What have we learned from atmospheric measurements of carbon isotopes and O_2/N_2

And what could we do next?

Ralph Keeling

Scripps Institution of Oceanography

Andrew Manning

Schoo of Environmental Sciences

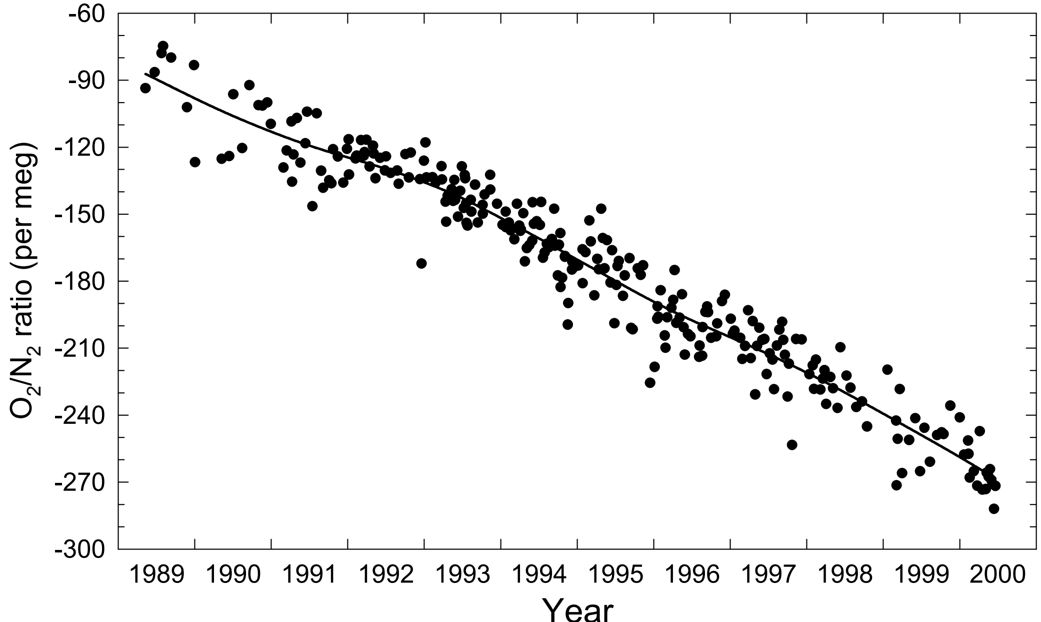
University of East Anglia

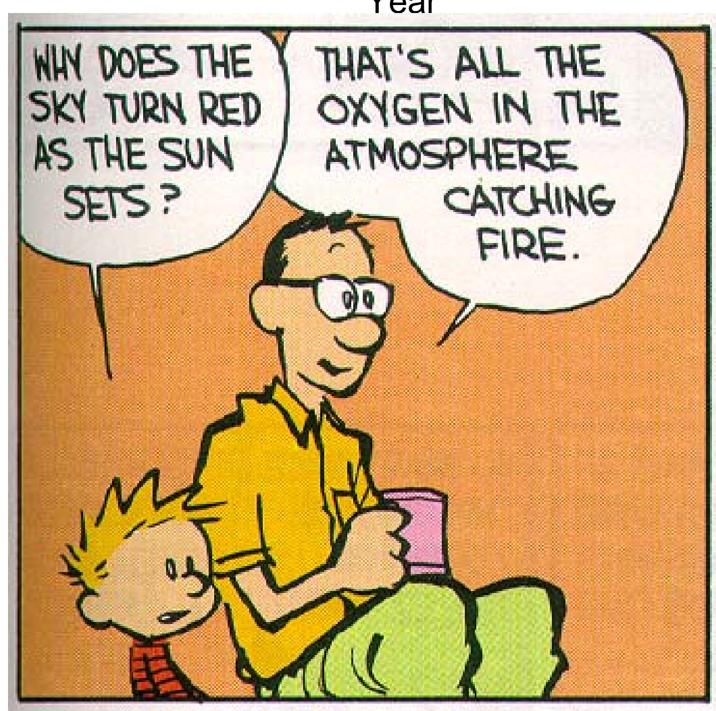
University of East Anglia

School of Environmental Sciences

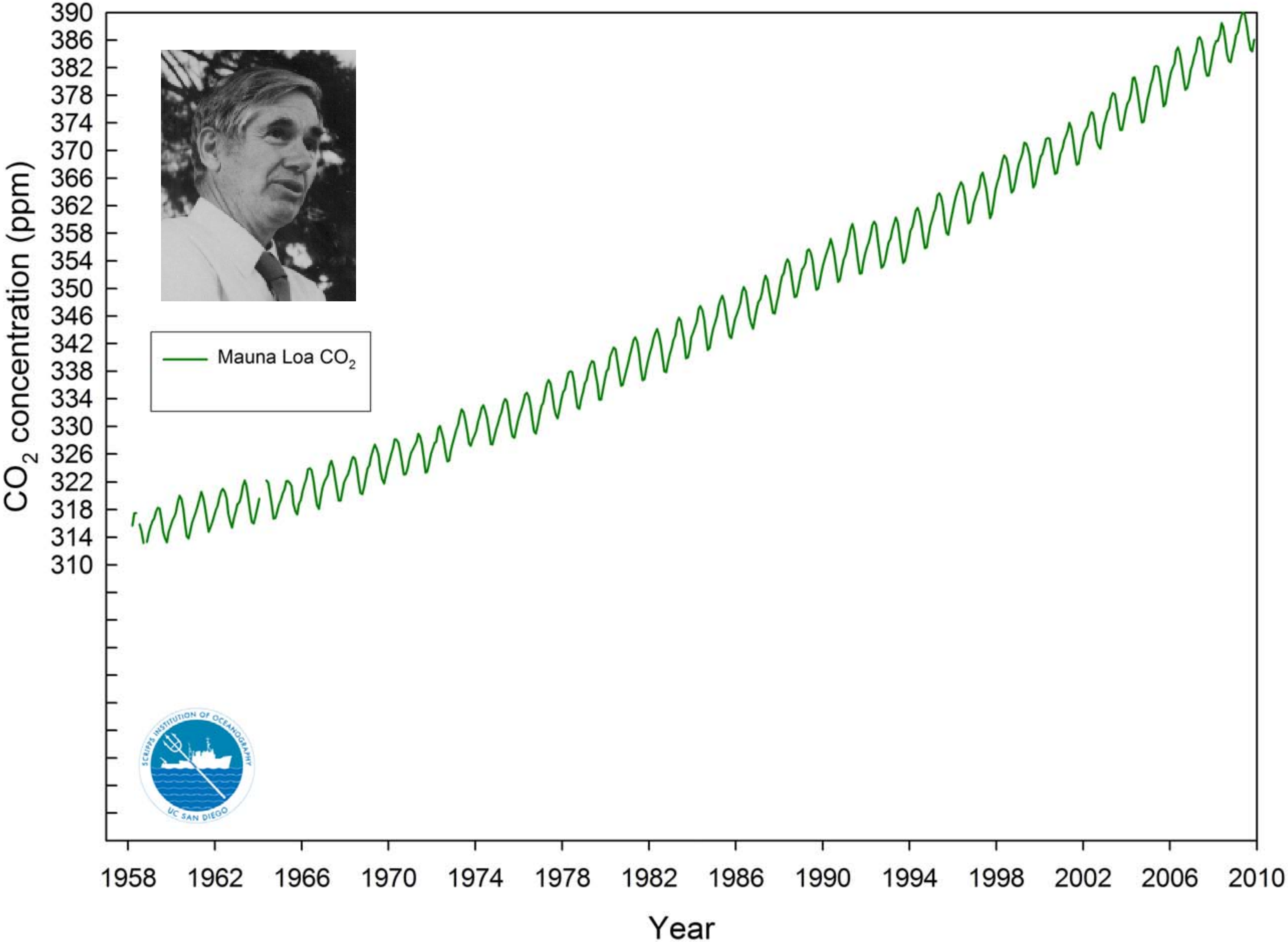
CRAM Laboratory

Deseasonalised O_2/N_2 ratio at La Jolla

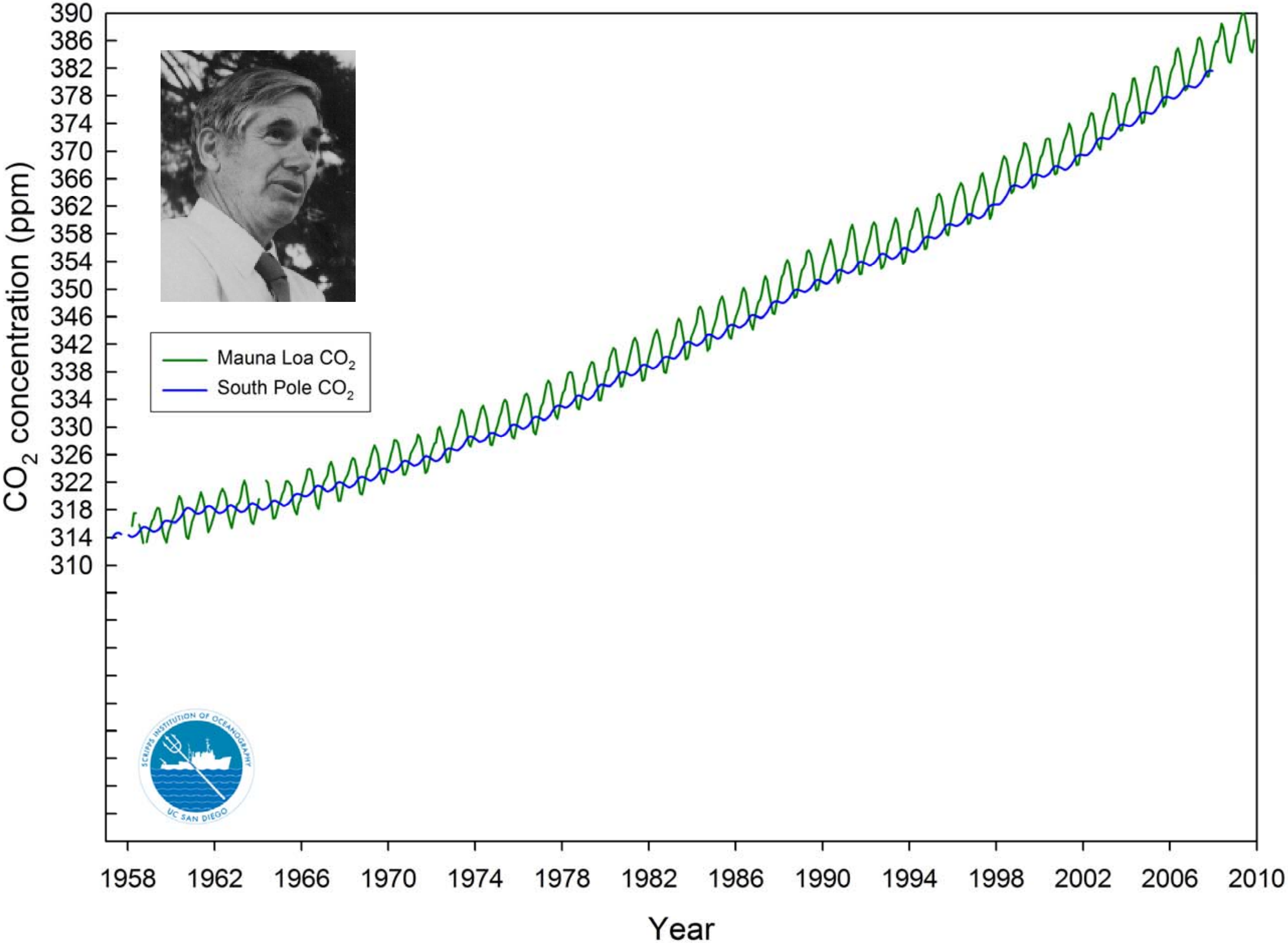




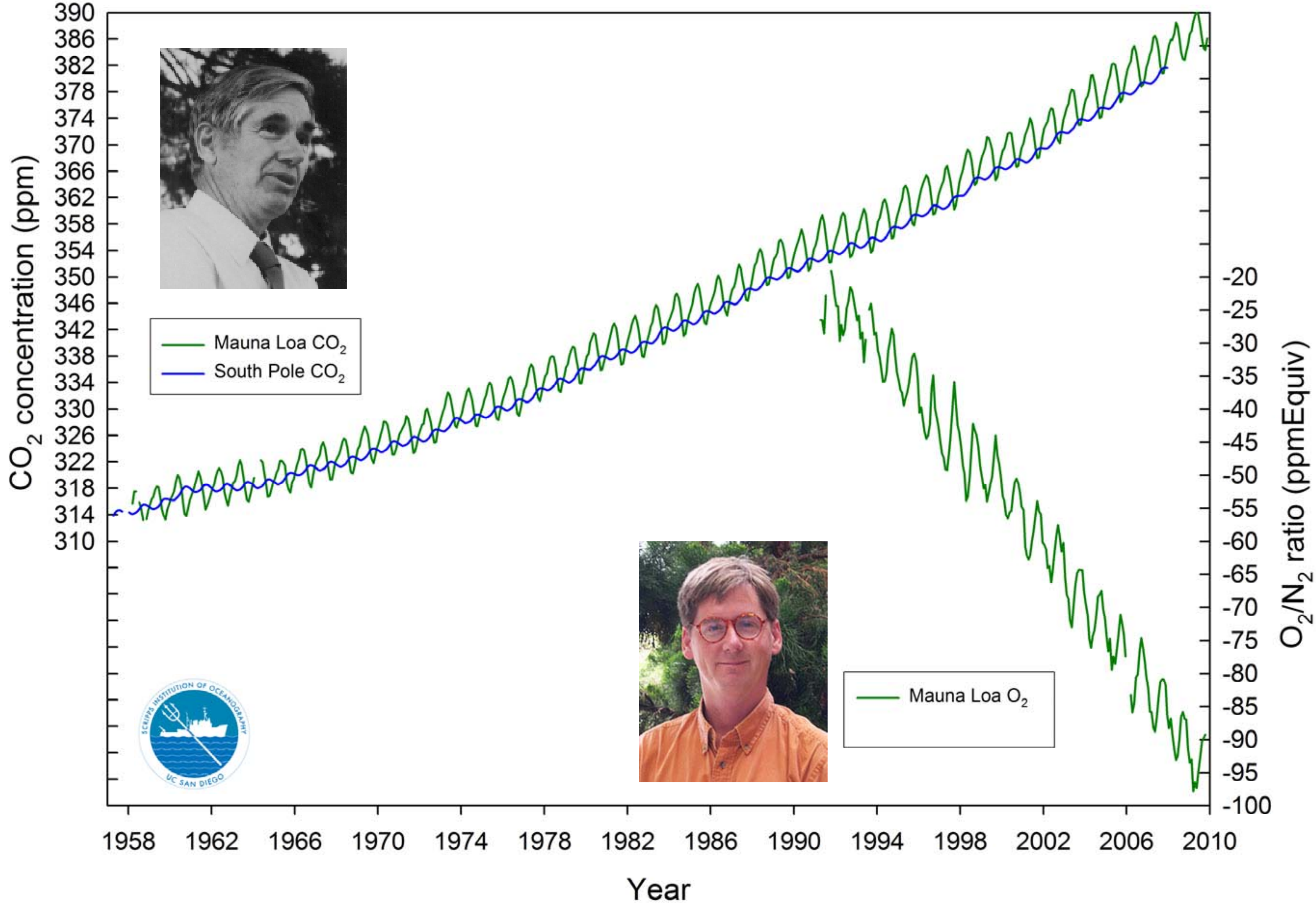
© Bill Watterson,
Calvin and Hobbes.

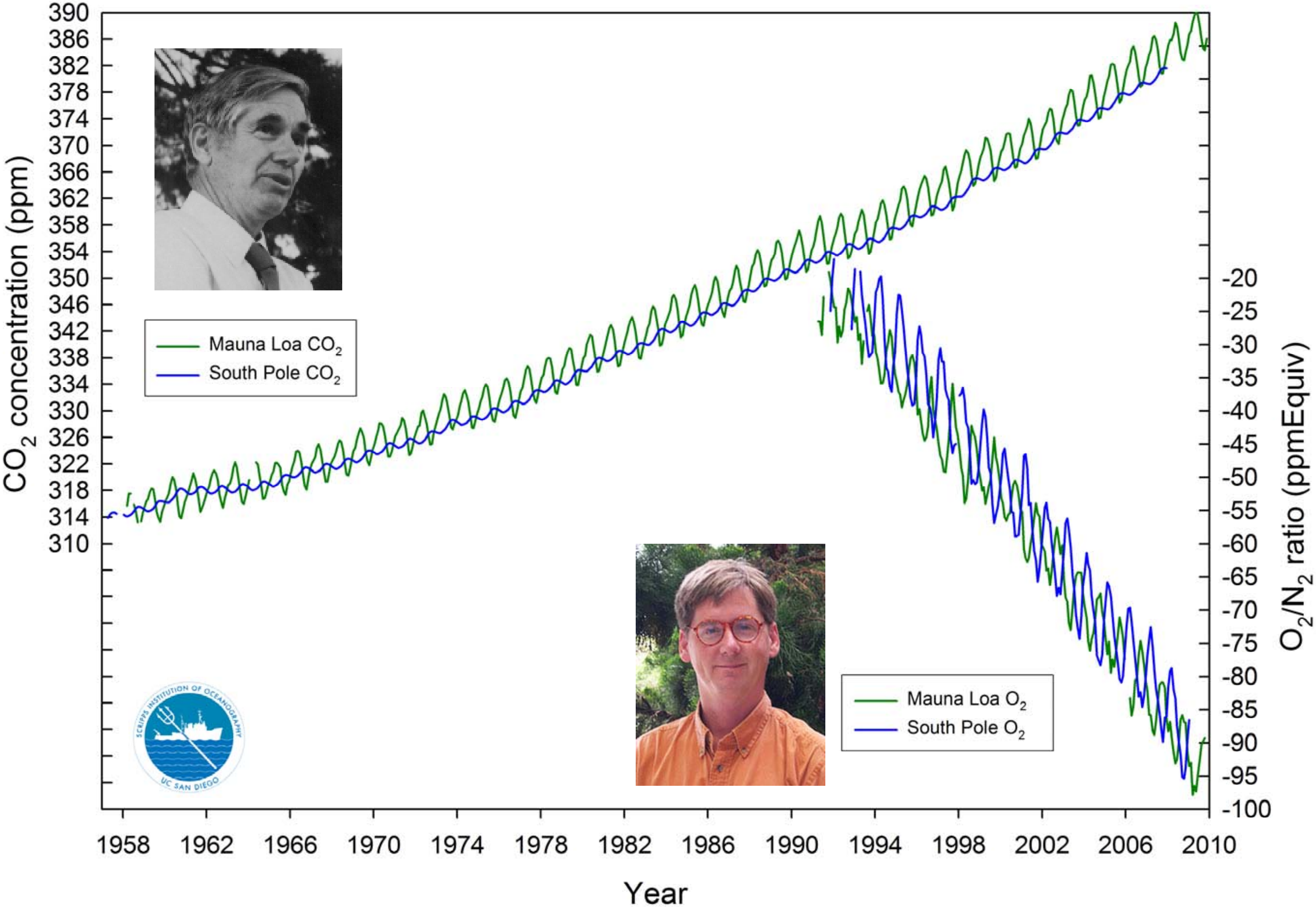


390
386
382
378
374
370
366
362
358
354
350
346
342
338
334
330
326
322
318
314
310
CO_2 concentration (ppm)
Mauna Loa CO_2
SCRIPPS INSTITUTION OF OCEANOGRAPHY
UC SAN DIEGO
1958
1962
1966
1970
1974
1978
1982
1986
1990
1994
1998
2002
2006
2010
Year



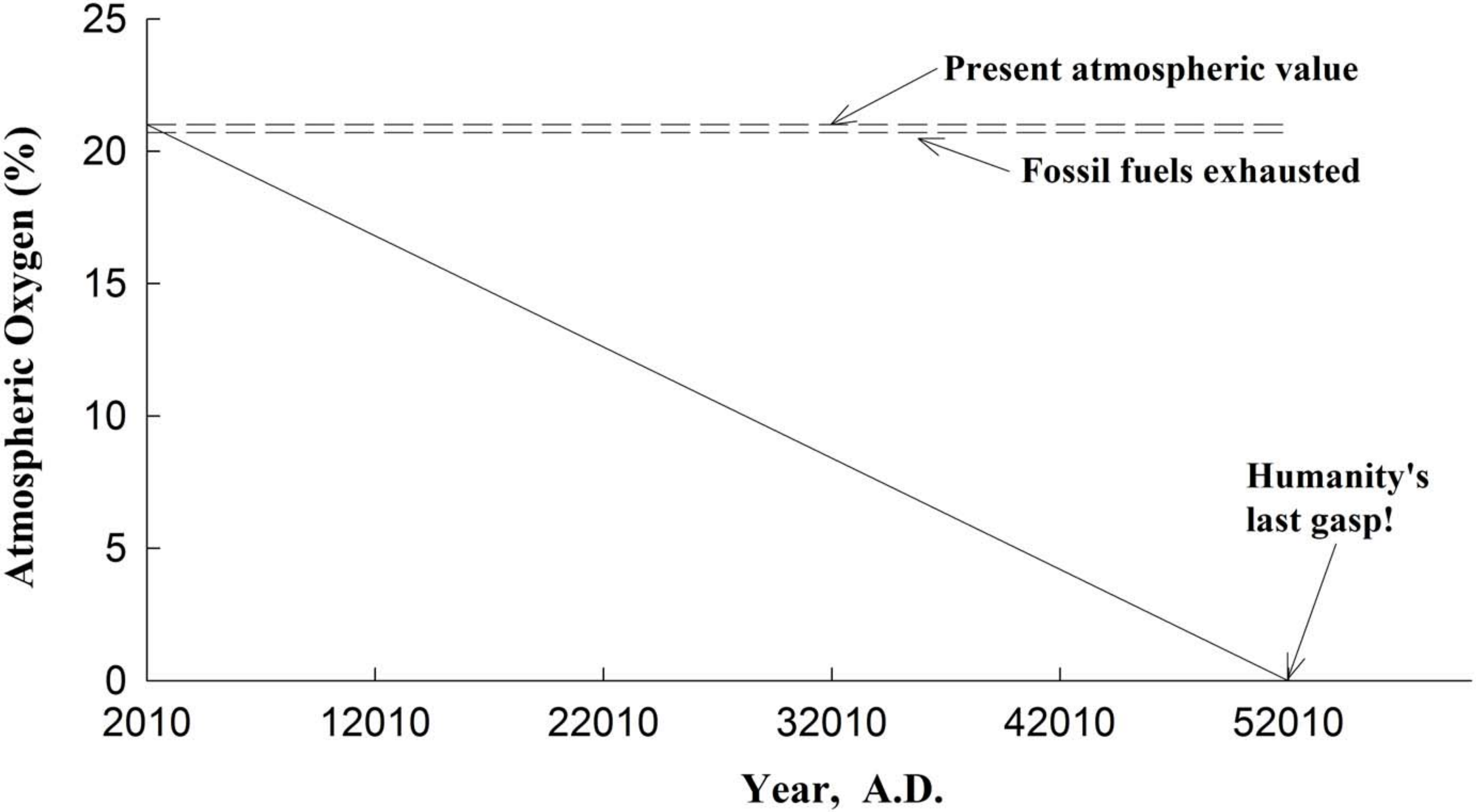
390
386
382
378
374
370
366
362
358
354
350
346
342
338
334
330
326
322
318
314
310
CO_2 concentration (ppm)
Mauna Loa CO_2
South Pole CO_2
SCRIPPS INSTITUTION OF OCEANOGRAPHY
UC SAN DIEGO
1958
1962
1966
1970
1974
1978
1982
1986
1990
1994
1998
2002
2006
2010
Year


CO2 concentration (ppm)
O2/N2 ratio (ppmEquiv)
Year
Mauna Loa CO2
South Pole CO2
Mauna Loa O2
390
386
382
378
374
370
366
362
358
354
350
346
342
338
334
330
326
322
318
314
310
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
1958
1962
1966
1970
1974
1978
1982
1986
1990
1994
1998
2002
2006
2010

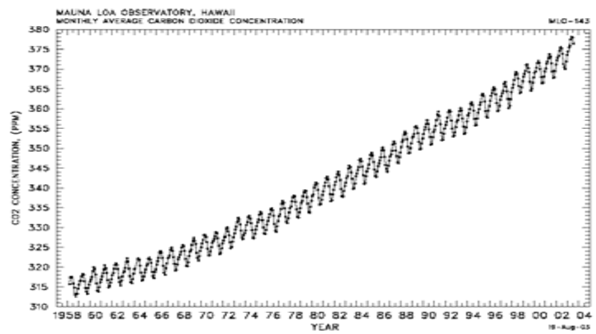


Mauna Loa CO_2
South Pole CO_2
Mauna Loa O_2
South Pole O_2
CO_2 concentration (ppm)
O_2/N_2 ratio (ppmEquiv)
Year
390
386
382
378
374
370
366
362
358
354
350
346
342
338
334
330
326
322
318
314
310
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
1958
1962
1966
1970
1974
1978
1982
1986
1990
1994
1998
2002
2006
2010

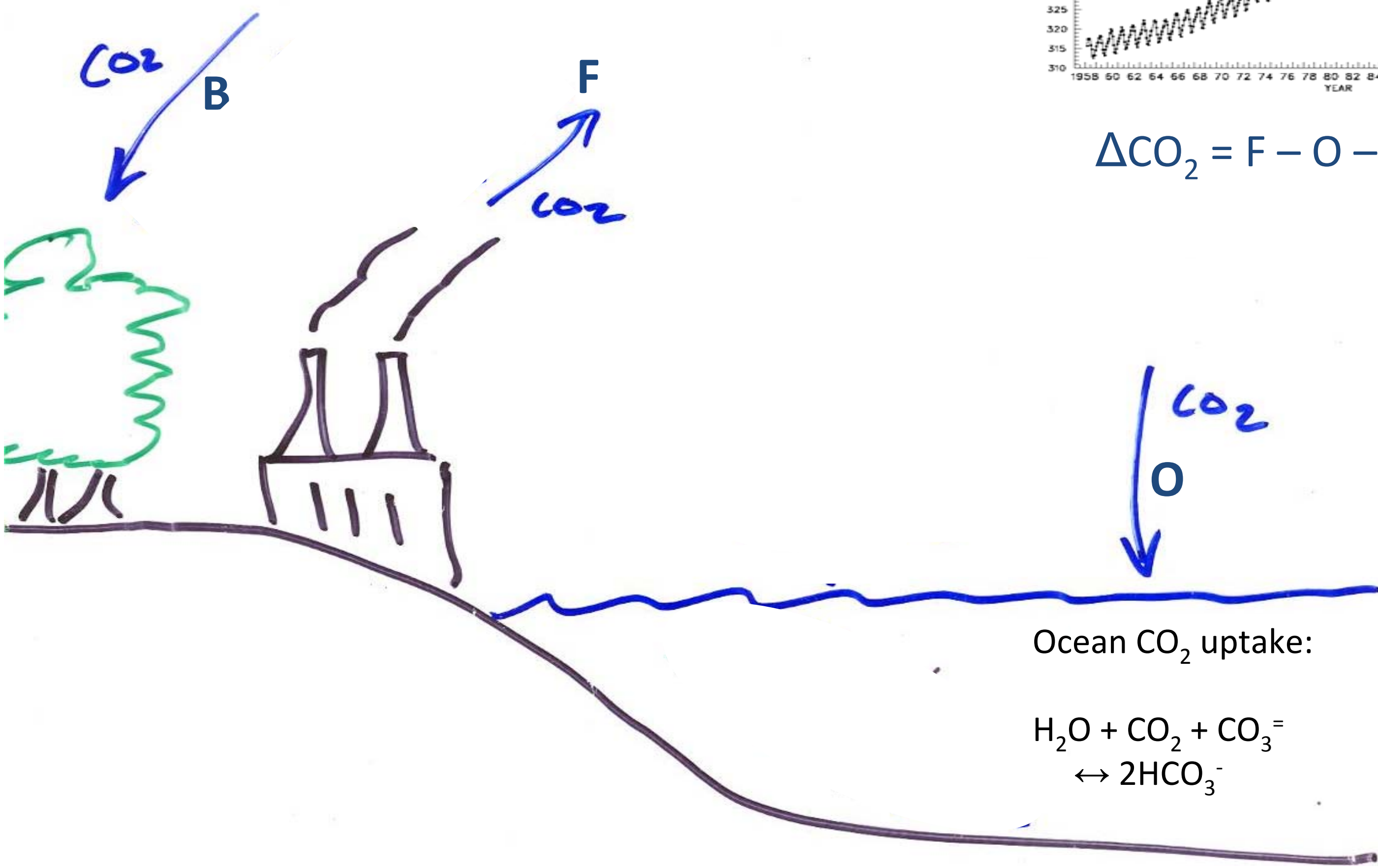
Projected Decreasing Trend in Atmospheric Oxygen



Atmospheric CO_2 budget



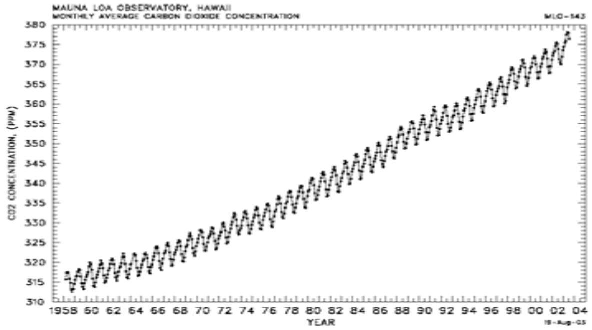
$\Delta CO_2 = F - O - B$

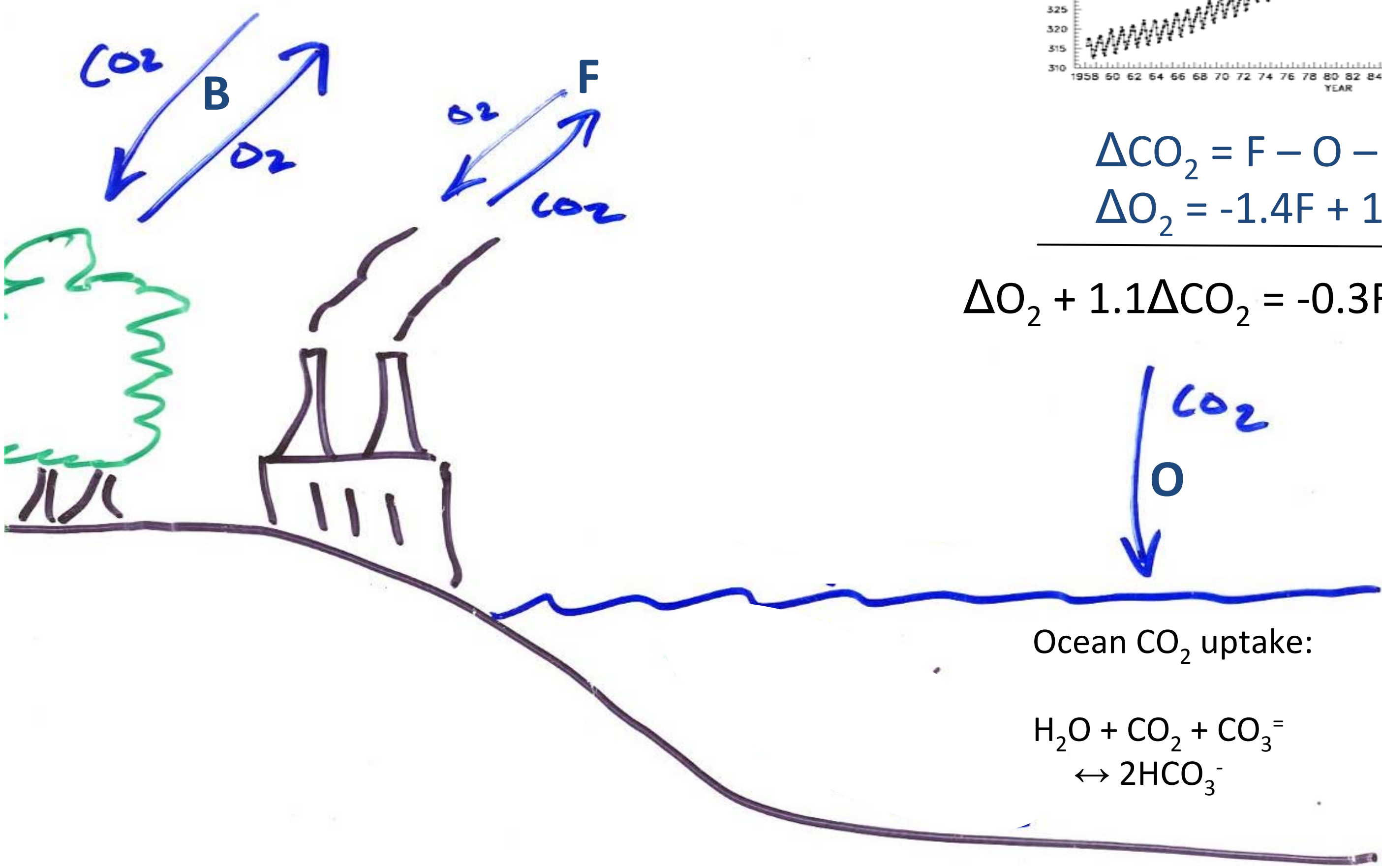


Ocean CO_2 uptake:

$H_2O + CO_2 + CO_3^{=}$
$\leftrightarrow 2HCO_3^-$

Atmospheric CO_2 & O_2 budgets





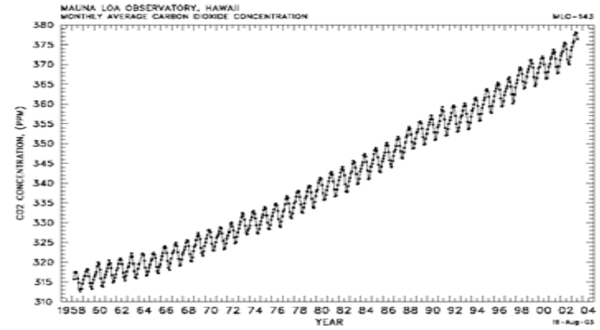
$$\Delta CO_2 = F - O - B$$
$$\Delta O_2 = -1.4F + 1.1B$$

$$\Delta O_2 + 1.1\Delta CO_2 = -0.3F - 1.1O$$

Ocean CO_2 uptake:

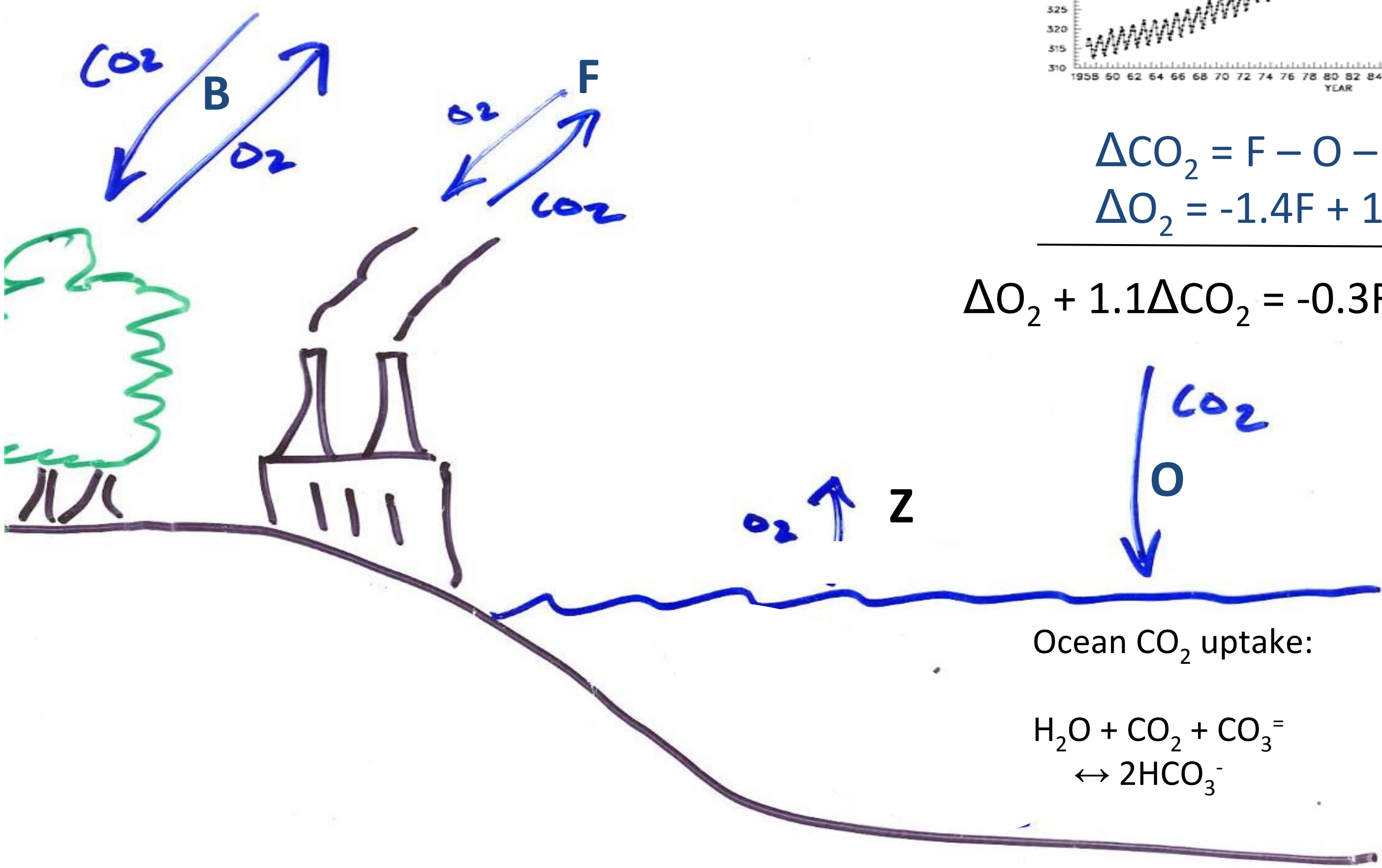
$$H_2O + CO_2 + CO_3^{=} \leftrightarrow 2HCO_3^{-}$$

Atmospheric CO_2 & O_2 budgets



$$\Delta CO_2 = F - O - B$$
$$\Delta O_2 = -1.4F + 1.1B + Z$$

$$\Delta O_2 + 1.1\Delta CO_2 = -0.3F - 1.1O + Z$$



Ocean CO_2 uptake:

$$H_2O + CO_2 + CO_3^{=} \leftrightarrow 2HCO_3^{-}$$

Atmospheric O_2/N_2 applications

- <u>Original motivation:</u>
  separate and quantify land and ocean sinks. Limited by uncertainty in ocean O_2 flux, Z.

- <u>Emergent application:</u>
  solve for ocean O_2 flux Z, by building on improved estimates of ocean carbon sink.

Ocean Acidification
Ocean Deoxygenation

Models suggest global warming will reduce dissolved O_2 levels in the ocean interior (1 to 7% loss in total inventory by 2100).

<u>Causes in models:</u>

(1) Warming reduces O_2 solubility
(2) Warming increases upper ocean stratification, reducing ventilation rates

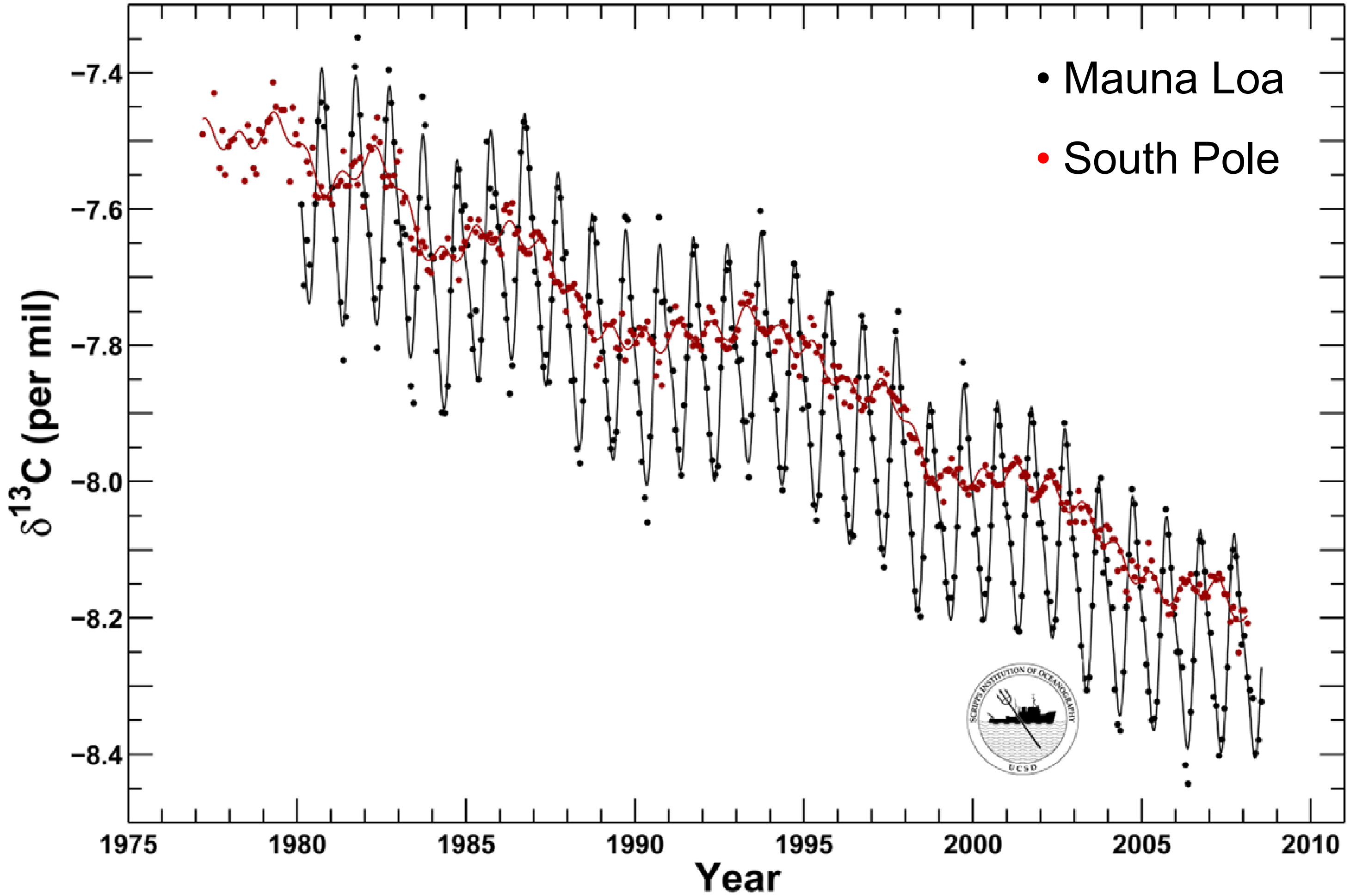
<u>Potential consequences:</u>

(1) Expanded O_2 minimum and “dead” zones
(2) Impacts on fisheries
(3) Interaction with N, P, C, & trace element cycles

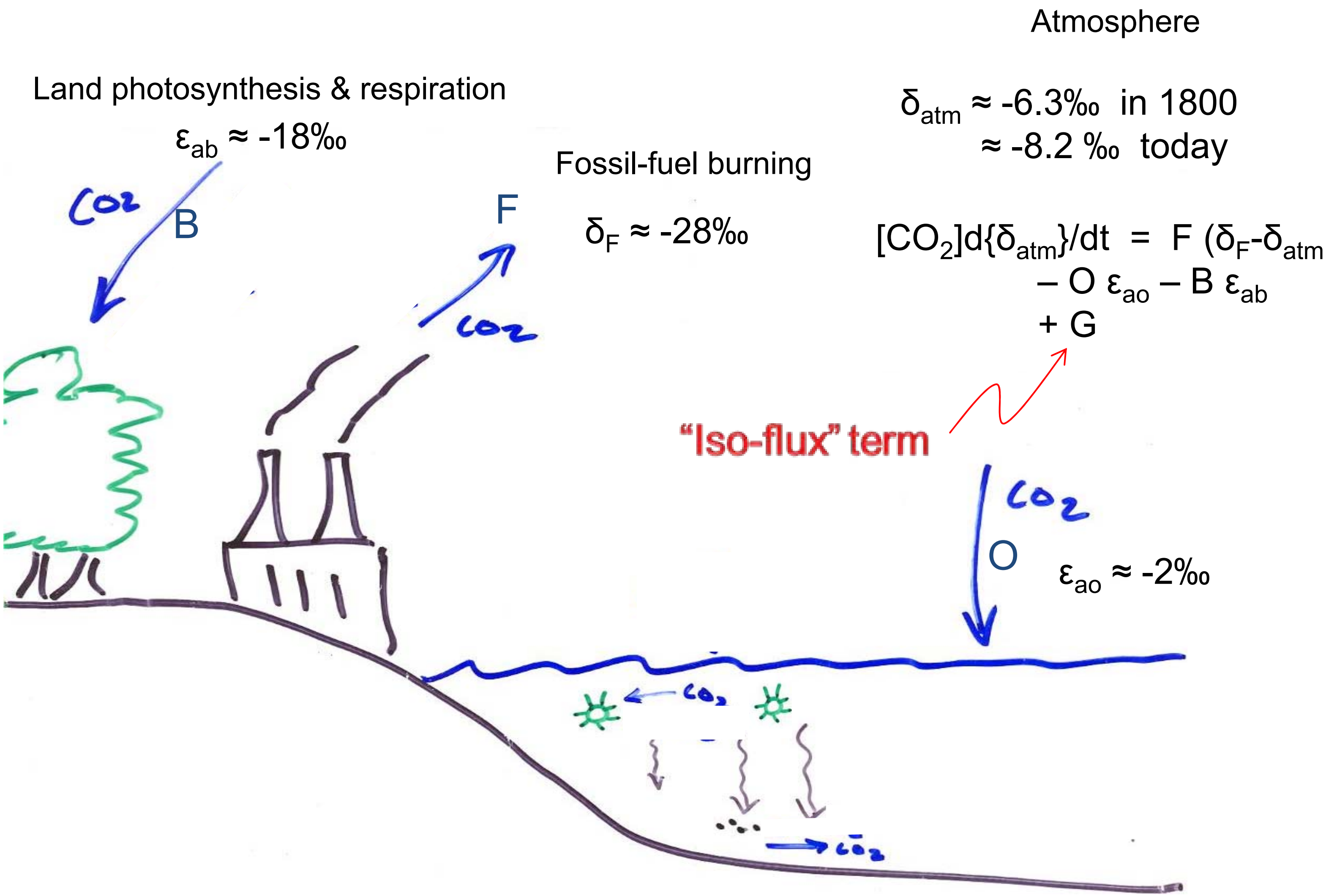
<u>Evidence for deoxygenation:</u>

(1) Repeat hydrography shows declines in North Pacific, Tropics and Antarctic zones)
(2) Atmospheric O_2 budget seems to require Z>0, but with large uncertainty.

$\delta^{13}C$ trends at Mauna Loa and the South Pole



Atmospheric $^{13}CO_2$ budget

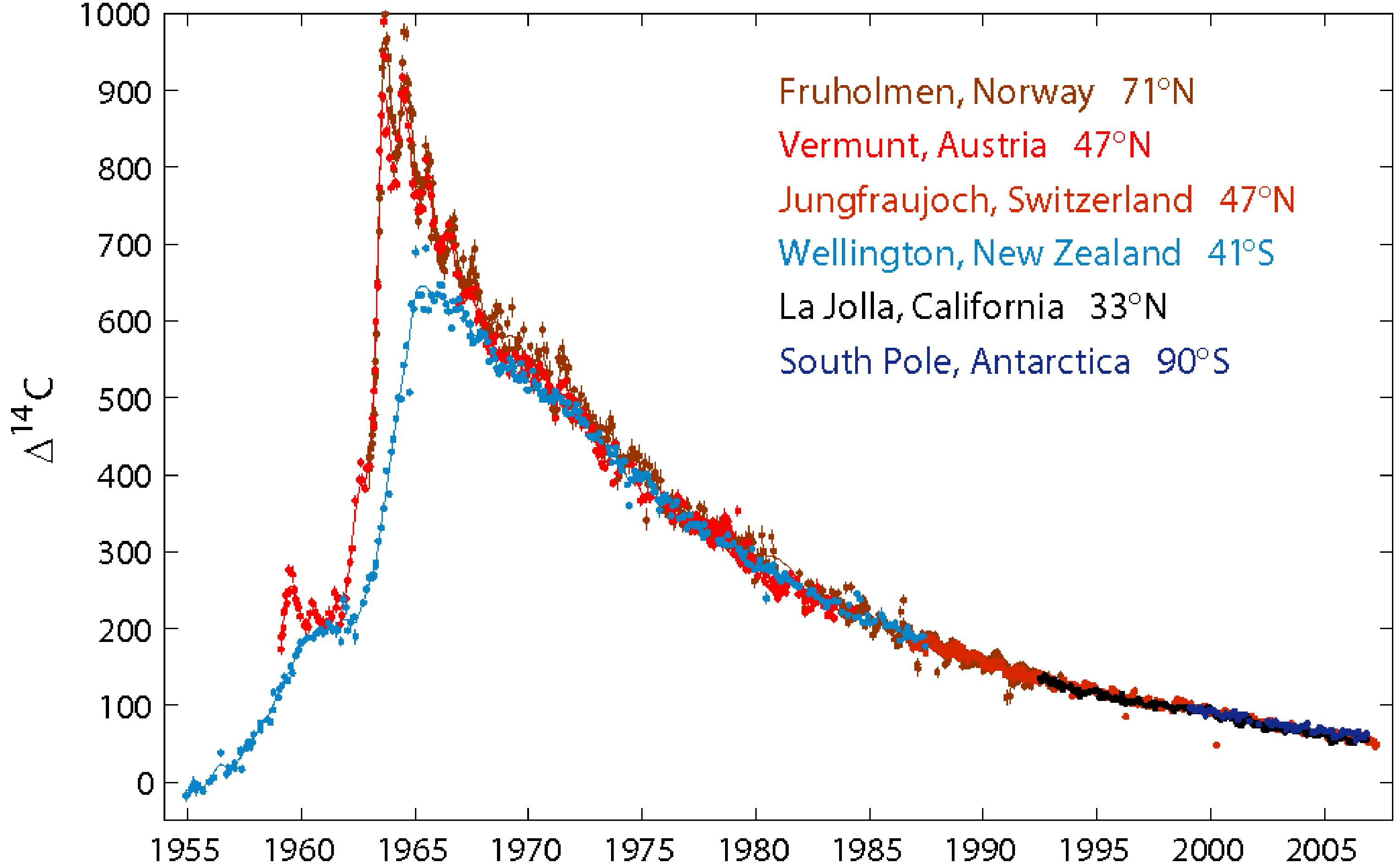


Atmospheric $^{13}CO_2/^{12}CO_2$ applications

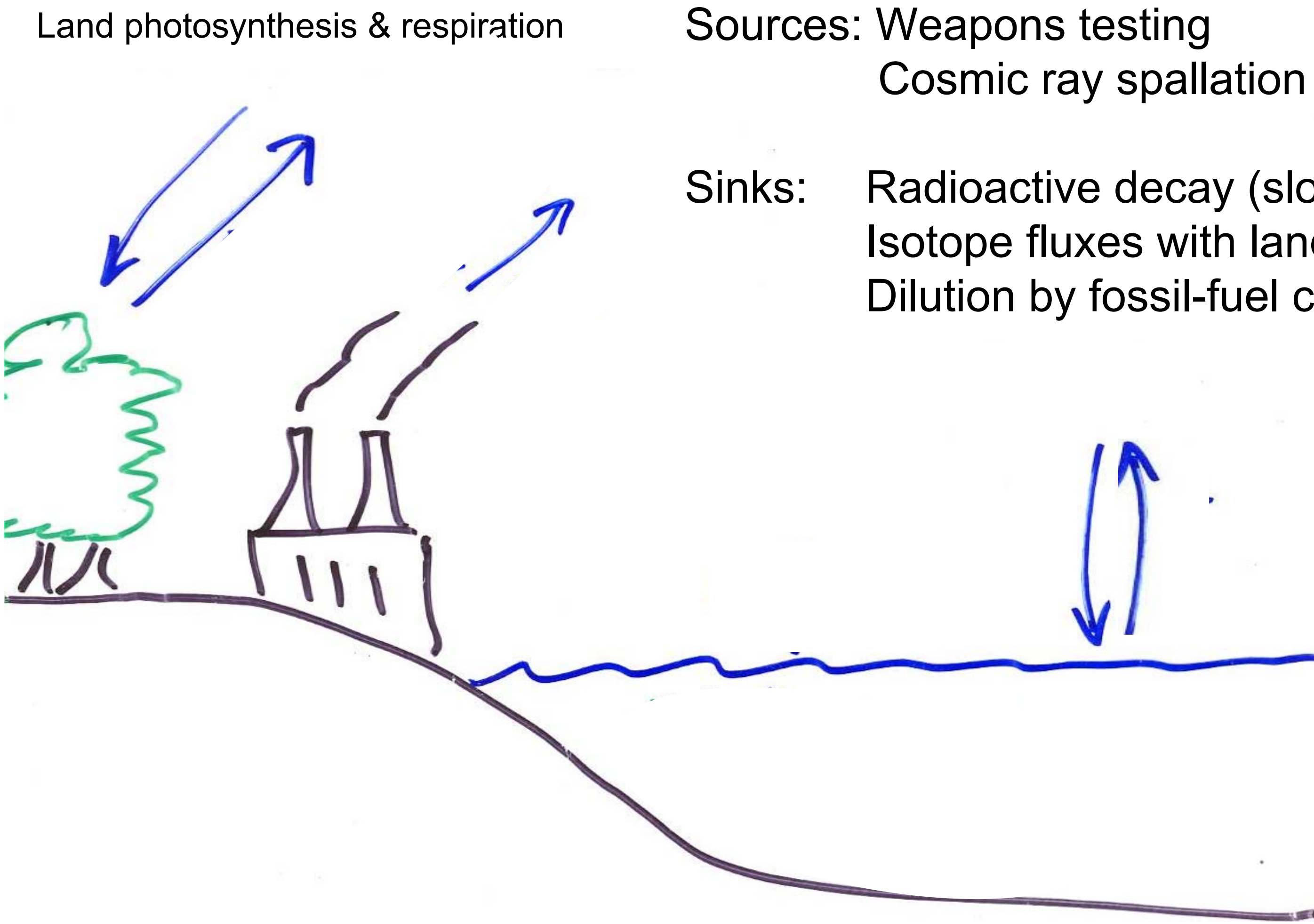
- Original motivation:
  separate and quantify land and ocean sinks.
  (Large uncertainties in isofluxes limited this application to El Niño time scales).

- Emergent application:
  resolve changes in ε_{ab}, related to shifts in water-use efficiency.

Atmospheric $^{14}CO_2$ trends



Atmospheric $^{14}CO_2$ budget



Sources: Weapons testing
Cosmic ray spallation

Sinks: Radioactive decay (slow)
Isotope fluxes with land and oceans
Dilution by fossil-fuel carbon

Atmospheric $^{14}CO_2$ applications

- Original motivation:
  tracing nuclear bomb fallout.

- 1970-present motivation:
  determine air-sea exchange rates and ocean mixing rates.

- Emergent application:
  constraining fossil-fuel burning.

How applications of atmospheric measurements have evolved:

- Measurements of O_2/N_2, $^{13}CO_2/^{12}CO_2$, $^{14}CO_2/^{12}CO_2$ provide constraints on many processes acting simultaneously.

- The “hottest” application has always been to solve for the least known process in terms of all the others.

- This is a moving target, depending on which processes are known well independently.

How the playing field may change:

"Until now, there has been no financial penalty for producing emissions and no benefit from carbon sequestration. Now that money enters the picture, so also can fraud." - Euan Nisbet (Nature, **433**, 2005)

How the playing field may change:

Old Maths: $\Delta CO_2 = F - O - B$

ΔCO_2	F	O	B
known	known	unknown	unknown

New Maths?: $\Delta CO_2 = F - O - B$

ΔCO_2	F	O	B
known	unknown	known?	known?

New Maths Needs:

- Land and ocean observing systems.

- Atmospheric observing system with multiple tracers.

- Mesoscale transport modelling for regional verification.

Example: Atmospheric verification of carbon capture and storage

Carbon capture signature:

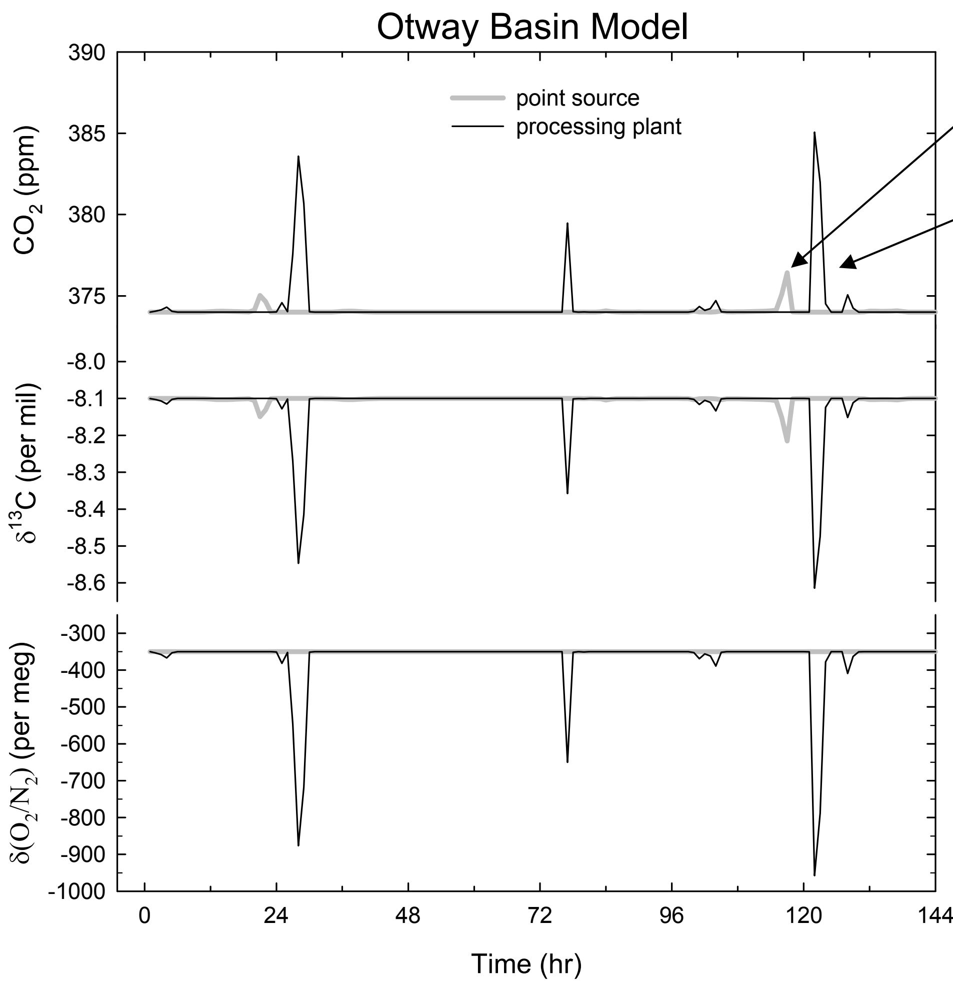
CCS: O_2 loss (from combustion) without normal CO_2 release.

DAC: CO_2 sink with no O_2 change.

Leakage signature:

CO_2 source with no O_2 change.

Example: Atmospheric verification of carbon capture and storage

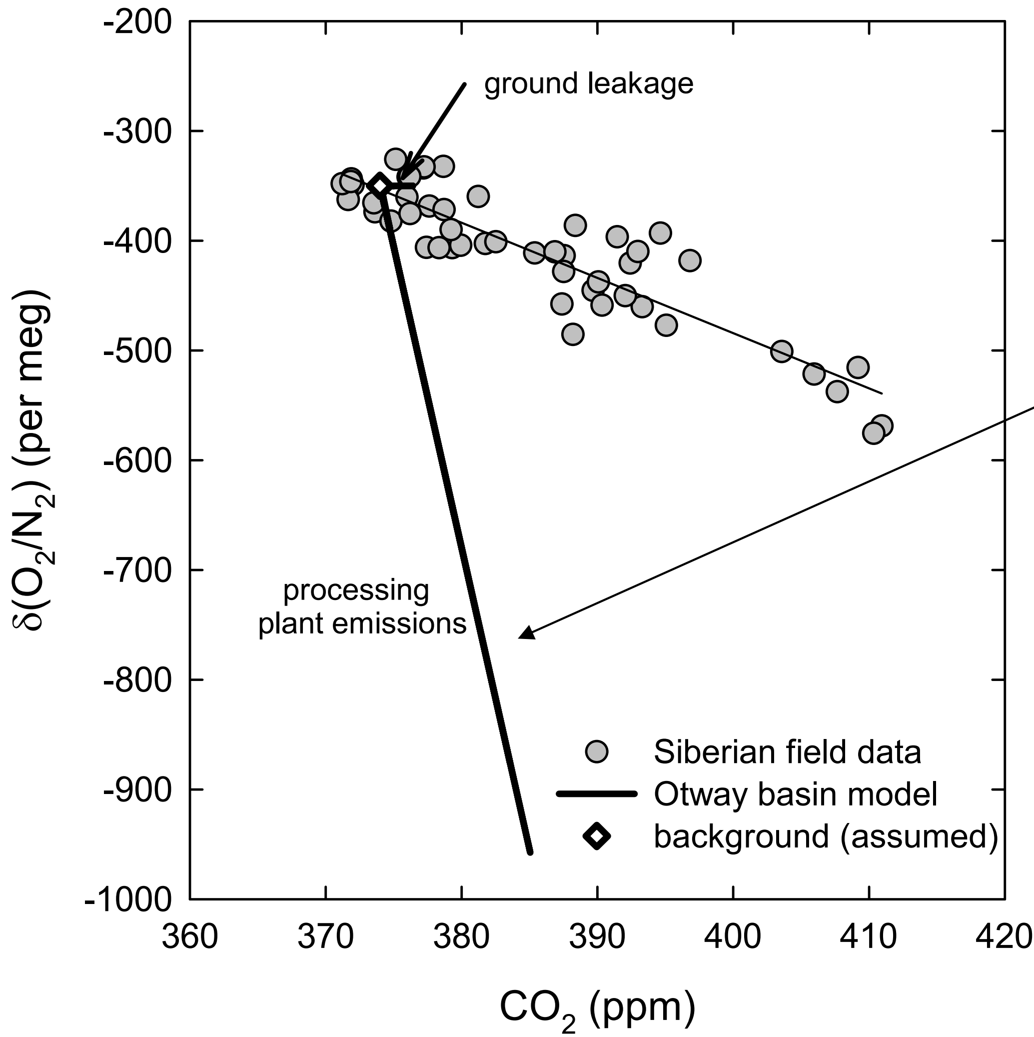


Point source leak.

Coal power plant w/ CCS at 90% efficiency.

CO_2 Model results from Leuning et al., International Journal of Greenhouse Gas Control (2006).

Example: Atmospheric verification of carbon capture and storage



Slope depends on efficiency of carbon capture.

Siberian data from Kozlova et al., GBC (2008).

Conclusions:

- Atmospheric measurement is an extremely powerful tool for improving understanding of the Earth System.

- The longer the time series (e.g. multiple decades), the more valuable the record. Funding agencies take note!

- "Best" application of these measurements changes over time:
    - O_2/N_2: quantify ocean O_2 flux (Z).
    - $^{13}CO_2/^{12}CO_2$: resolve changes in ε_{ab}, related to shifts in water-use efficiency.
    - $^{14}CO_2$: constraining fossil-fuel burning.

Conclusions:

• Emerging financial and political incentives for fraud in reporting emissions

→ Measure the atmosphere (+ oceans) – it can not lie.

• Emerging importance for quantifying regional emissions

→ Requires higher density observation networks and improved high resolution models.

• Using O_2/N_2 measurements to check for carbon capture and storage efficiency and leaks.

• <u>Questions?:</u>

O_2/N_2 – Andrew Manning
$^{13}CO_2$ – Philippe Ciais / Euan Nisbet
$^{14}CO_2$ – Ingeborg Levin / Martin Manning
rkeeling@ucsd.edu