baring Head $^{14}CO_2$

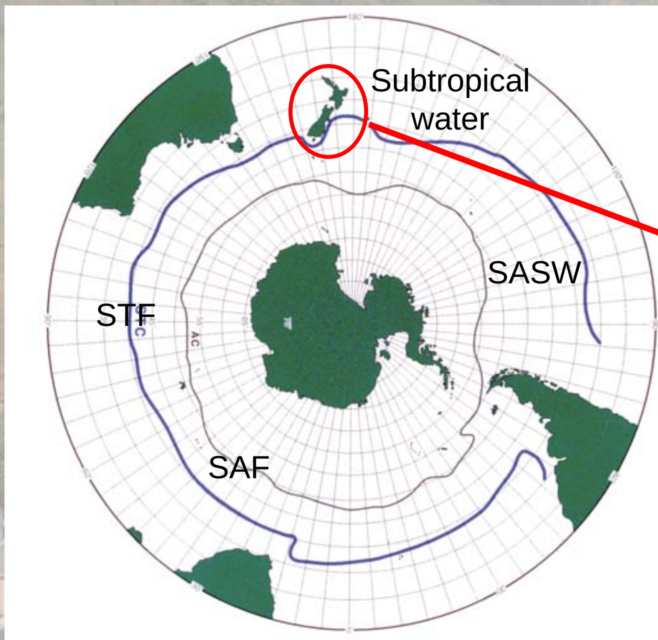


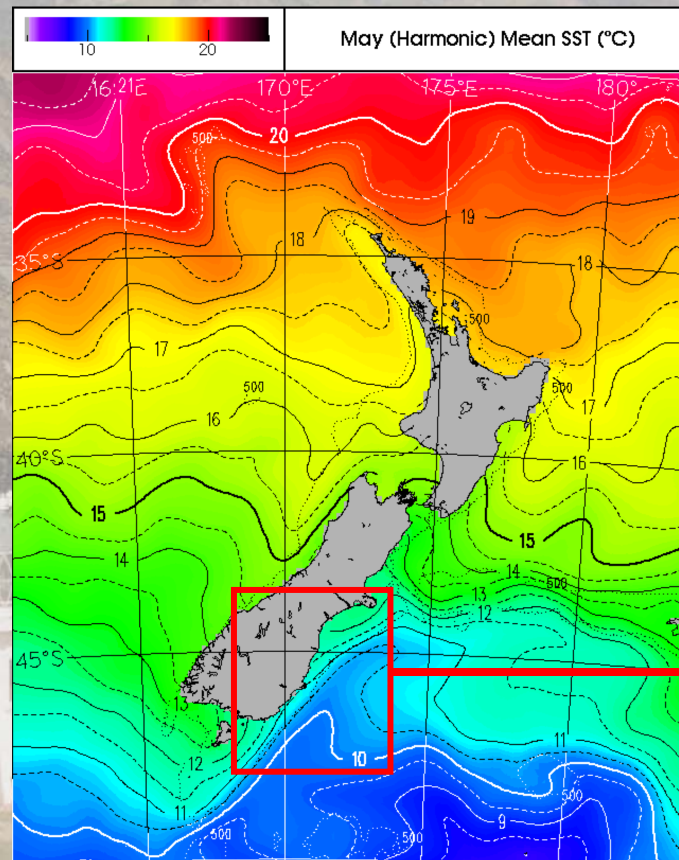
Baring Head $\Delta^{14}CO_2$

- **Visionary commencement of measurements, pre-dating the "bomb-^{14}C pulse"**
- **Near-unique and valuable dataset:**
  - **long-term evolution of $\Delta^{14}CO_2$ critical to carbon-dating calibration [eg, Hua & Barbetti, 2004]**
  - **response of C reservoirs to bomb-^{14}C injection pivotal to understanding C-cycling [eg, Lassey et al., 1996; Peacock, 2004]**

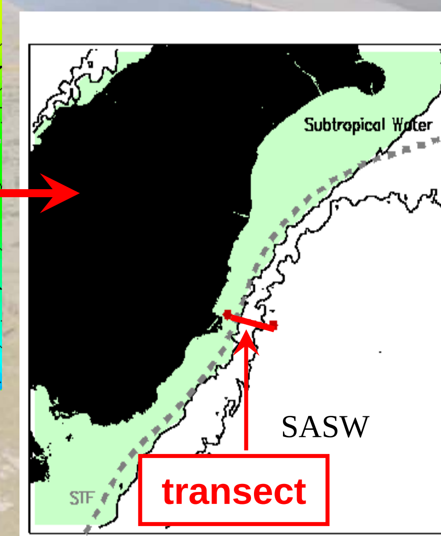
Hua, Q.; Barbetti, M. (2004). *Radiocarbon 46*: 1273–1298.
Lassey, K.R. et al. (1996). *Tellus 48B*: 487–501.
Peacock, S. (2004). *GBC 18*: GB2022,

pCO_2 time series along a sub-Antarctic surface transect





May SSTs



Attribution: Work of Kim Currie et al.

pCO_2 time series along a sub-Antarctic surface transect

‘Munida’ time series since 1998, led by Kim Currie

Measurements of:

- temperature
- salinity
- pCO2
- pH
- alkalinity
- etc

bi-monthly since 1998

RV Polaris
(Munida replacement)

SASW Seasonal Cycles

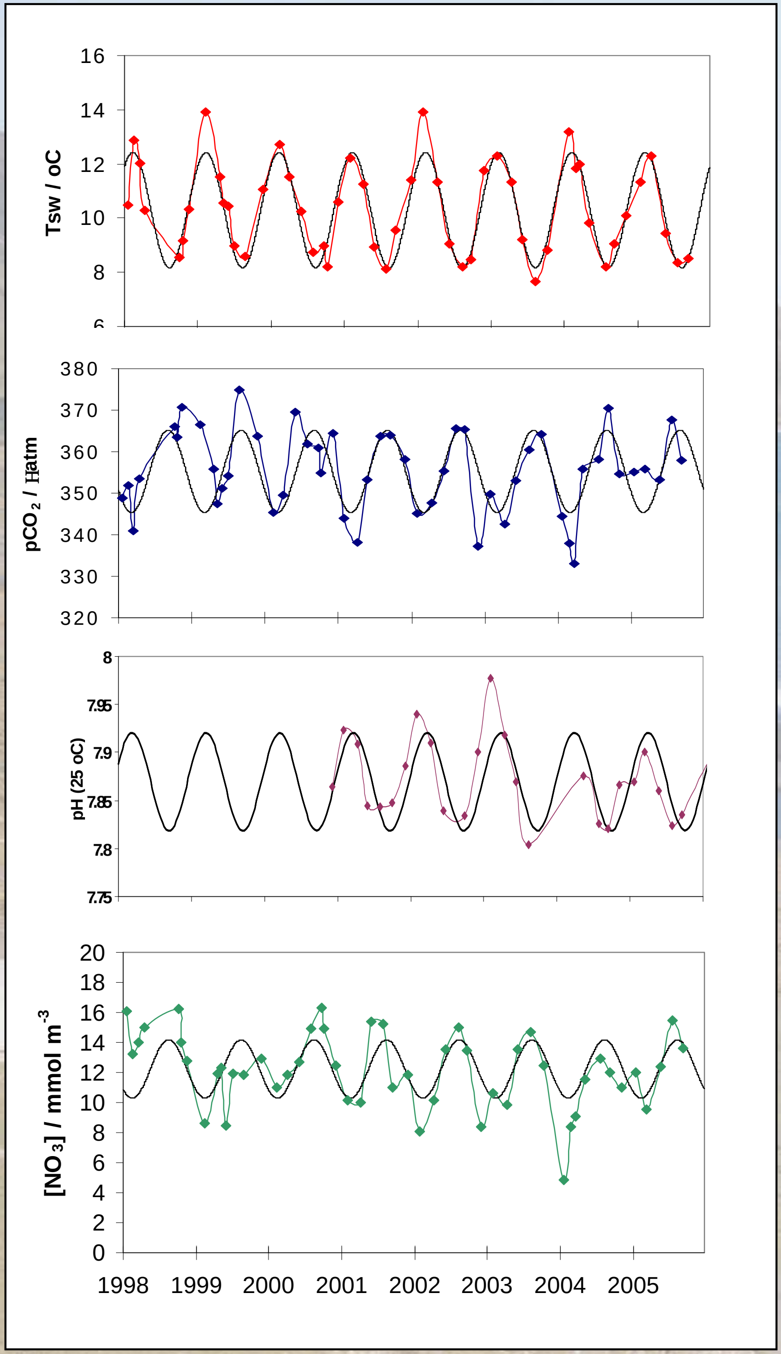
No indication of a trend!

$$T = 10.3 + 2.1\sin\left(2\pi\frac{t-317}{365}\right)$$

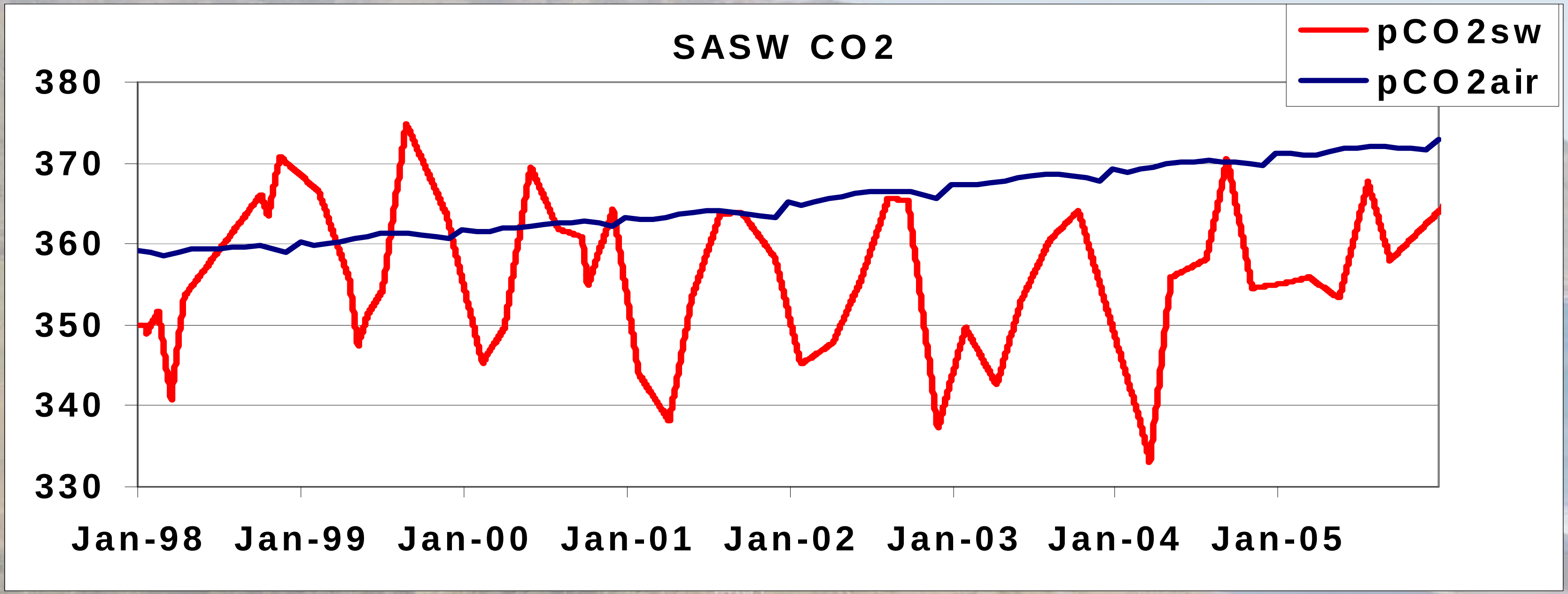
$$pCO_2 = 355 + 10\sin\left(2\pi\frac{t-156}{365}\right)$$

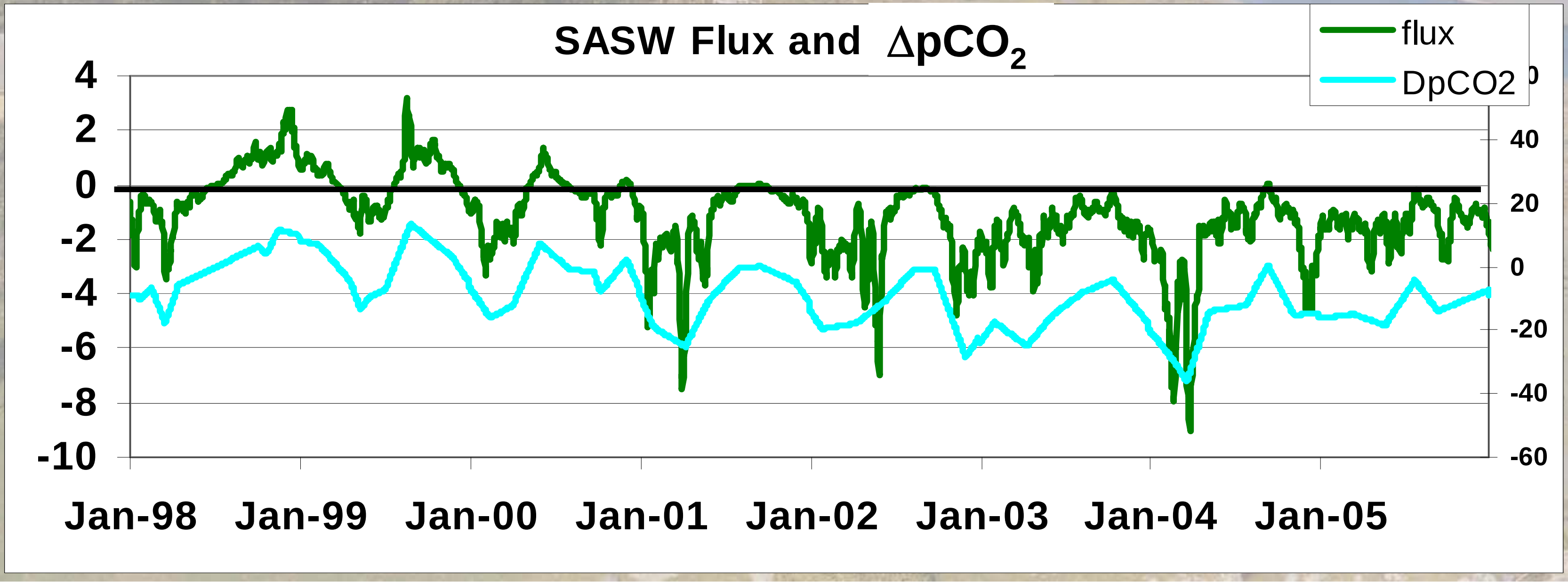
$$pH = 7.869 + 0.05\sin\left(2\pi\frac{t-162}{365}\right)$$

$$NO_3 = 12.2 + 1.9\sin\left(2\pi\frac{t-138}{365}\right)$$



SASW Air-Sea flux of CO_2

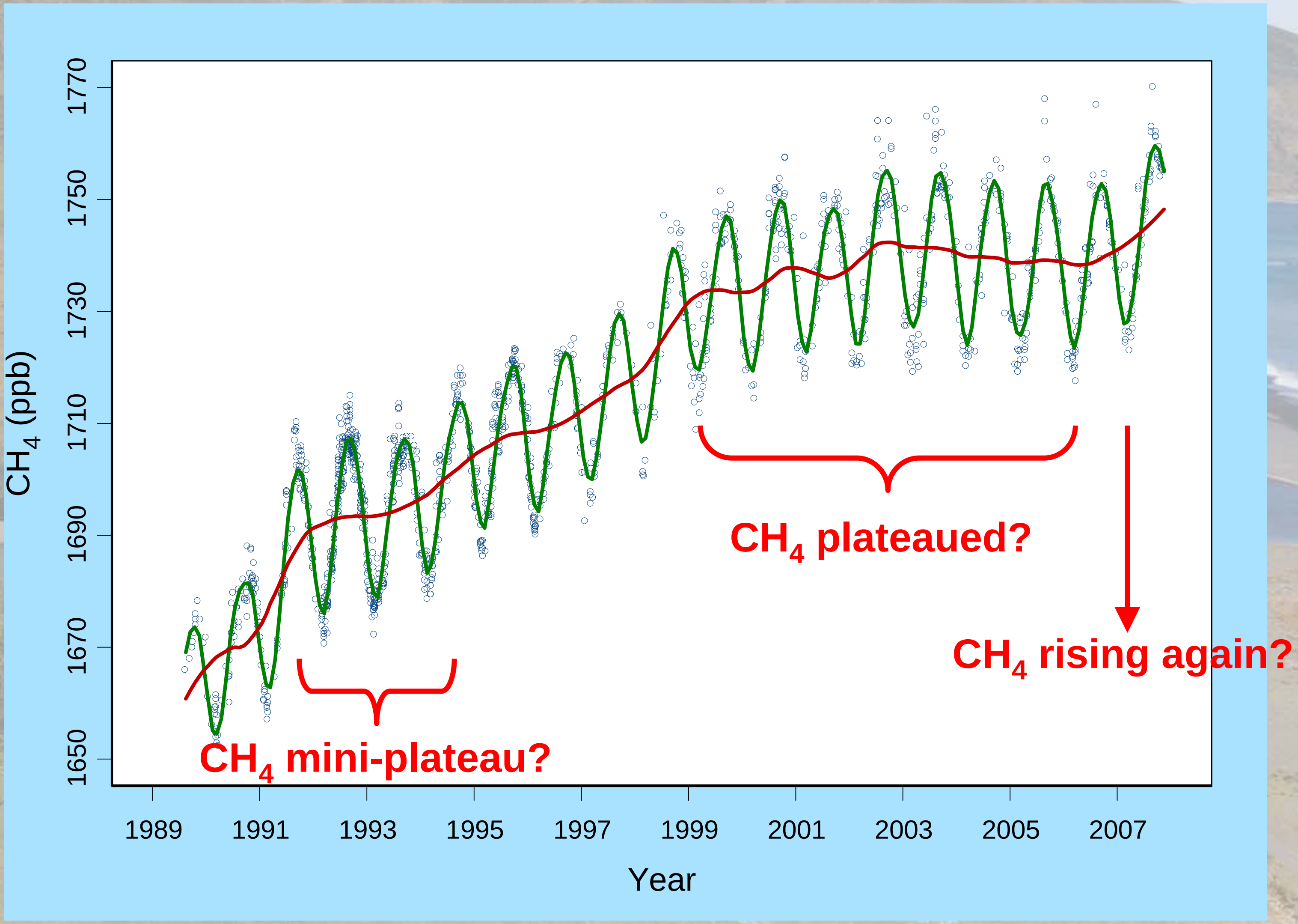




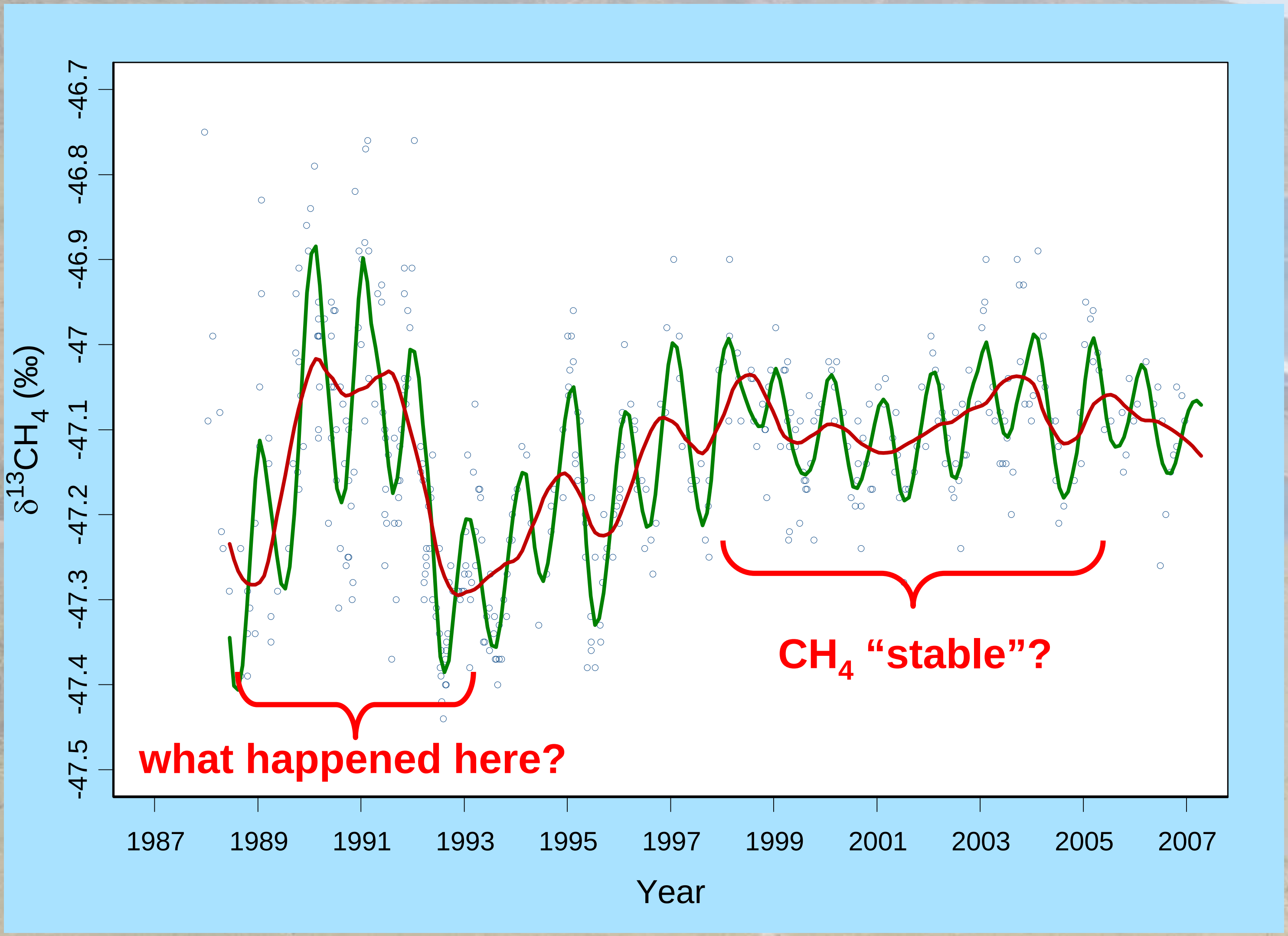
Baring Head CH_4 and $\delta^{13}C(CH_4)$

- monitoring of $\delta^{13}C(CH_4)$ commenced in 1987; $[CH_4]$ commenced in 1989
- $[CH_4]$ measured by GC/FID, $\delta^{13}C(CH_4)$ by IRMS, on grab samples
- inter-calibrated with recognised standards
- $[CH_4]$ complements NOAA record; $\delta^{13}C(CH_4)$ arguably the best record globally

Baring Head CH_4

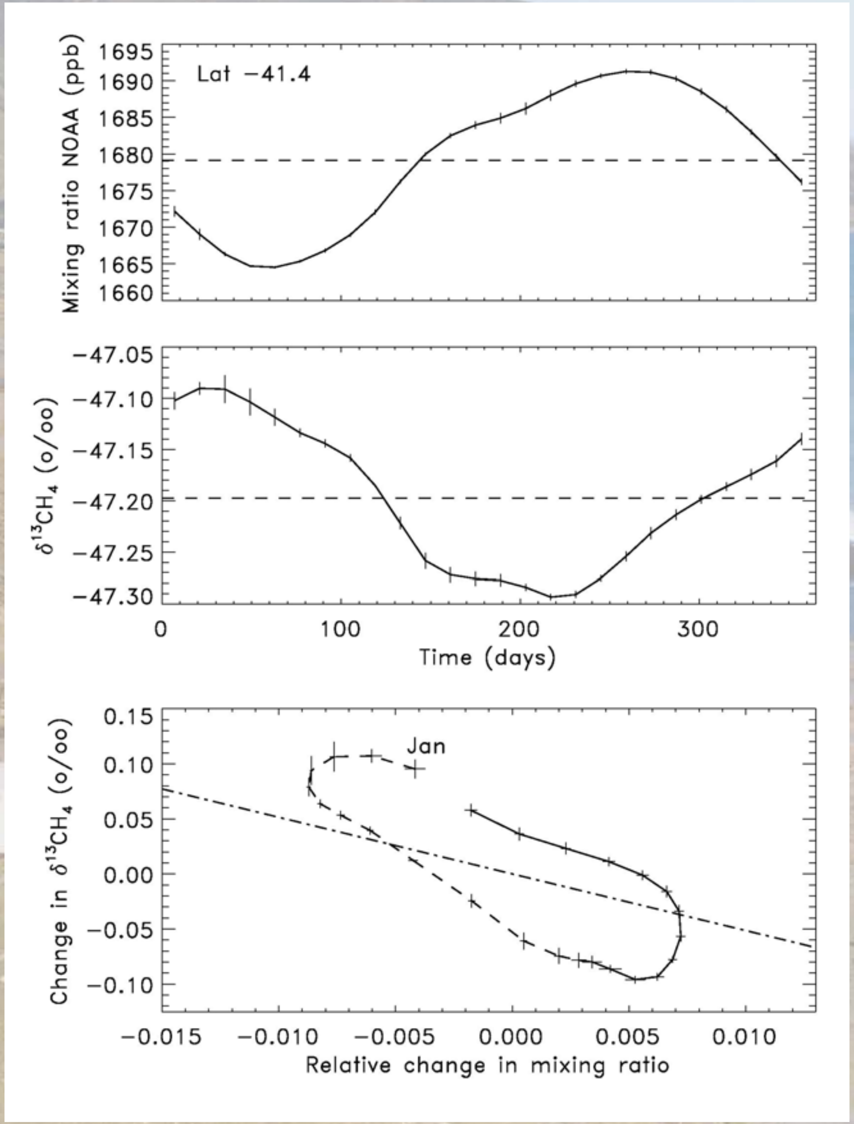


Baring Head $\delta^{13}C(CH_4)$



An important chlorine sink for CH_4?

- **Upper plot:**
  - composite seasonality of $[CH_4]$
- **Centre plot**
  - composite seasonality of $\delta^{13}CH_4$
- **Lower plot:**
  - $[CH_4]$ *vs* $\delta^{13}CH_4$: “phase ellipse”
  - Slope of ellipse axis determined by isotope fractionation in sink
  - Dash-dot line corresponds to ‘accepted’ fractionation of 5.4‰
  - Actual slope ⇒ fraction’n ~13‰



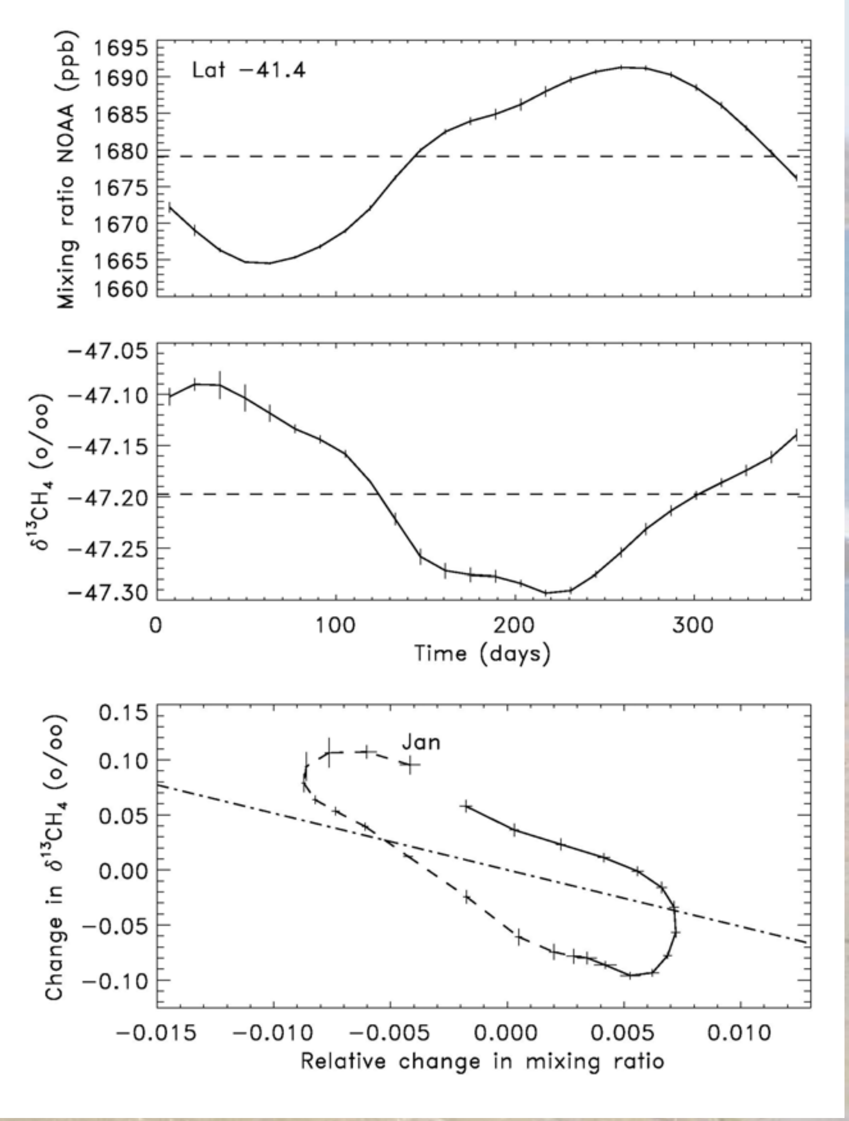
Source: Allan et al. (2001)

📖 Allan, W. et al. (2001). *GBC 15*: 467-481.

📖 Allan, W. et al. (2007). *JGR 112*: D04306.

An important chlorine sink for CH_4?

- **Why is sink fractionation as high as ~13‰? (OH sink has fractionation ~5.4‰ or less)**
- **Likely answer: role by active Cl (fractionation ~60‰)**
- **Allan et al. (2007) argue that a Cl sink that removes 13–37 $TgCH_4$/yr globally can account for observations**
- **Cl sink absent from current global budgets**



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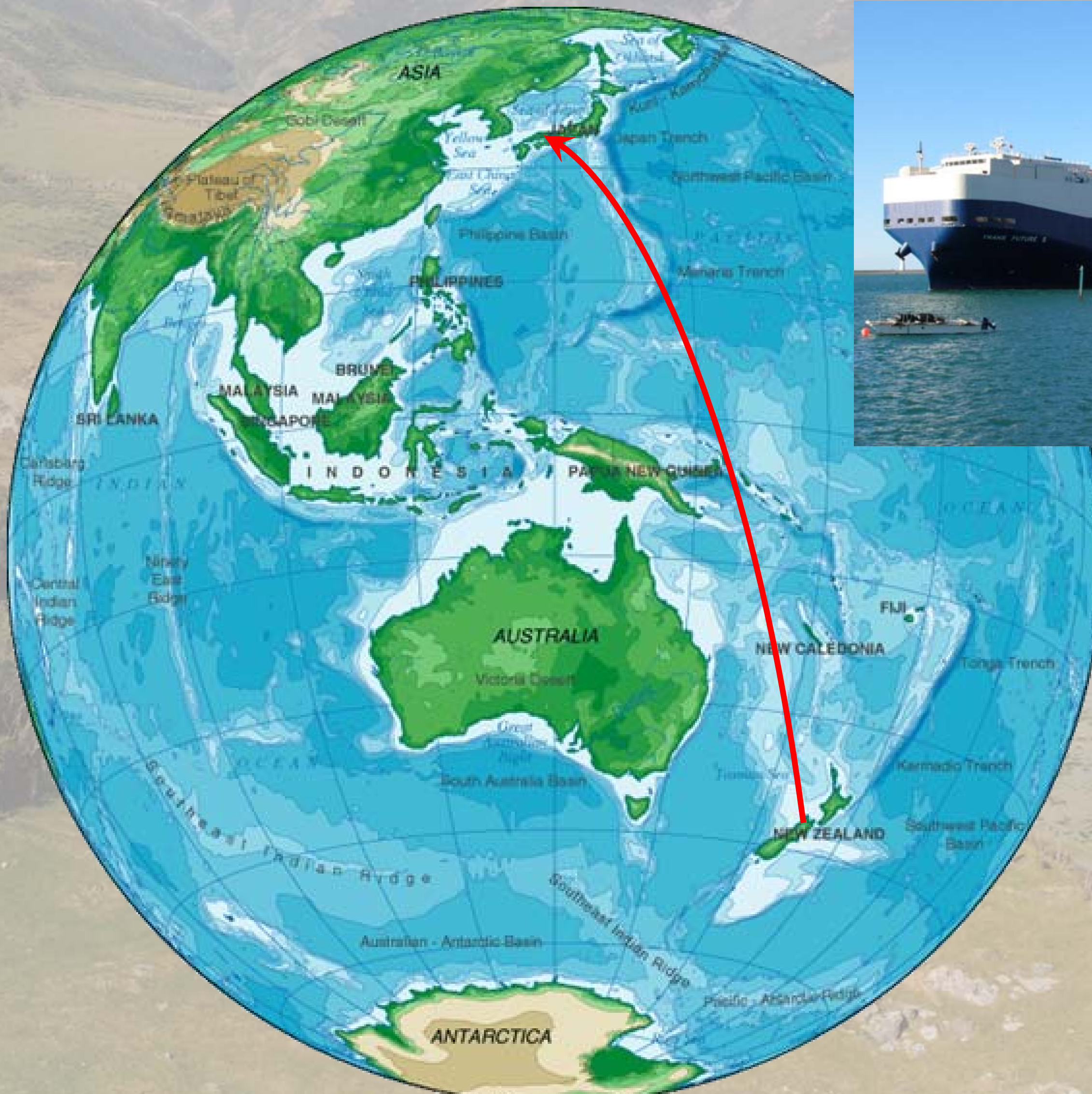
Ship voyages, Nelson (NZ) to Osaka

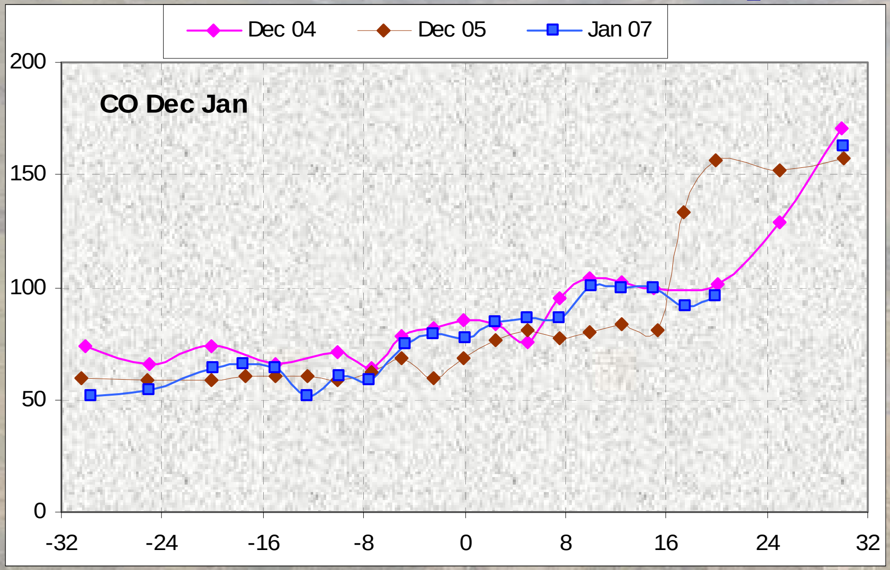


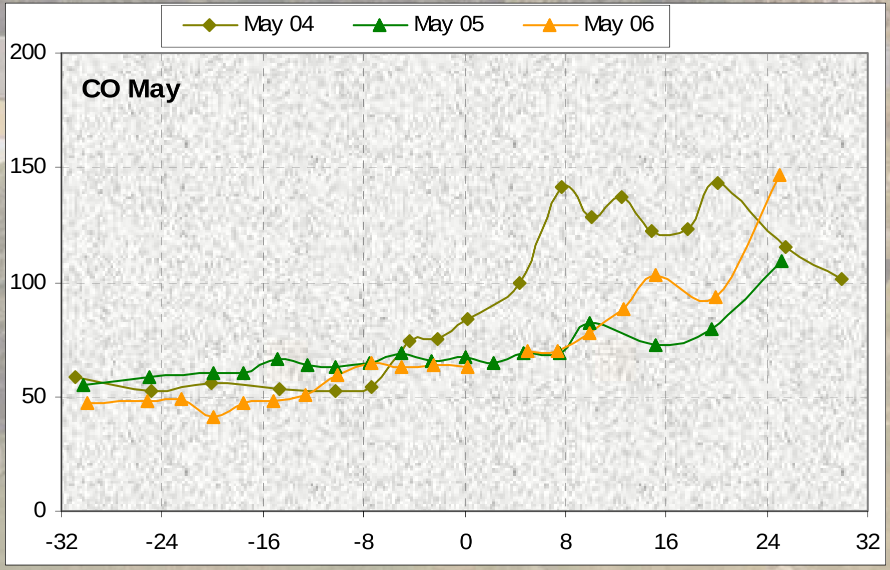
Shipboard measurements

- transect: 41.3°S, 174.3°E to 34.7°N, 135.5°E
- 8 voyages on two bulk-carrier vessels*, May 2004 to May 2007
- collect dried air samples every 2.5° between latitudes –20° to +20°, every 5° elsewhere
- record meteorology at time of sampling
- analyse samples in NIWA laboratory for:
  - CH_4, $^{13}CH_4$, CO, ^{13}CO, ^{14}CO, $C^{18}O$
- measure real-time CN densities
- 24-hr particulate aerosols (hi-vol filtration)

* Vessels *Fujitrans World* then *Transfuture 5*, Toyofuji Shipping Company Ltd, Nagoya

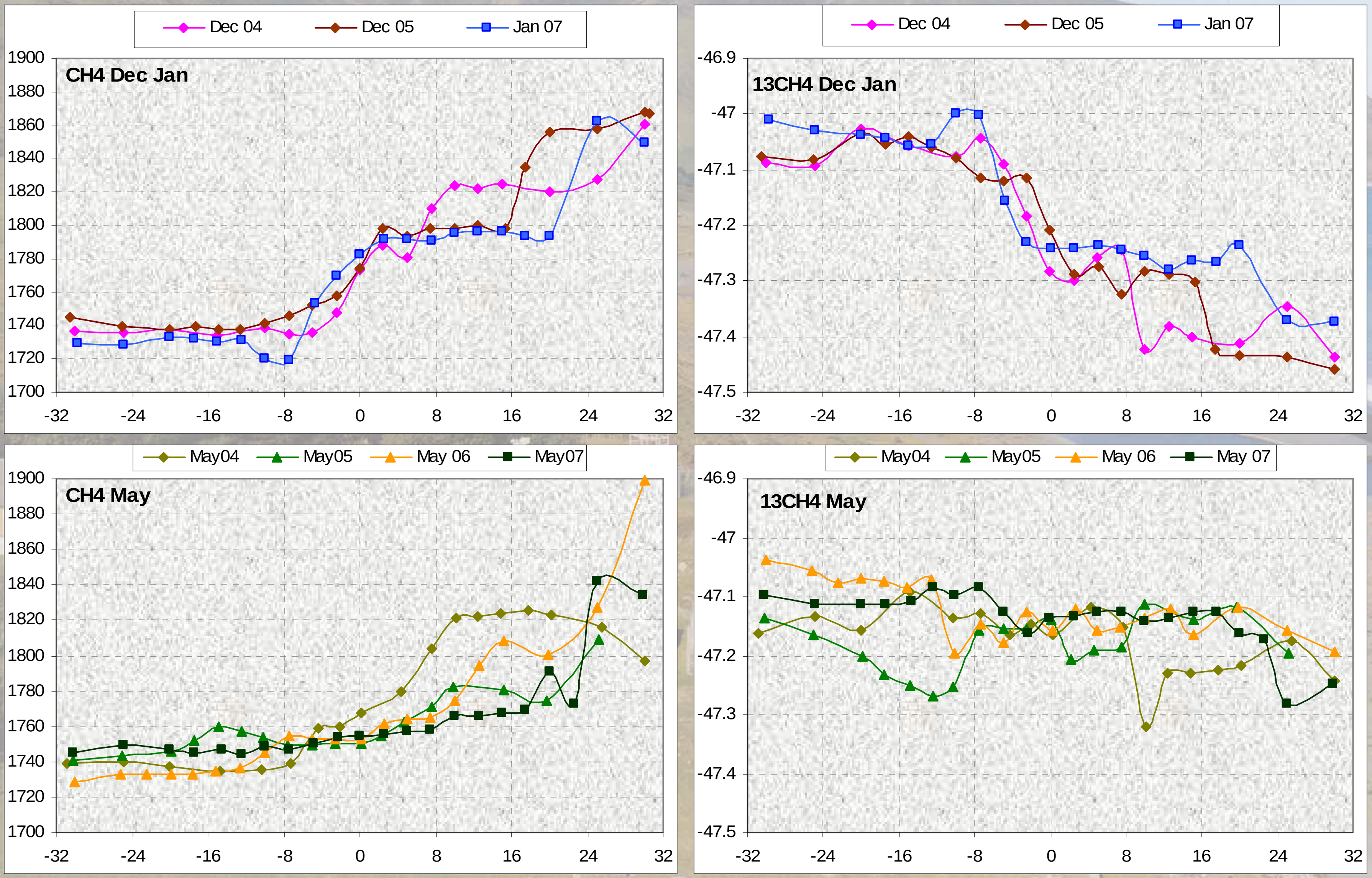
Shipboard CO





- **Inter-comparisons of CO:**
  - **3 voyages, Dec – early Jan**
  - **4 voyages in May (but CO unavailable for May 2007)**
- **approx. NH seasonality:**
  - **peak ~150ppb in Mar**
  - **trough ~90 ppb in Aug**
- **approx. SH seasonality:**
  - **peak ~60ppb in Sep**
  - **trough ~40 ppb in Feb**
- **Note inter-annual variability north of ~10°S**

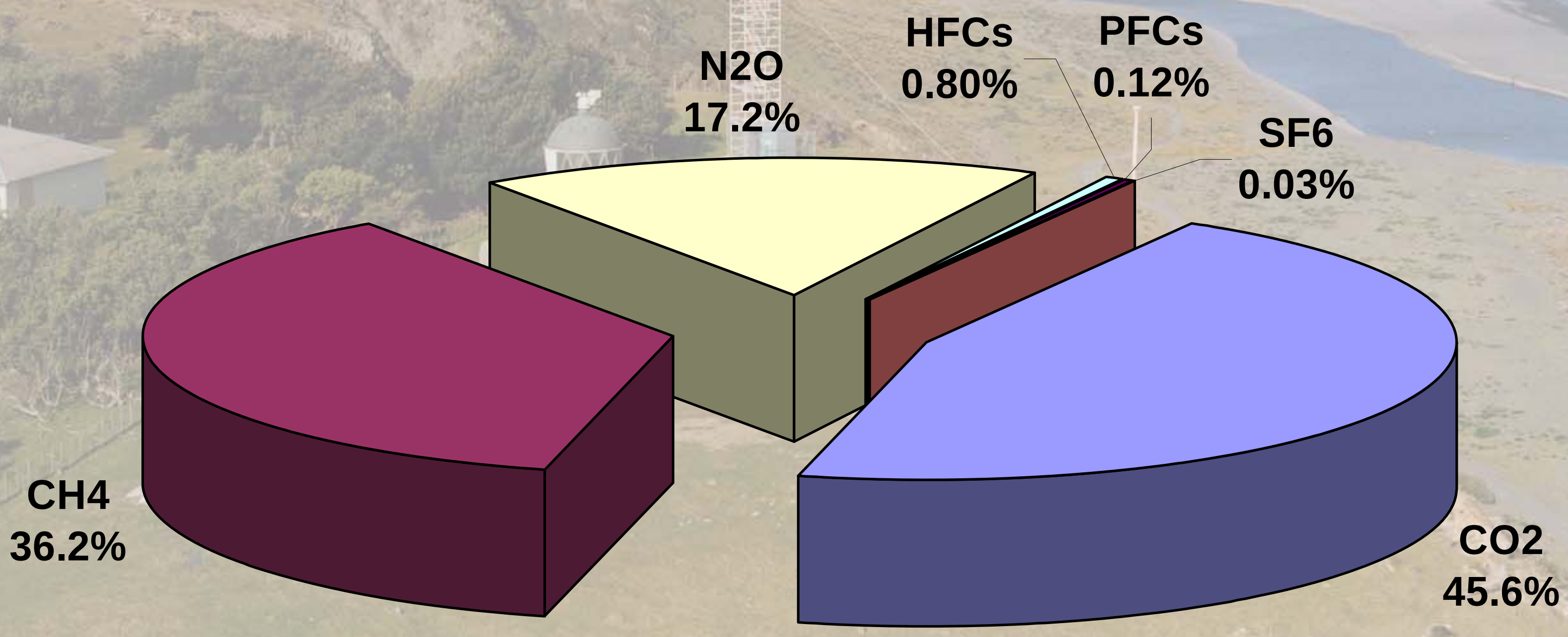
Shipboard CH_4 and $\delta^{13}C(CH_4)$



Why the NZ focus on CH_4?

The NZ GHG emission inventory (shown for 2004):

- approx 50% CO_2, 50% agricultural GHGs
  — highest ag. component of all developed countries
- 2/3 of ag. GHGs are CH_4 from ruminant livestock
- ruminant CH_4 has no known abatement prospects



Acknowledgements

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- Opportunities, facilities and hospitality aboard vessels of Toyofuji Shipping Company Ltd
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- Co-funding: NOAA GCOS programme


Thank you
ASIA
Gobi Desert
Japan Trench
Philippine Basin
PHILIPPINES
Mariana Trench
BRUNEI
MALAYSIA
MALAYSIA
SINGAPORE
SRI LANKA
Central Pacific Basin
AUSTRALIA
Victoria Desert
FIJI
Tonga Trench
South Australia Basin
Kermadic Trench
NEW ZEALAND
Southeast Indian Ridge
Australian - Antarctic Basin
ANTARCTICA