Terrestrial and Oceanic Budgets from Atmospheric O_2/N_2 Ratio Measurements

Yasunori Tohjima
National Institute for Environmental studies

Acknowledgements
H. Mukai, Y. Nojiri, T. Machida, H. Yamagishi, etc..

The 3rd GEOSS Asia-Pacific Symposium, Feb. 4-6 2009, Kyoto

Outline

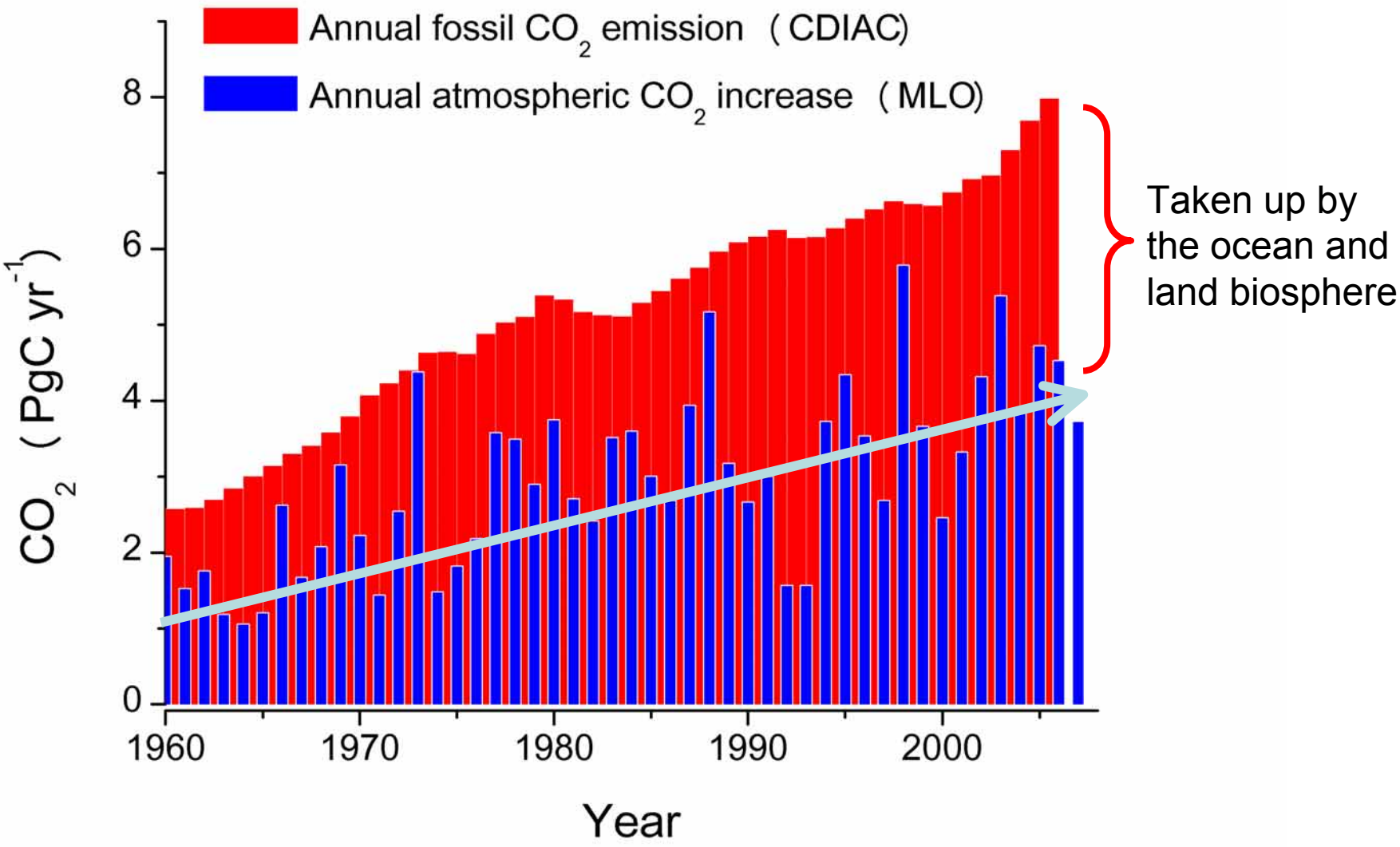
I. CO_2 and O_2 cycle on the earth surface
   - How to partition the global carbon sink between oceanic and terrestrial biosphere

II. Analytical techniques for the atmospheric O_2 change

III. CO_2 budget calculated from O_2 and CO_2 measurements by NIES

I. CO_2 and O_2 cycle on the earth surface

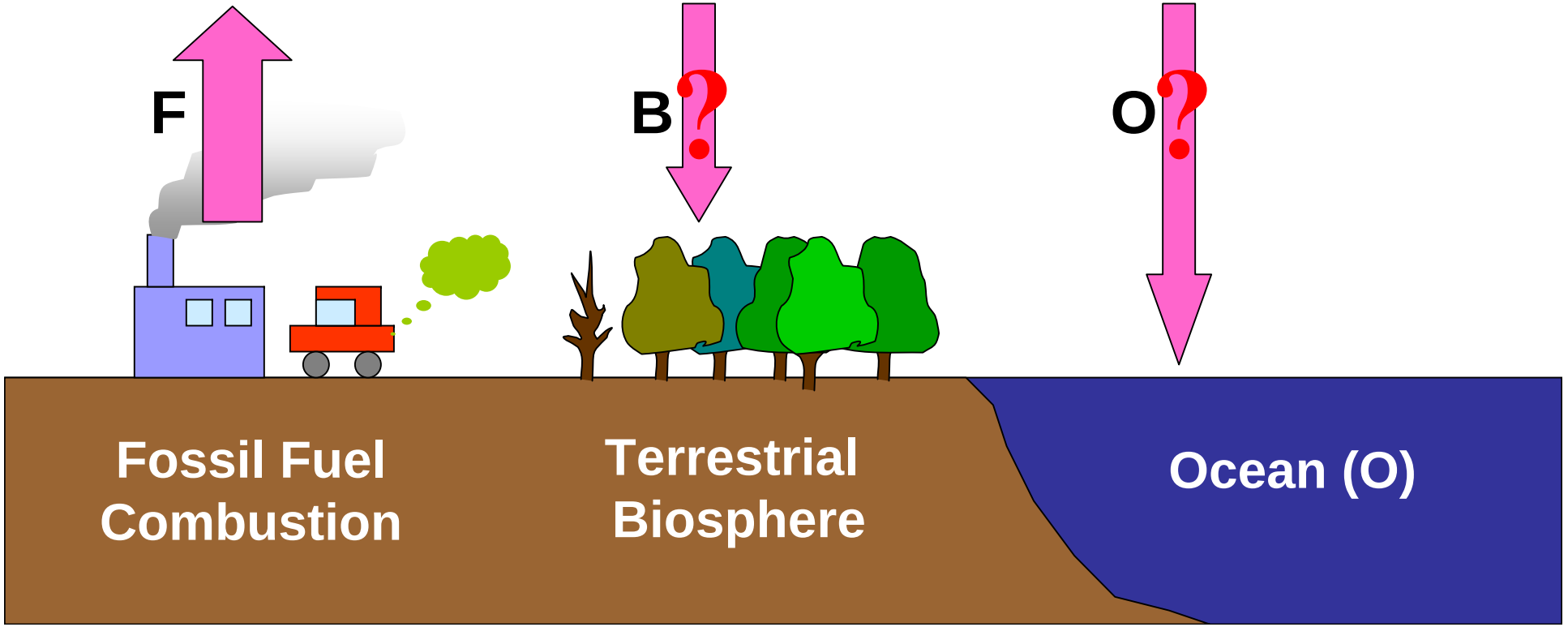
Fossil CO_2 emission and atmospheric accumulation



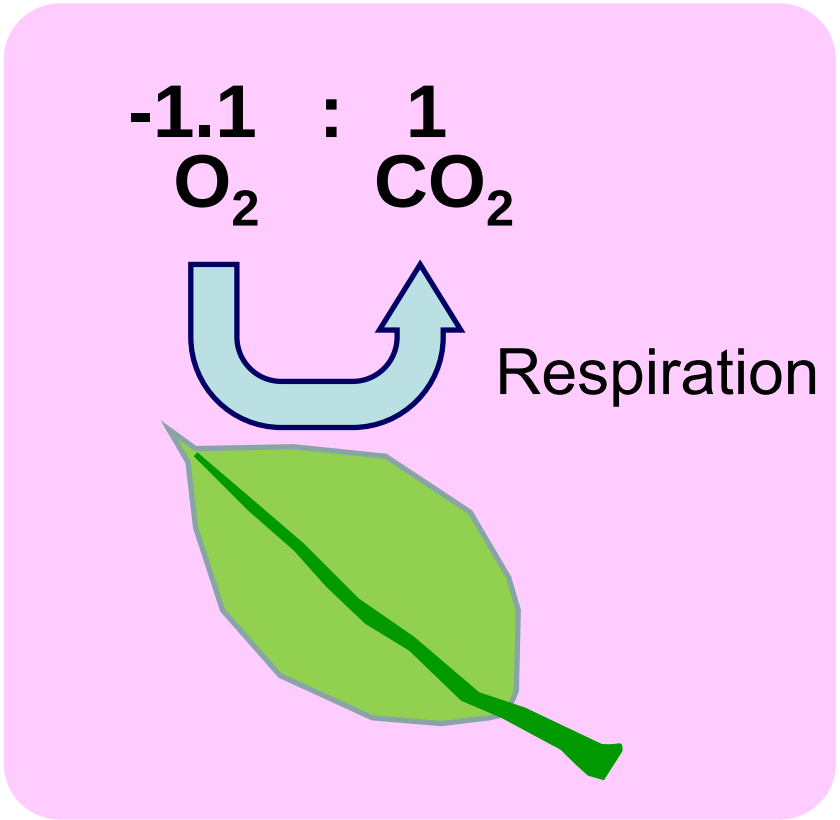
CO_2 (⇨) cycle

Mass balance in atmosphere

$$\Delta CO_2 = F - B - O$$



O_2 and CO_2 exchange during photosynthesis/respiration



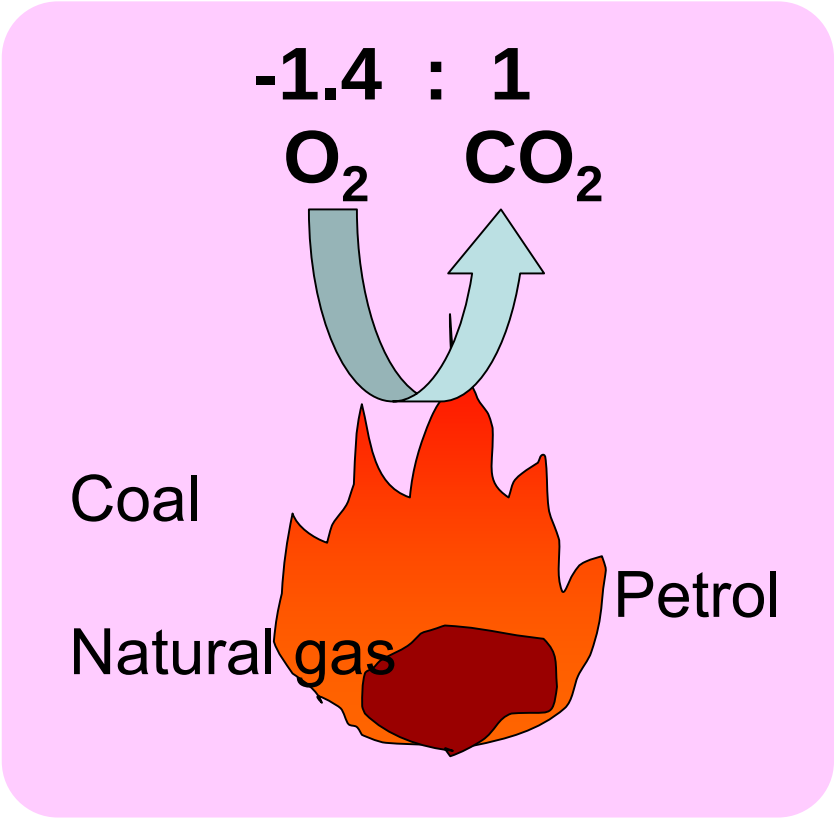
photosynthesis

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2$$

respiration

$$R_{O2/CO2} = -1$$

O_2 and CO_2 exchange during fossil fuel burning



Global average

Coal

$C+O_2 \rightarrow CO_2$

$R_{O2/CO2} = -1$

Natural gas (Methane)

$CH_4+2O_2 \rightarrow CO_2+2H_2O$

$R_{O2/CO2} = -2$

Petrol (e.g. C_7H_{16})

$C_7H_{16}+11O_2 \rightarrow 7CO_2+8H_2O$

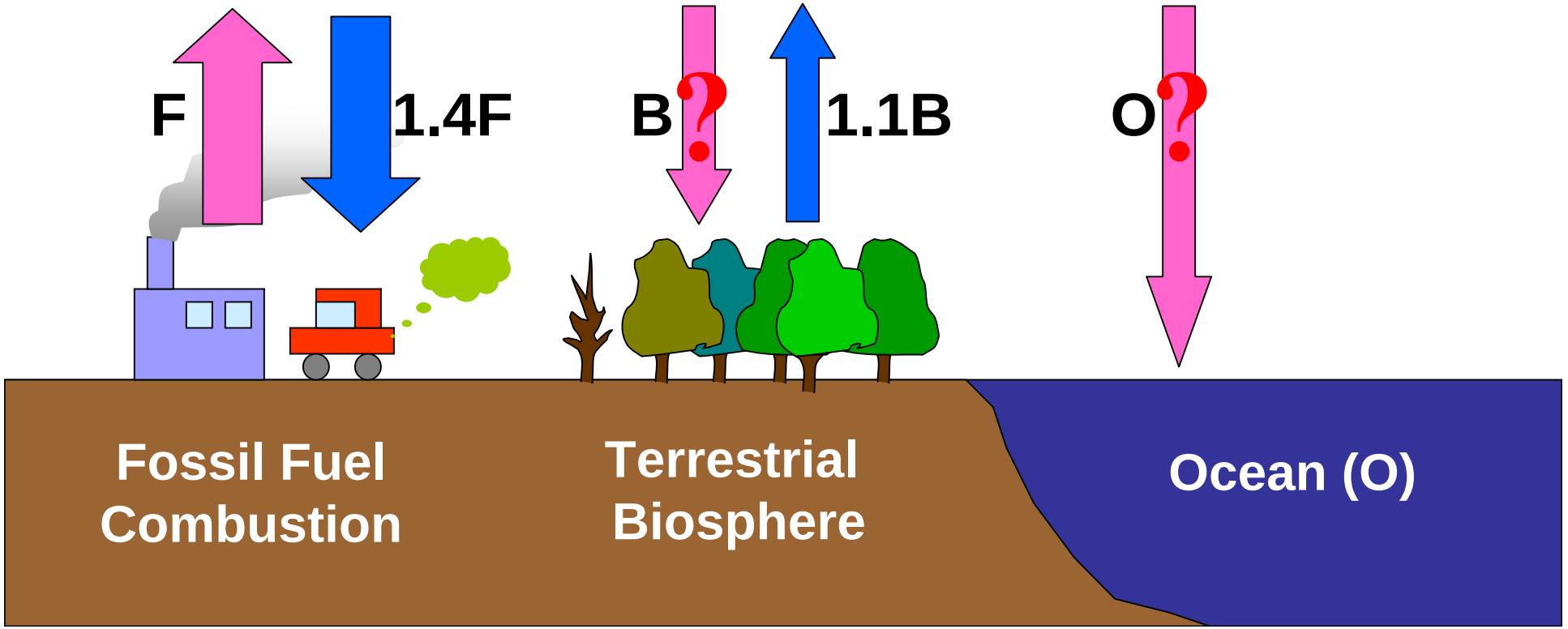
$R_{O2/CO2} = -1.6$

CO_2 (➡) cycle & O_2 (➡) cycle

Mass balance in atmosphere

$$\Delta CO_2 = F - B - O$$

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

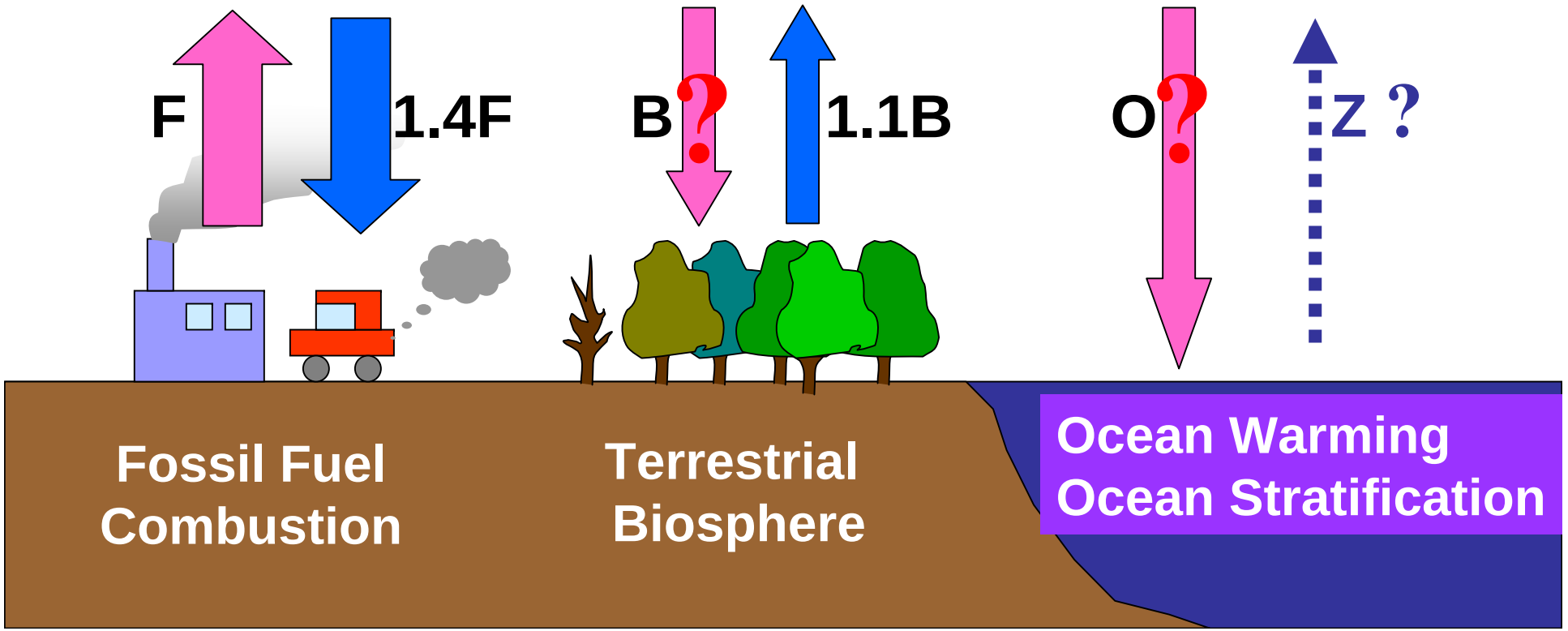


CO_2 (➡) cycle & O_2 (➡) cycle

Mass balance in atmosphere

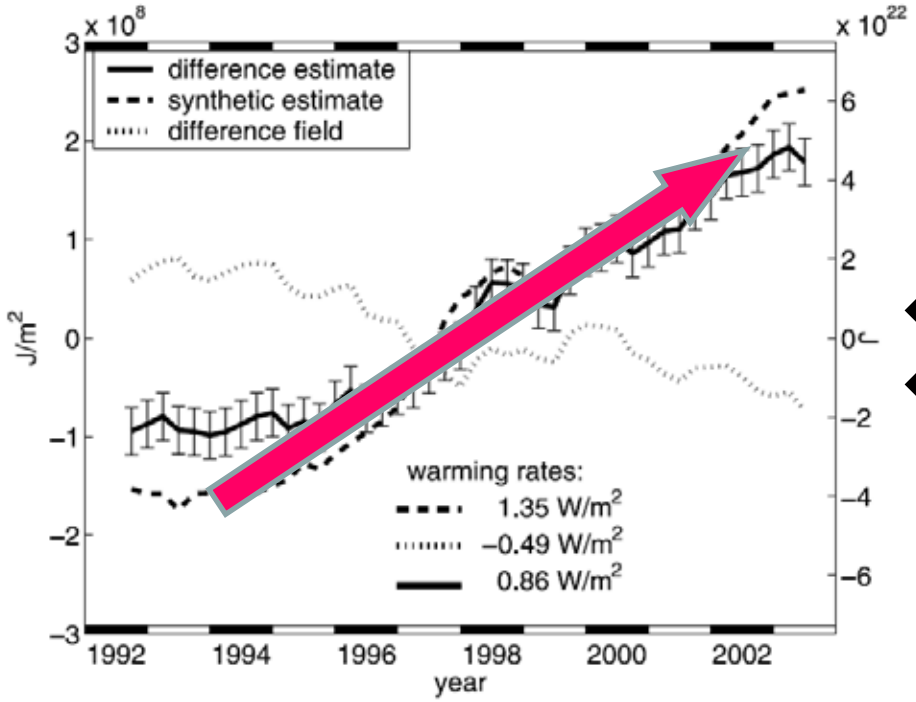
$$\Delta CO_2 = F - B - O$$

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



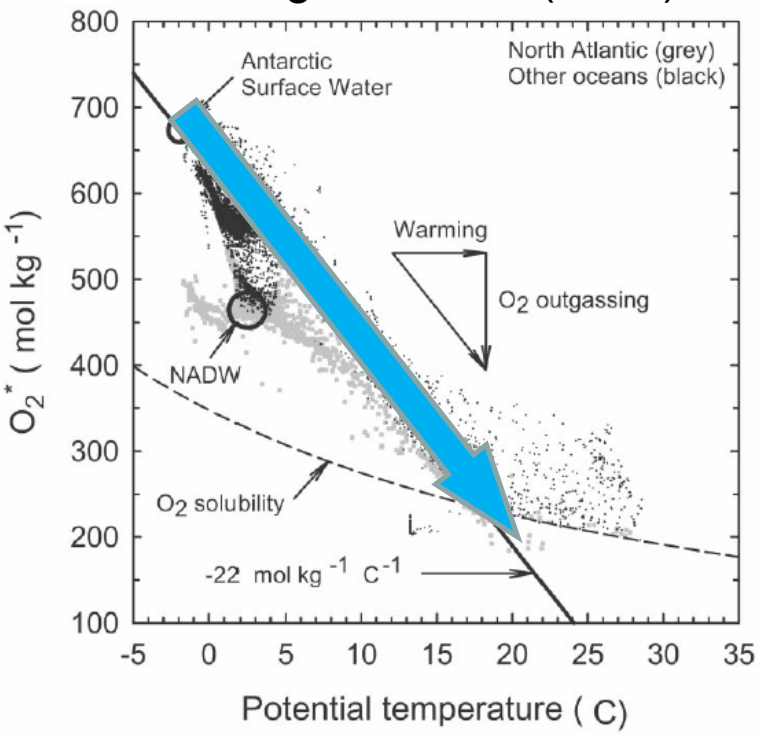
Estimation of the ocean outgassing effect

Willis et al. (2004)



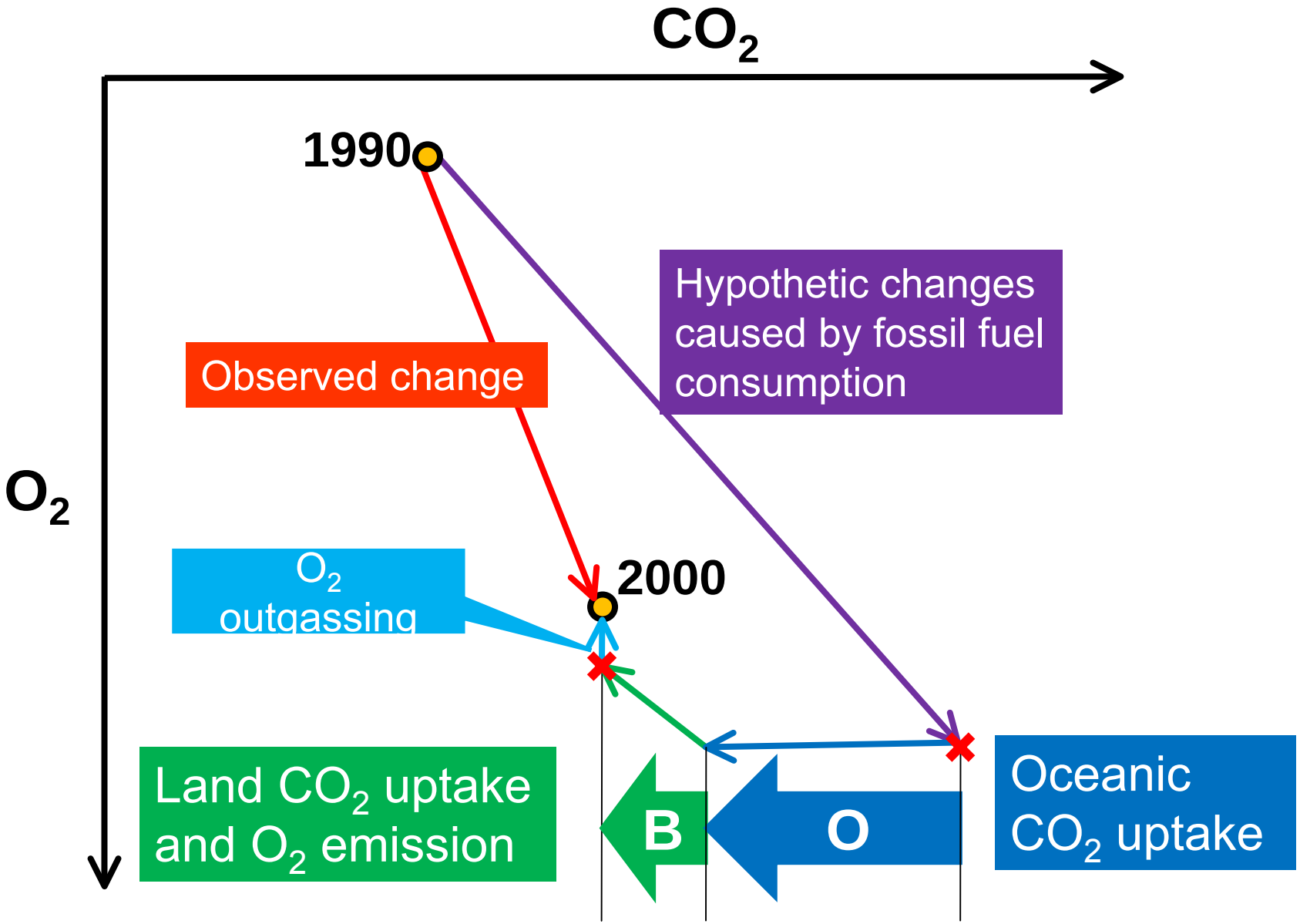
×

Keeling & Garcia. (2002)



O_2 outgussing = Net Ocean Heat Flux × Oceanic $\frac{O_2 \text{ Flux}}{\text{Heat Flux}}$ Ratio

Graphical explanation of budget calculation

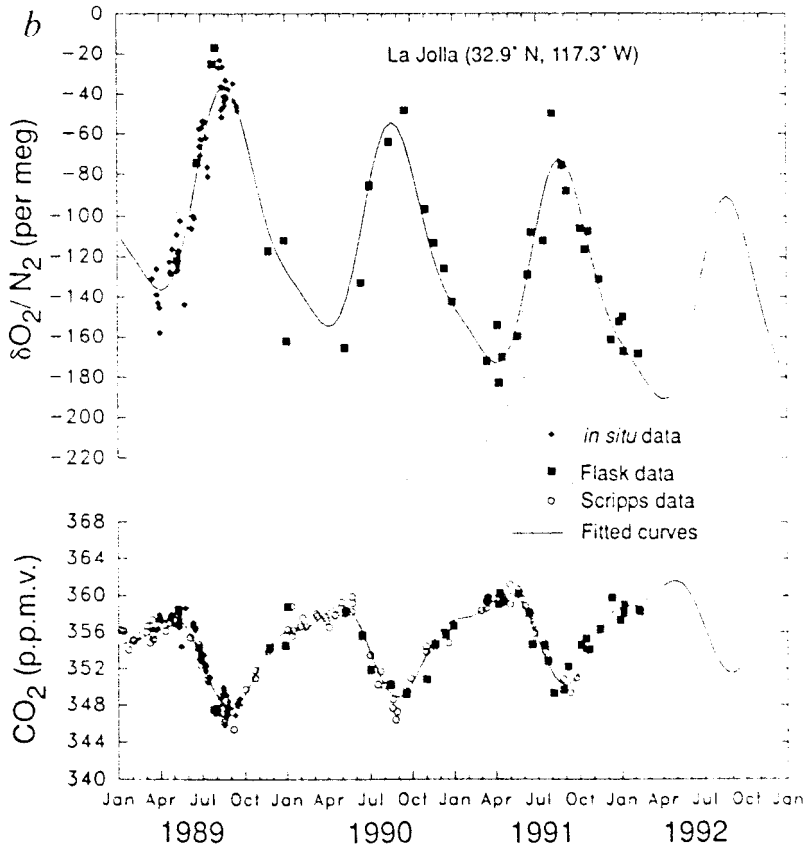


II. Analytical technique for the atmospheric O_2 change

Seasonal and interannual variations in atmospheric oxygen and implications for the global carbon cycle

Ralph F. Keeling & Stephen R. Sherze (1992)

Nature **358**, 723 (1992)



Methods to detect O_2 change in the atmosphere

Methods	Principle	References
Interferometer	Detecting Changes in the relative refractivity.	Keeling (1988)
Mass Spectrometer	Detecting Beams of masses 29 ($^{15}N^{14}N$) and 32 ($^{16}O_2$).	Bender et al. (1994)
Paramagnetic Oxygen Analyzer	Modifying a commercially available paramagnetic oxygen analyzer	Manning & Keeling (1999)
Fuel Cell	Garvanic fuel cell generates current proportional to O_2 partial pressure	Stephens et al. (2001)
VUV absorption	Measuring the absorption of VUV radiation (147nm)	Stephens et al. (2003)
Gas Chromatography	Detecting O_2 (+Ar) and N_2 peaks by TCD	Tohjima (2000)

Definition of $\delta(O_2/N_2)$
(Keeling & Shertz, 1992)

$$\delta(O_2/N_2) = \left\{ \frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{reference}} - 1 \right\} \times 10^6$$

Arbitrary reference scale

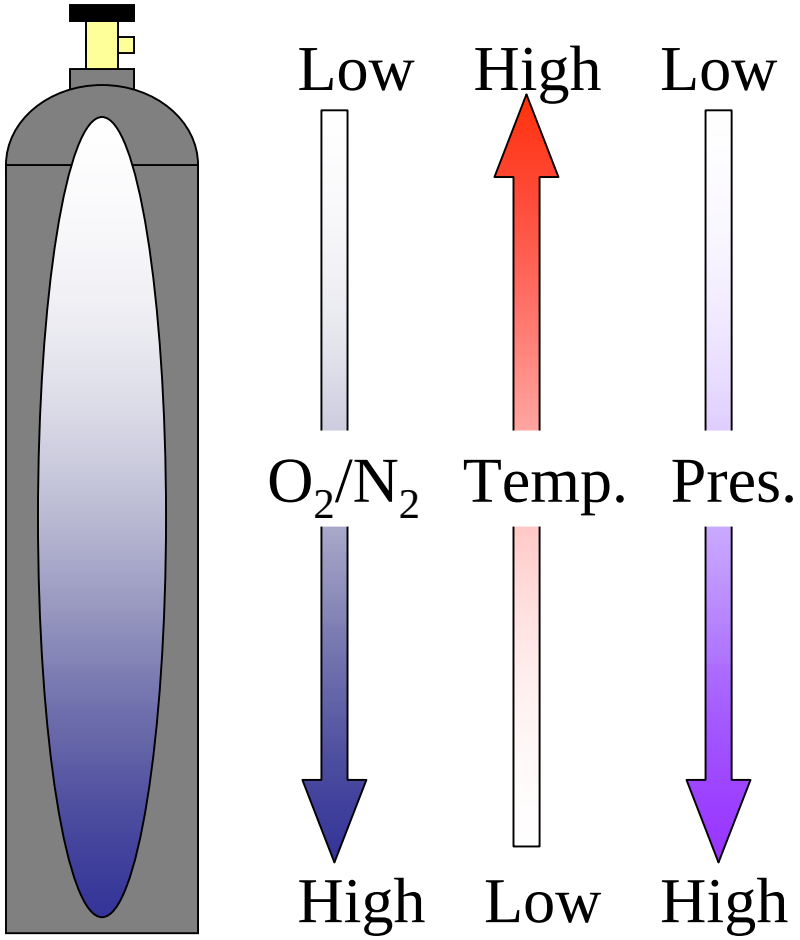
"per meg" unit;

4.8 per meg = 1 ppm of CO_2 in dry air

Atmospheric O_2 measurement is very challenging!

- The atmospheric O_2 change (~4 ppm yr^{-1}) is very small in comparison with its concentration (~20%).
- The O_2 concentration is easily fractionated during air sampling, storing, gas handling, and gas analyzing processes.
- There is no authorized reference for the O_2 measurements.

Cylinders should be laid horizontally! Not vertically!!



III. CO_2 budget calculated from O_2 and CO_2 measurements by NIES

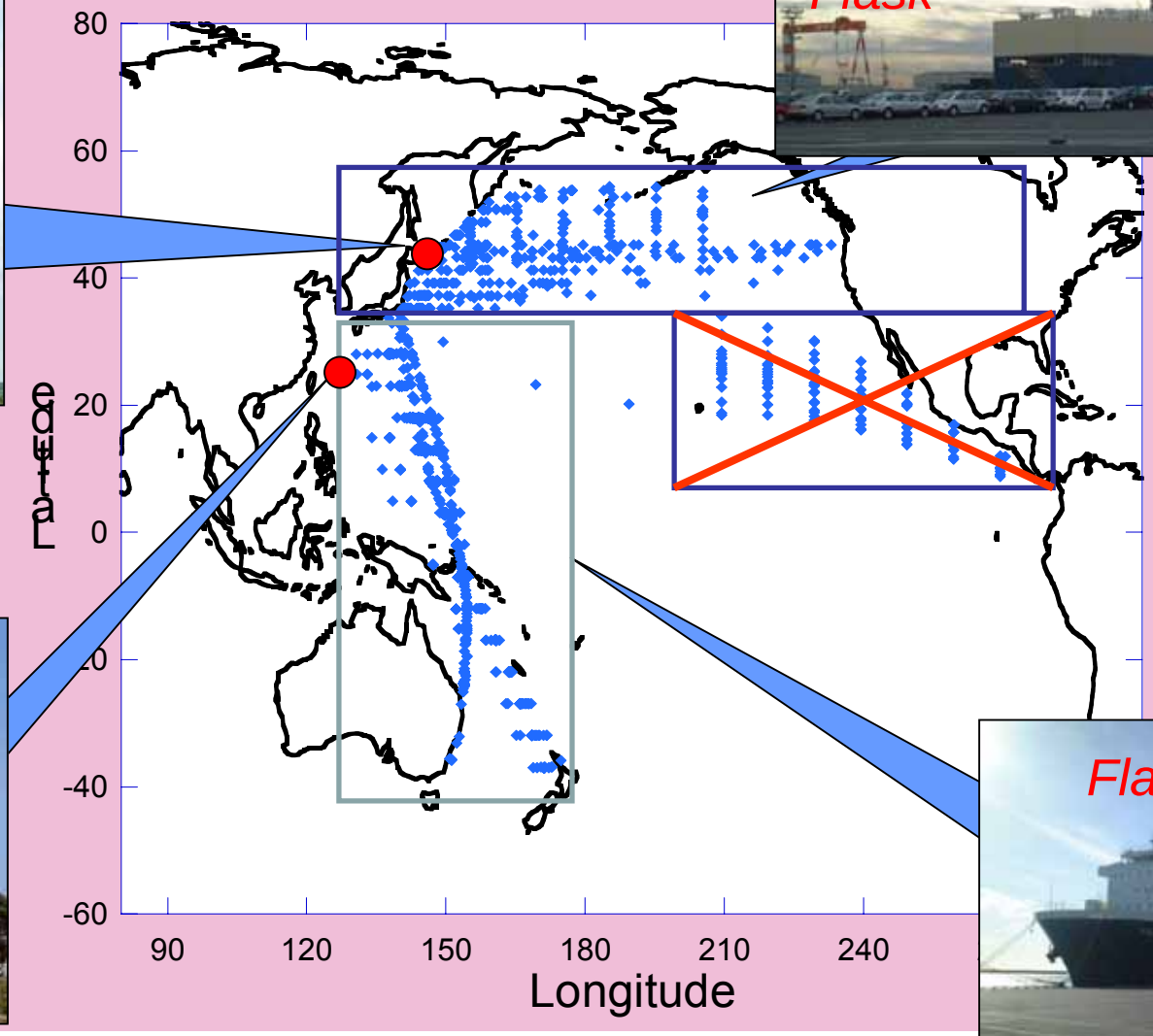
Distribution of flask sampling locations

Cape
Ochi-ishi

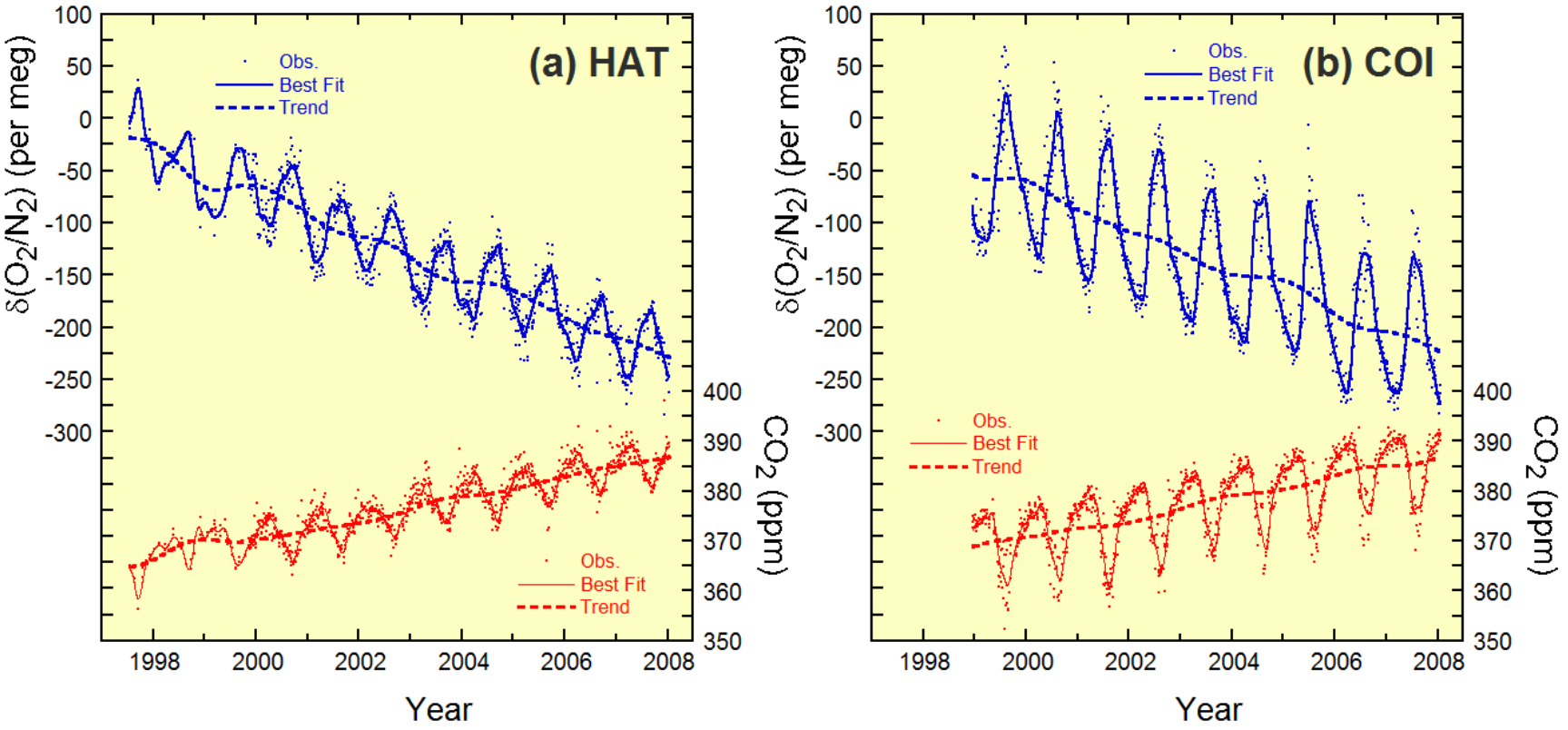
Hateruma Island

Skaubryn
& Pyxis

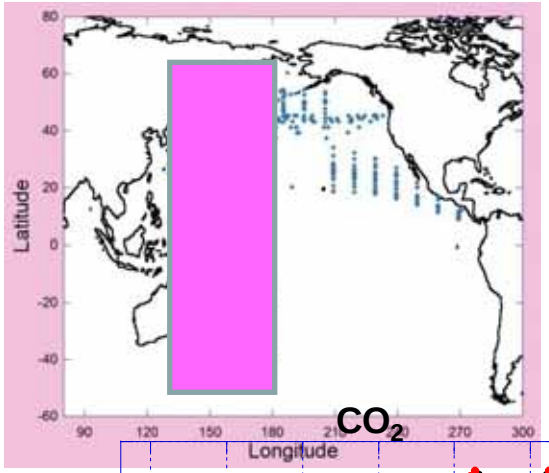
Fujitrans
Future

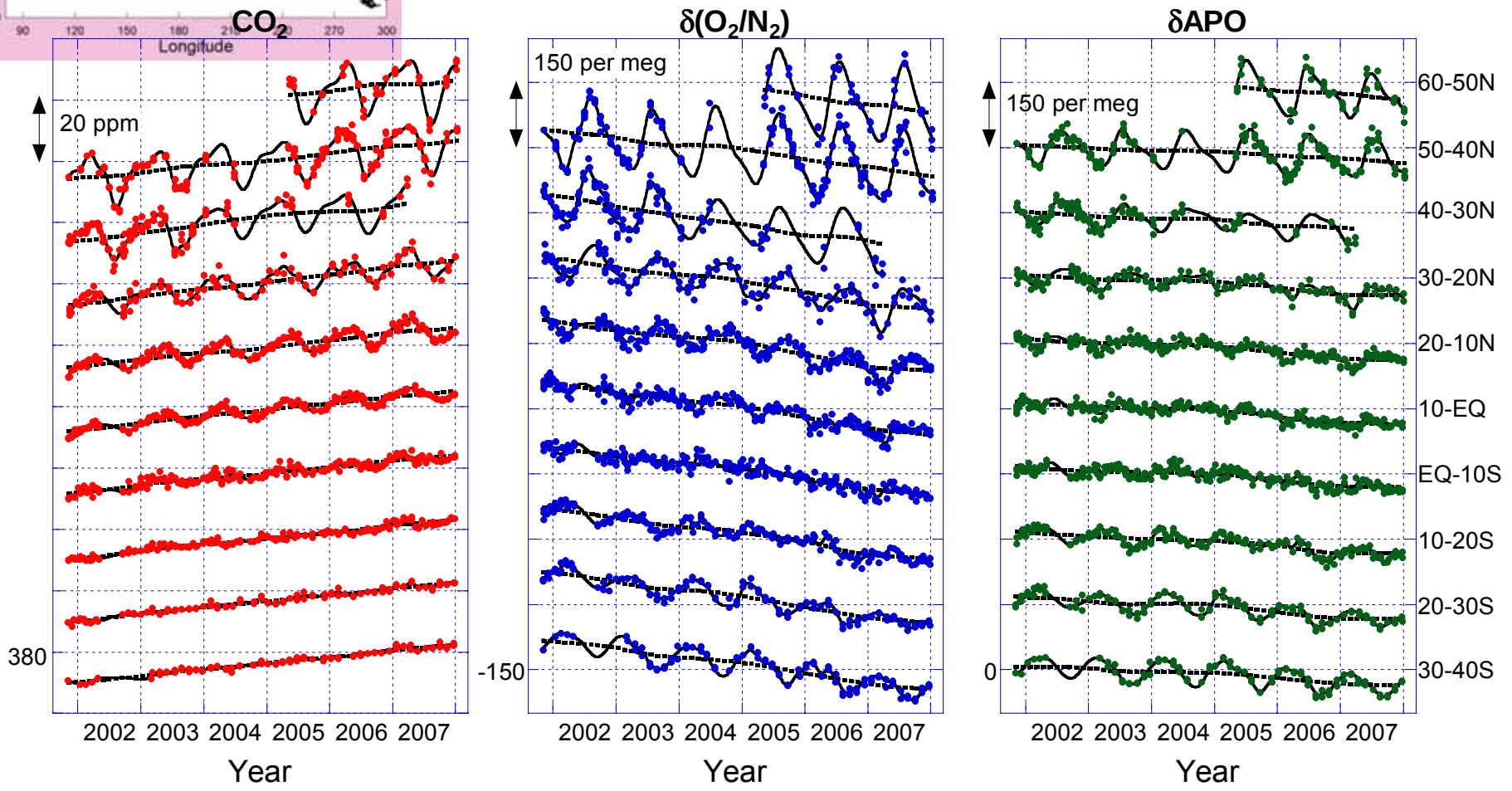


CO_2 and O_2/N_2 at HAT and COI

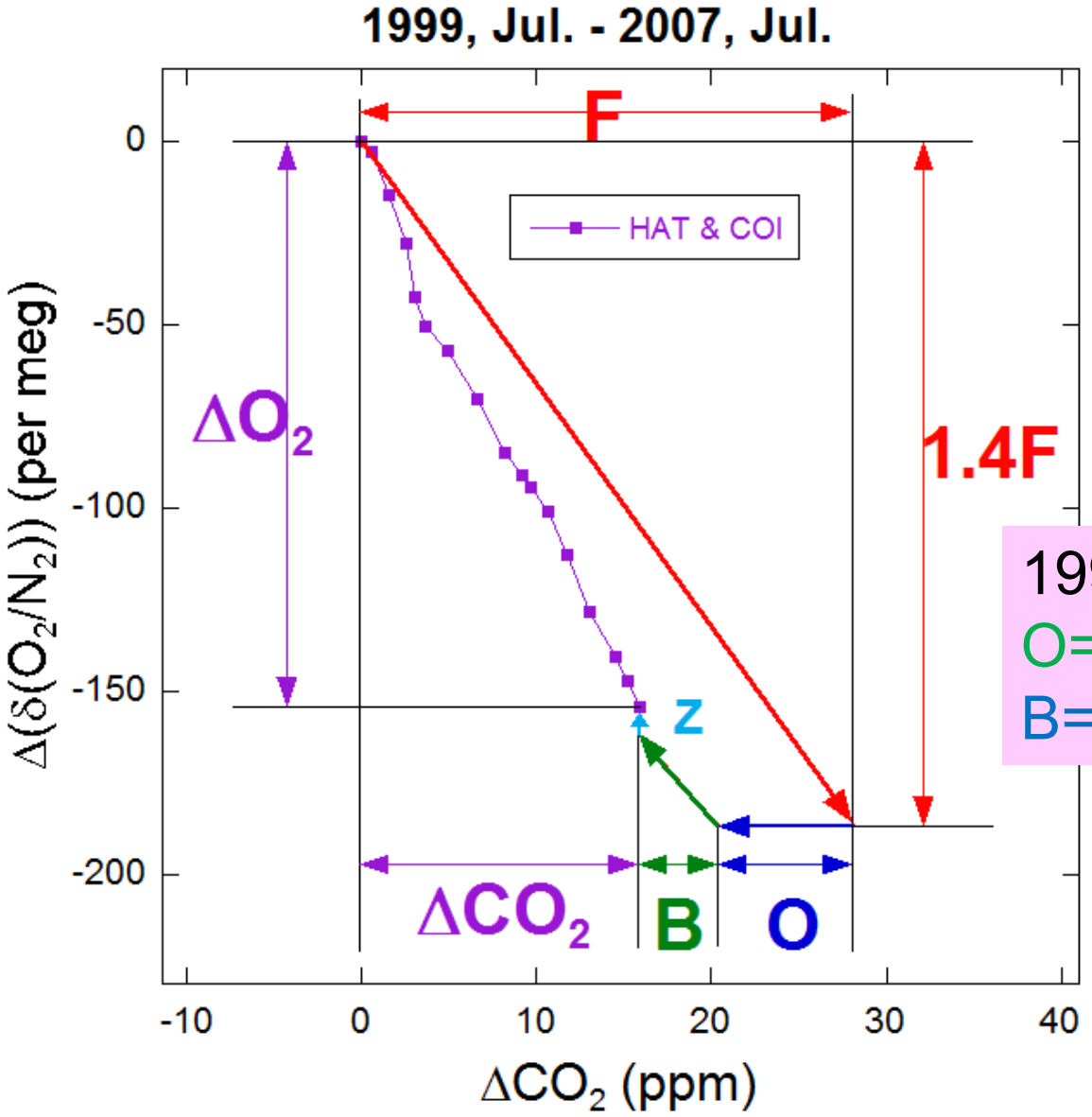


観測結果


Latitude
Longitude


CO2
20 ppm
380
2002 2003 2004 2005 2006 2007
Year
δ(O2/N2)
150 per meg
-150
2002 2003 2004 2005 2006 2007
Year
δAPO
150 per meg
0
60-50N
50-40N
40-30N
30-20N
20-10N
10-EQ
EQ-10S
10-20S
20-30S
30-40S
2002 2003 2004 2005 2006 2007
Year

Fossil CO_2 sequestration based on O_2 change



1999-2007
O=2.1 PgC yr^{-1}
B=1.1 PgC yr^{-1}

Recent O_2 based Carbon budgets

Time Periods	Sites	F	Z_{eff}	Ocean Sink	Land Sink
Tohjima et al., 2008 (Based on CDIAC 2008)					
99.5-05.5	HAT+COI	7.15	0.43	2.0±0.7	1.0±0.9
This study (Based on CDIAC 2008)					
99.5-07.5	HAT+COI	7.42	0.43	2.1±0.7	1.1±0.9
Bender et al., 2005 (Based on CDIAC 2008)					
93.5-02.5	CGO	6.58	0.43	2.3±0.5	0.6±0.6
Manning & Keeling, 2006 (Based on CDIAC 2008)					
93-03	ALT,LJO,CGO	6.58	0.43	2.2±0.6	0.6±0.7

(Units : GtC yr^{-1})

Estimates of uncertainties

Parameter	Sources	Uncertainty	Oceanic sink (Pg C yr^{-1})	Land sink (Pg C yr^{-1})
Fossil fuel	CDIAC	0.4 Pg C yr^{-1}	0.11	0.53
Z_{eff}	Manning & Keeling (2006)	0.48 Pg C yr^{-1}	0.44	0.44
ΔO_2	NIES	0.41 per meg yr^{-1}	0.17	0.17
Drift of O_2 scale	NIES	1.0 per meg yr^{-1}	0.40	0.40
O2:CO2 exchange ratio		0.04	0.25	0.25
Square root of the square sum			0.68	0.86

Summary

- The oceanic and terrestrial sinks are 2.1 PgC yr^{-1} and 1.1 PgC yr^{-1}, respectively, for the 8-year period (1999.5-2007.5).

- To achieve more accurate estimates, we need reduce the uncertainties of
  - Fossil fuel carbon emission
  - Ocean degassing effect
  - Reference scale stability

Thank you for your attention.