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High-accuracy atmospheric O_2 measurements. (Too) challenging for quantitative preparation of reference gases

Highgas stakeholder workshop

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High-accuracy atmospheric O_2 measurements. (Too) challenging for quantitative preparation of reference gases

Contents

Greenhouse gas CO_2 and the carbon cycle

Partitioning of terrestrial and oceanic uptake

Measuring atmospheric Oxygen

Relative accuracy and measurement systems

Reference gases

Conclusions: use the O_2 measurement capability as benchmark

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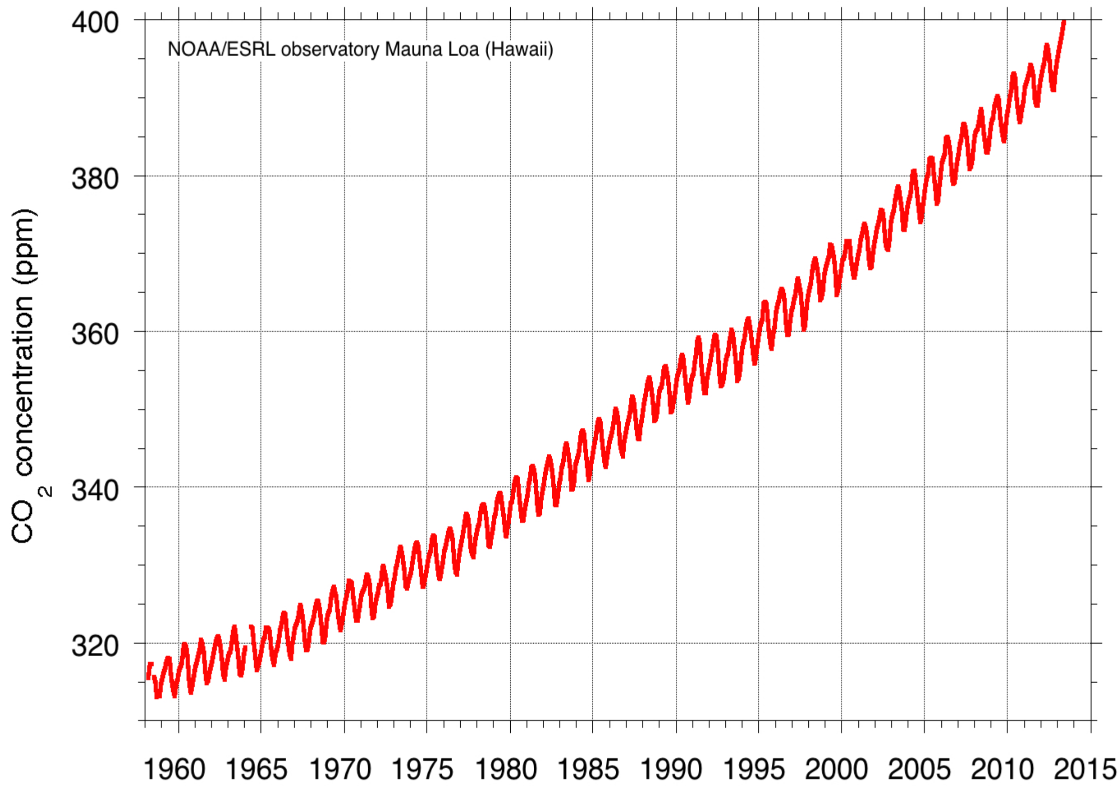
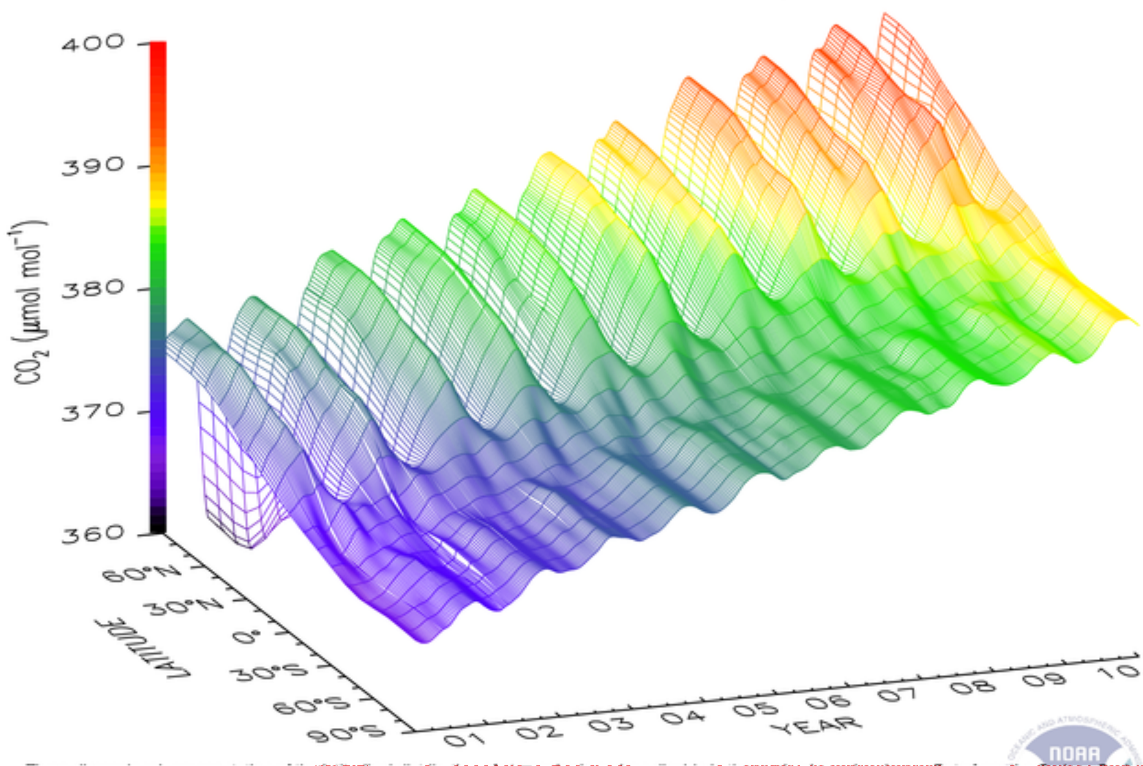
CO_2 concentration in the atmosphere



Global Distribution of Atmospheric Carbon Dioxide

NOAA ESRL Carbon Cycle



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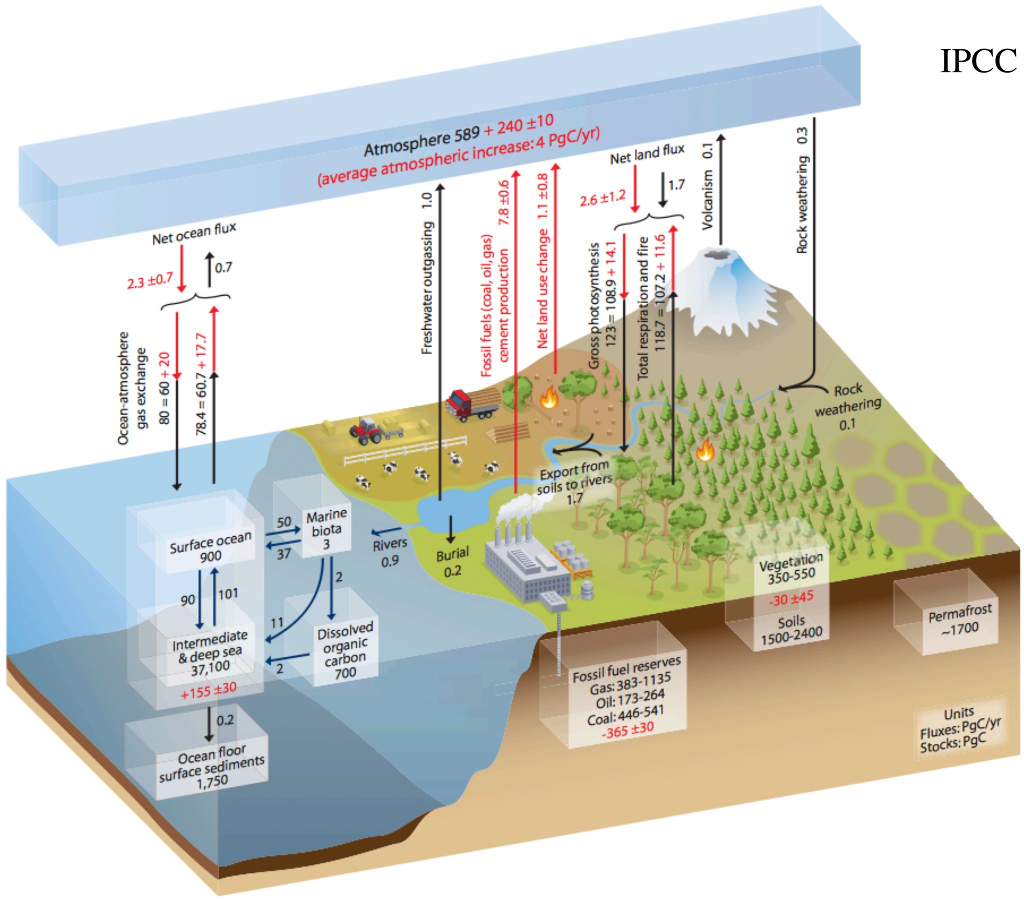
IPCC AR5



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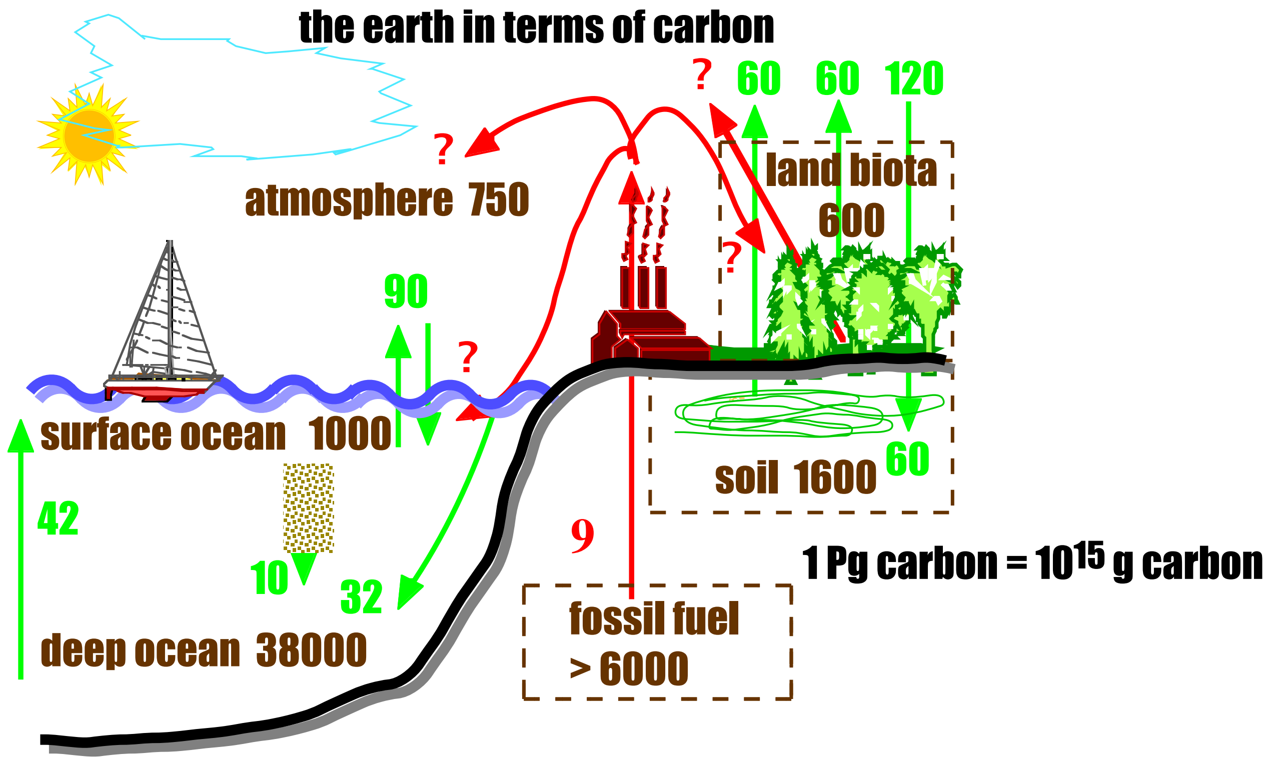


reservoirs in Pg C
natural cycle in Pg C/yr
fossil fuel usage in PgC/yr

Carbon Balance:a global view

well measurable in the atmosphere !

known from commercial statistics to ±10-15%

the sum follows, breakdown very uncertain

$$\Delta C_a = C_f + \Delta C_{oc} + \Delta C_{tb}$$

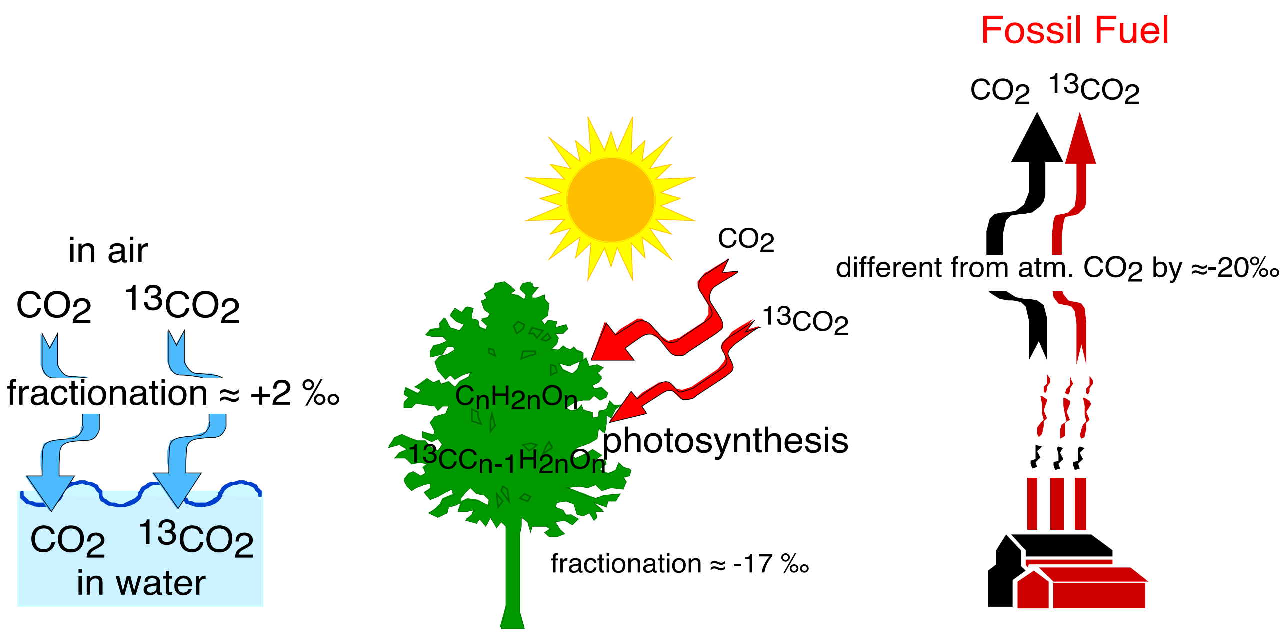
SINK: CO_2 dissolves

SINK: reforestation CO2 "fertilisation" SOURCE: deforrestation erosion

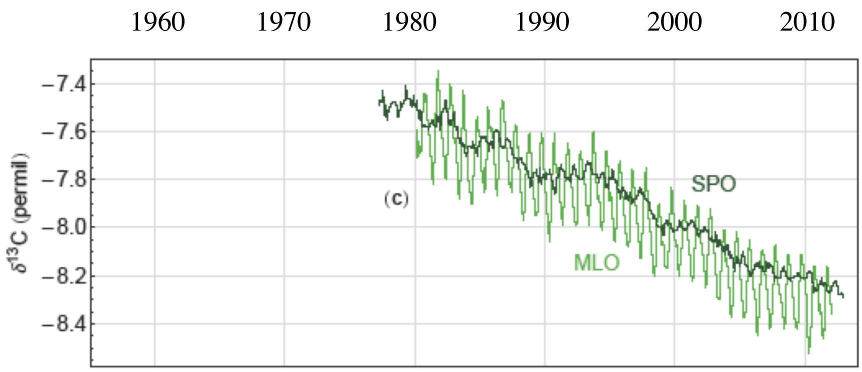
Years	FF input	Atmospheric Increase	Ocean uptake	Net Land Uptake
2002-2011	8.3 ± 0.7	4.3 ± 0.2	2.4 ± 0.7	1.6 ± 1.0

IPCC best numbers

Partitioning of land and ocean processes using $^{13}CO_2$



$\delta^{13}C$ is a very complicated parameter

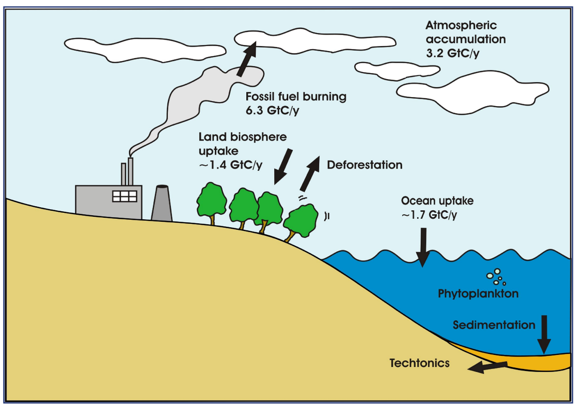


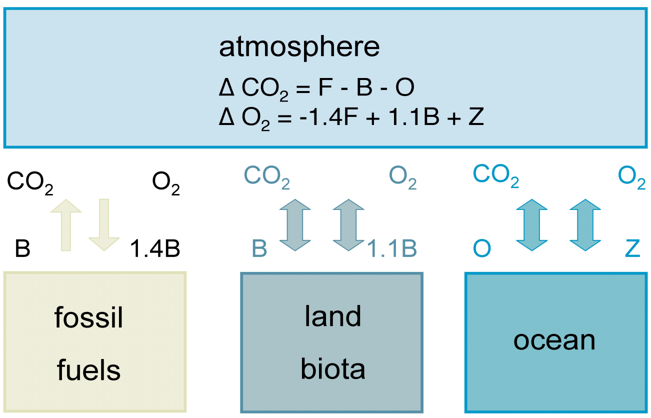
The signal is very small, variable, and influenced by a large number of effects

Also, the scale/calibration stability both intra- and interlaboratory over the years is a real challenge

Other valuable tracer: Atmospheric Oxygen

- O_2 and CO_2 show inverse behaviour in land processes: photosynthesis, respiration and fossil fuel combustion
- Independent behaviour in marine processes





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Atmospheric O_2 concentration

Concentration in air: ≈ 21%

Expected signals:

seasonal cycle	ca 20 ppm
annual trend	ca -2 ppm

Accuracy required :

≤ 1 ppm; equivalent to ≤ 1:2 x 10^5 !!

Relative measurements $[O_2] / [N_2]$ using Isotope Ratio Mass Spectrometry :

"as if O_2 and N_2 were each others isotopes"

$$\delta (O_2/N_2) = \frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{ref}} - 1$$ in "permeg"

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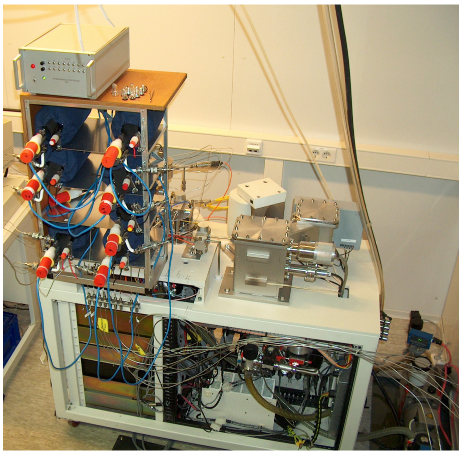
Measuring atmospheric Oxygen

- O_2 originally measured vs (almost constant) N_2 (using IRMS):

$$\delta(O_2/N_2) = \left[\frac{(O_2/N_2)_{sample}}{(O_2/N_2)_{reference}}\right] - 1 \quad \text{(in per meg)}$$

"as if O_2 and N_2 were each others' isotopes"



- 1 per meg = 0.20946 ppm (but....)
- O_2/N_2 unaffected by other variable atmospheric gases
- Only flask samples (not on-line)
- For other measurement methods, that measure oxygen abundances, scale conversion using reference gases is needed

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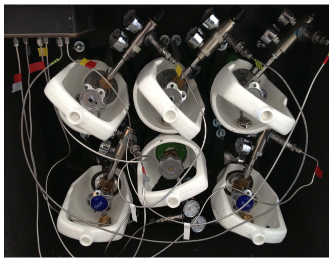
Design of a semi-continuous O_2 instrument

the equipment in three “flight cases” (or road cases)

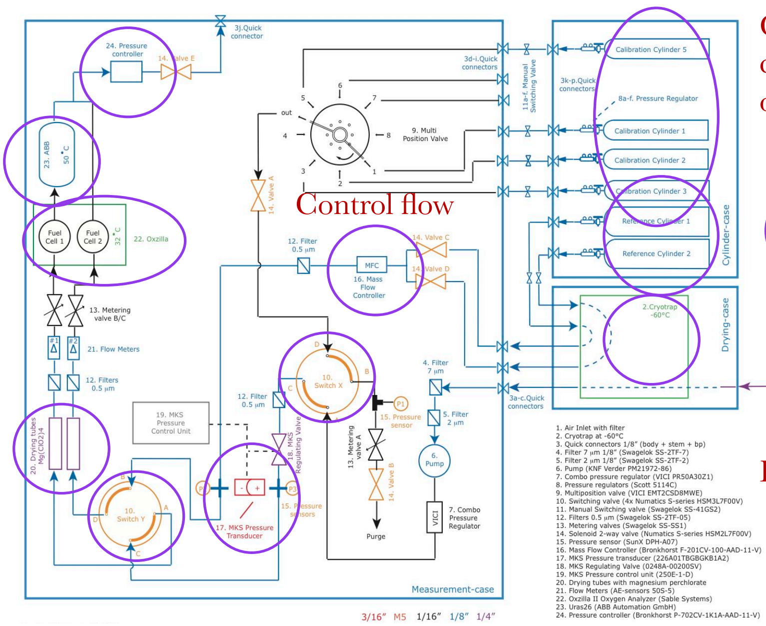
the heart of the system: **“differential” fuel cell** oxygen measurement system



the reference and calibration cylinders

-60°C **drying system,** with $Mg(ClO_4)_2$ trap follow-up

The CO_2 / O_2 device: under the hood



Once in a while calibration cylinders are measured instead of air

Regulate the pressure

Air inlet

Reference cylinder

Dry the air

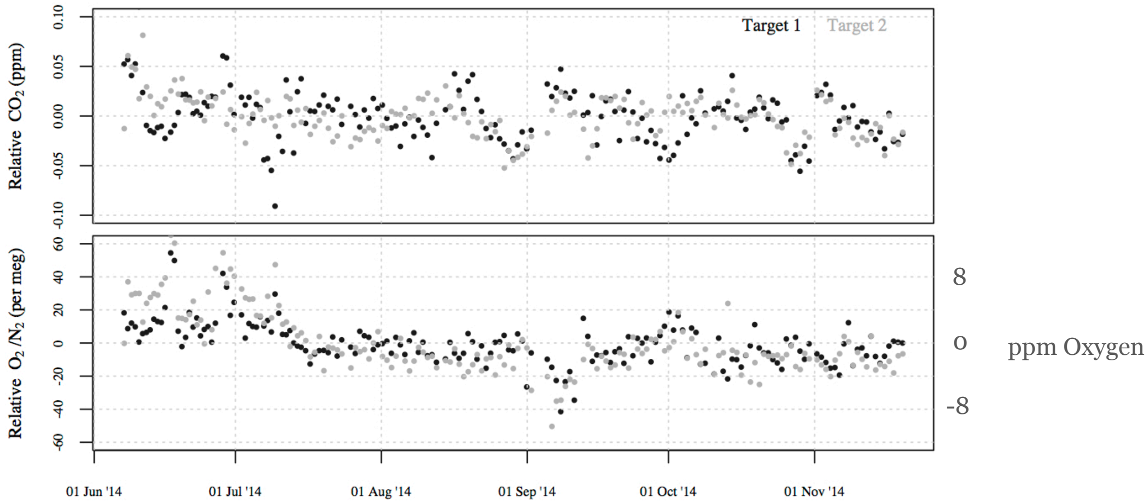
Equalize the pressure in both lines

Reference and air are switched every 3 minutes

Measure oxygen concentration in two lines (Oxzilla dual fuel cell device)

Measure CO_2 concentration using the ABB NDIR device (URAS 26)

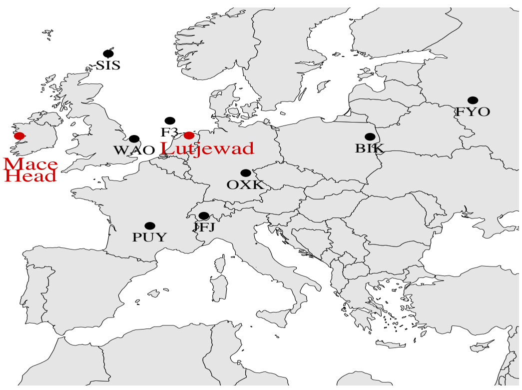
Quality of the measurements



	CO_2 (ppm)		O_2 / N_2 (per meg)	
	Target 1	Target 2	Target 1	Target 2
Average stdev within a target run (n = 48)	0.011	0.010	12	15
Stdev of all target runs (n = 48)	0.021	0.018	8	8
Stdev of pairs, averaged (n = 47)	0.011	0.009	5	6

so in the 2-3 ppm range!

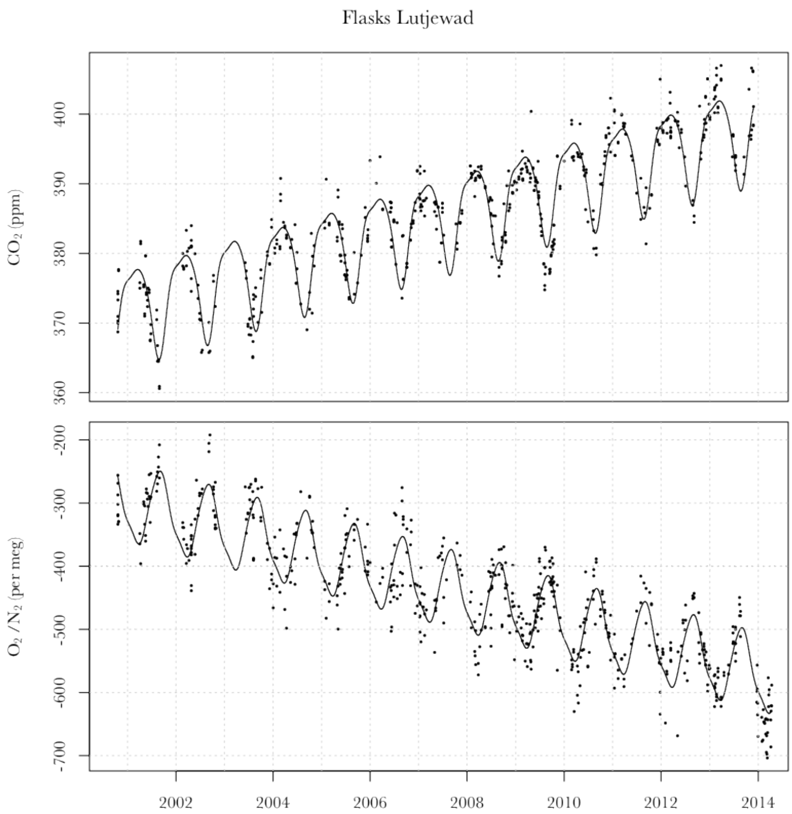
Atmospheric O_2 in Europe



Groups capable of O_2 measurements:

UEA, Norwich, UK
UoG, Groningen, NL
MPI BGC Jena, D
UBern, Bern, CH

(and LSCE, Gif, F, but currently no station in Europe)



Atmospheric monitoring station Lutjewad

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System Performance in Groningen

O_2 DI Optima IRMS
flask precision (duplicates) ≤ 4 per meg
internal scale stability ≈ 2 per meg
Cylinder precision (single mm) :≈ 10 per meg until Jan 2015 (regulators!)
after that date improved to ≈ 6 per meg

5 per meg ≈ 1 ppm

Calibration on the "Scripps" scale depends on
infrequent and few **cylinder measurements**.
The scale is maintained at Scripps Institute of Oceanography, UC San Diego
Cylinders shipped world-wide
Intercomparison rounds organised in Europe by UEA

Compare:
CO_2 (GC and Picarro CRDS)
Accuracy < 0.1 ppm (WMO X2007 scale)

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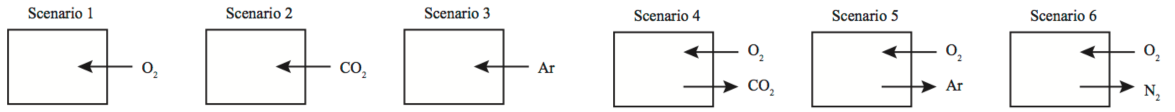
per megs and ppm's, a complicated matter



Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5	Scenario 6
The O_2 mole fraction changes: $\left(\frac{209461}{1000001}-\frac{209460}{1000000}\right)$ **= 0.79 µmol/mol**	**The O_2 mole fraction changes:** $\left(\frac{209460}{1000001}-\frac{209460}{1000000}\right)$ **= -0.21 µmol/mol**	**The O_2 mole fraction changes:** $\left(\frac{209460}{1000001}-\frac{209460}{1000000}\right)$ **= -0.21 µmol/mol**	**The O_2 mole fraction changes:** $\left(\frac{209461}{1000000}-\frac{209460}{1000000}\right)$ **= 1 µmol/mol**	**The O_2 mole fraction changes:** $\left(\frac{209461}{1000000}-\frac{209460}{1000000}\right)$ **= 1 µmol/mol**	**The O_2 mole fraction changes:** $\left(\frac{209461}{1000000}-\frac{209460}{1000000}\right)$ **= 1 µmol/mol**
The O_2/N_2 ratio changes by: $\left(\frac{209461/780800}{209460/780800}-1\right)$ **= 4.77 per meg**	**The O_2/N_2 ratio changes by:** $\left(\frac{209460/780800}{209460/780800}-1\right)$ **= 0 per meg**	**The O_2/N_2 ratio changes by:** $\left(\frac{209460/780800}{209460/780800}-1\right)$ **= 0 per meg**	**The O_2/N_2 ratio changes by:** $\left(\frac{209461/780800}{209460/780800}-1\right)$ **= 4.77 per meg**	**The O_2/N_2 ratio changes by:** $\left(\frac{209461/780800}{209460/780800}-1\right)$ **= 4.77 per meg**	**The O_2/N_2 ratio changes by:** $\left(\frac{209461/780800}{209460/780800}-1\right)$ **= 6.05 per meg**
Using equation 1.2: $\frac{0.79+0}{(1-0.20946)*0.20946}$ **=4.77 per meg**	**Using equation 1.2:** $\frac{-0.21+1*0.20946}{(1-0.20946)*0.20946}$ **0 per meg**	**Using equation 1.2:** $\frac{-0.21+0}{(1-0.20946)*0.20946}$ **=-1.26 per meg**	**Using equation 1.2:** $\frac{1+1*0.20946}{(1-0.20946)*0.20946}$ **=4.77 per meg**	**Using equation 1.2:** $\frac{1+0}{(1-0.20946)*0.20946}$ **6.04 per meg**	**Using equation 1.2:** $\frac{1+0}{(1-0.20946)*0.20946}$ **=6.04 per meg**
per meg / ppm: **4.77 / 0.79 = 6.04**	**per meg / ppm:** **0**	**per meg / ppm:** **0 or 6.05**	**per meg / ppm:** **4.77 / 1 = 4.77**	**per meg / ppm:** **4.77 or 6.04**	**per meg / ppm:** **6.05 or 6.04**

	Start situation	New situation	Change in ppm
Total number of molecules	1,000,000	1,000,001	
Number of O_2 molecules	210,000	210,000	
Percentage O_2 molecules	21	20.999979	0.21
Number of CO_2 molecules	400	400	
Percentage CO_2 molecules	0.04	0.0003999996	0.0004

Reference gases

Typical demand: O_2/N_2 ≤ 2 per meg (WMO) (≅ 0.4 ppm)

Relative accuracy of the instrumentation is much better than the absolute one

All gases matter: O_2, N_2, Ar, CO_2,...

Air needs to be absolutely dry (1ppm H_2O corresponds to 0.2 ppm deviation)

dew point ≈ -80 °C

O_2/N_2 measurements are less vulnerable than O_2 abundance measurements, but both need to be accomodated

So: gravimetrical mixing with accuracy ≤1 ppm N_2 on 78%, ≤1 ppm O_2 on 21%,...

Probably still out of reach??

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The bright side

The developed O_2 measurement techniques offer an unsurpassed scrutiny on mixing capabilities:

"do the best you can, and O_2/N_2 measurements will tell how good you really are"

The extremely high relative O_2 precision has brought many small effects to light:

- pressure regulator effects
- "fractionation" caused by splitting of inlet lines (flow and temperature-dependent)
- Gravitational settling in (vertical) cylinders, therefore all O_2 reference cylinders are kept horizontal, at constant temperature, and with a dip tube
- "aspirated" inlets are necessary in stations
- the great majority of materials influences the O_2 concentration
- getting and keeping cylinder air dry is a challenge
- ...

So: use the O_2/N_2 measurement capacity as benchmark for gravimetrical mixing quality

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