

Towards on-line monitoring of ^{14}C in atmospheric CO_2

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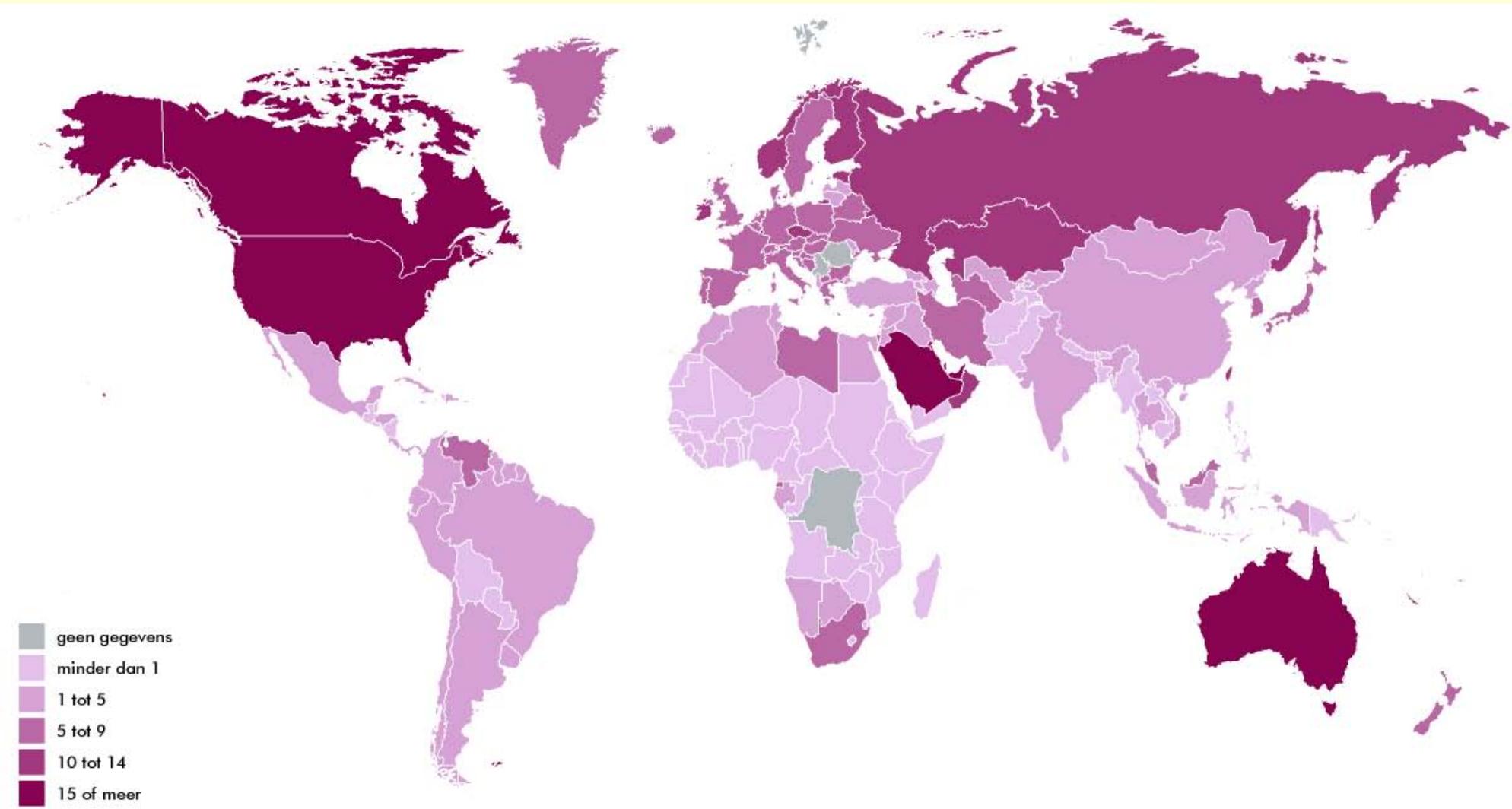
*NOAA Earth System Research Laboratory
Global Monitoring Annual Conference
Boulder, May 18&19, 2011*

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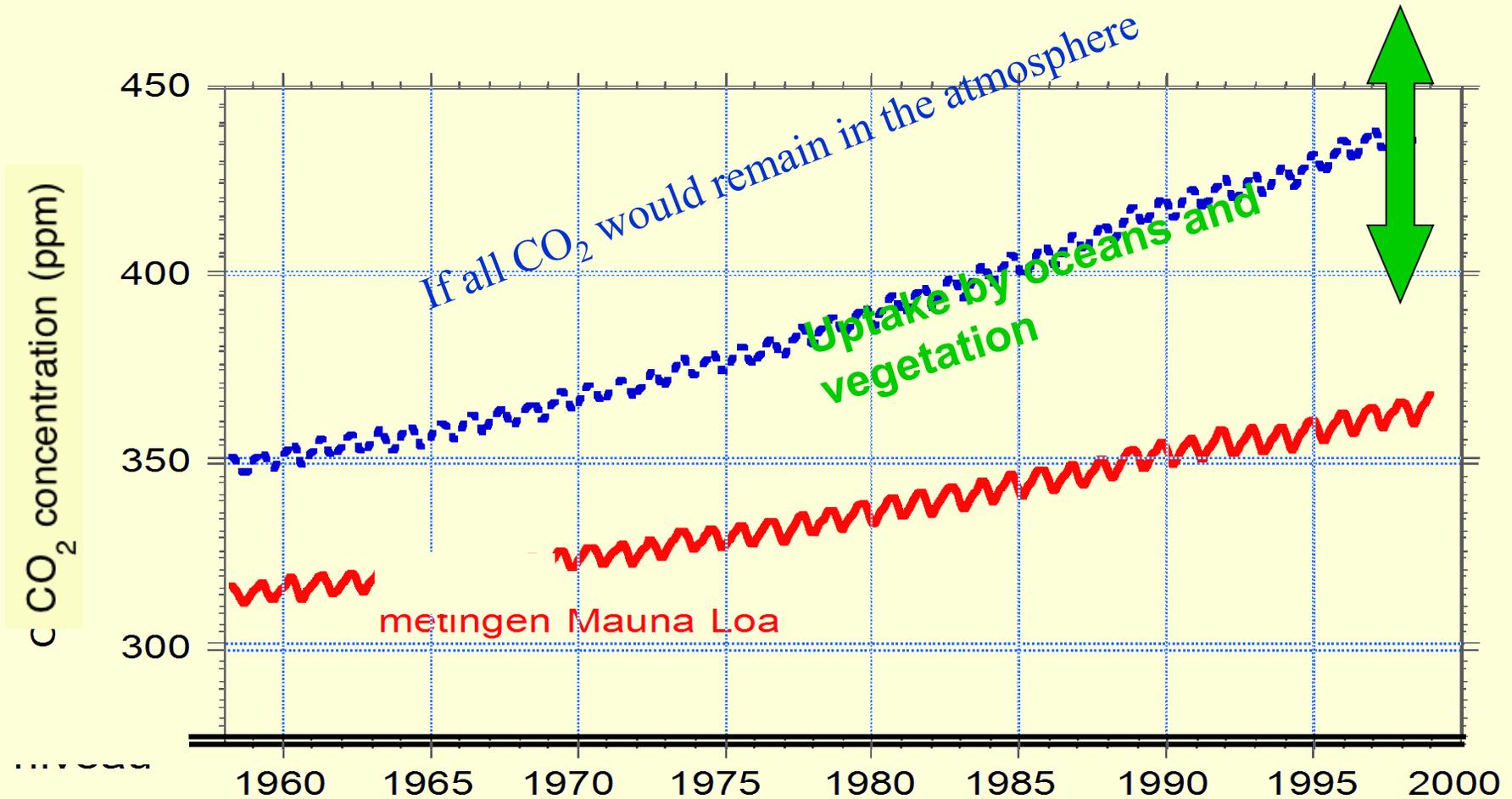
◆ Why?

◆ How?

Anthropogenic CO₂ production

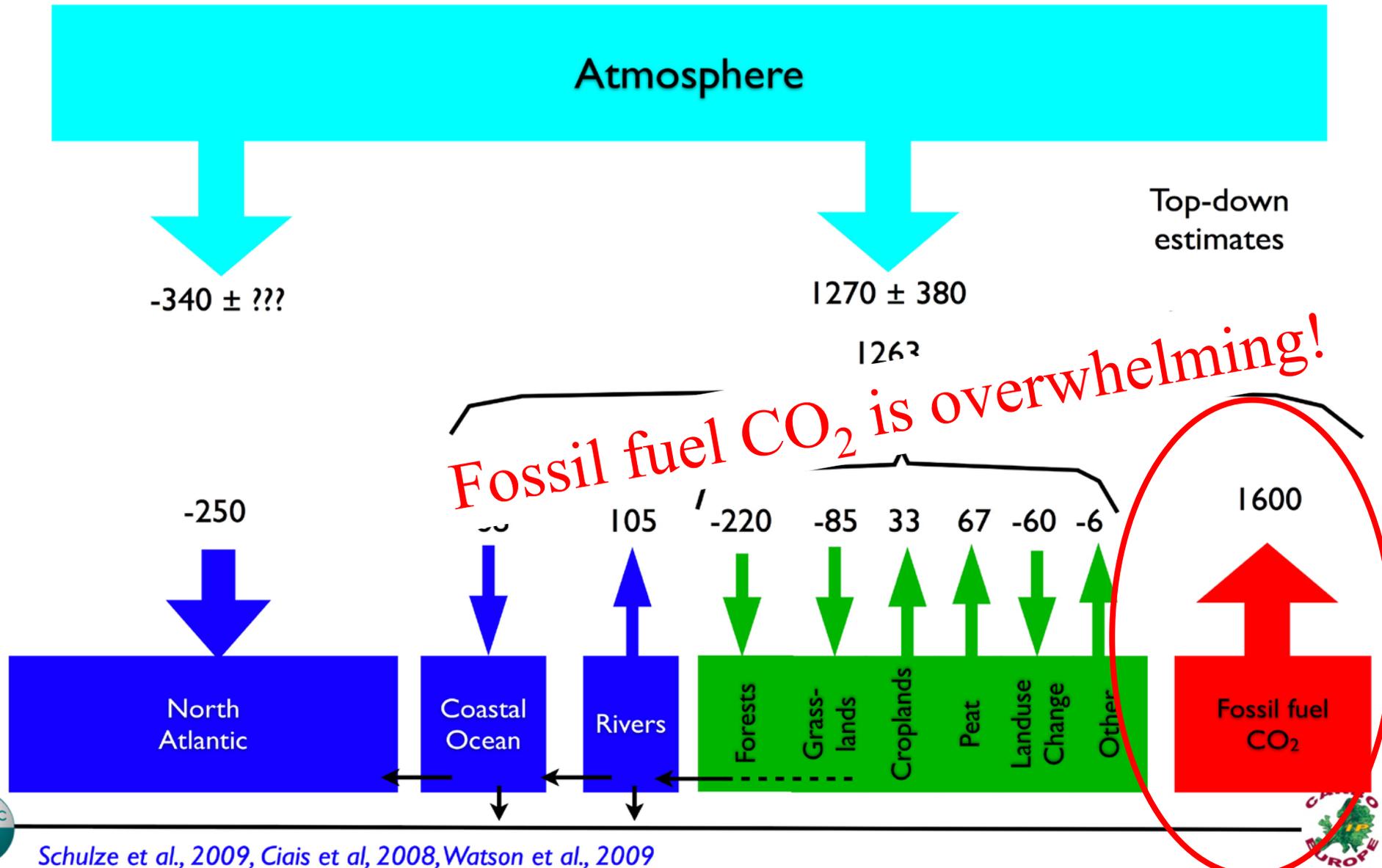


The increase of atmospheric CO₂ is half of what we expect



The European carbon balance (TgC/yr)

(positive numbers: flux into the atmosphere)



Need of methods to distinguish “natural” from fossil CO₂

- Fossil fuel CO₂ is by far the dominant net source
- Commercial statistics are not accurate enough: neither in place, nor in time
- The Kyoto (and successor!) treaties require reliable and verifiable CO₂ emission data to independently check measures and agreements

#1 candidate:

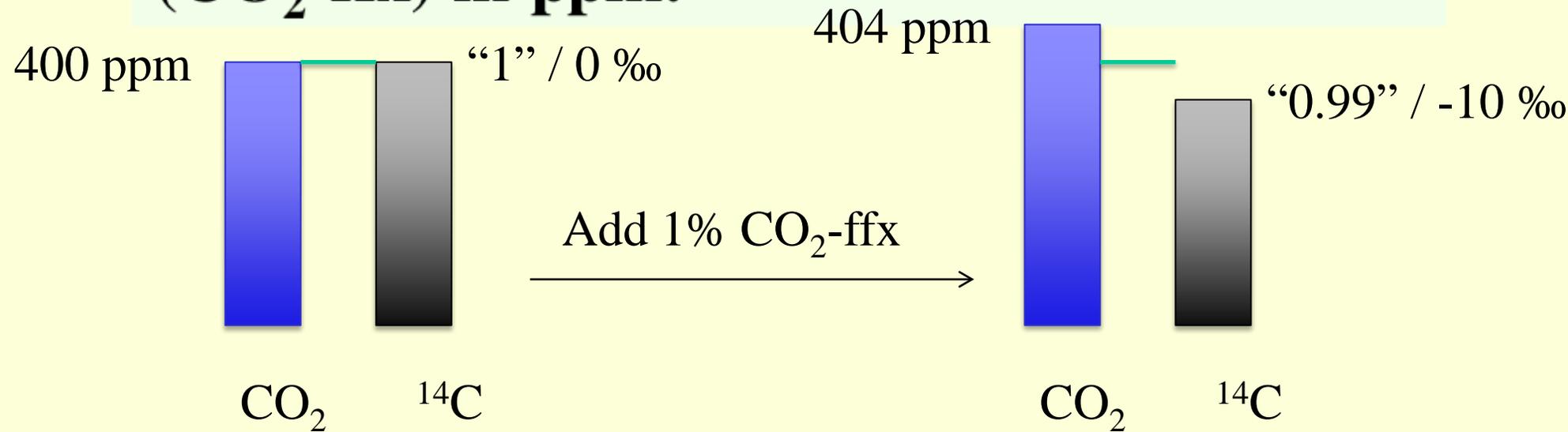
¹⁴C: “Radiocarbon”



^{14}C or Radiocarbon

- Radio-active (half life 5730 yrs), so fossil fuel is ^{14}C -free
- Extremely rare: abundance of 10^{-12} in modern carbon

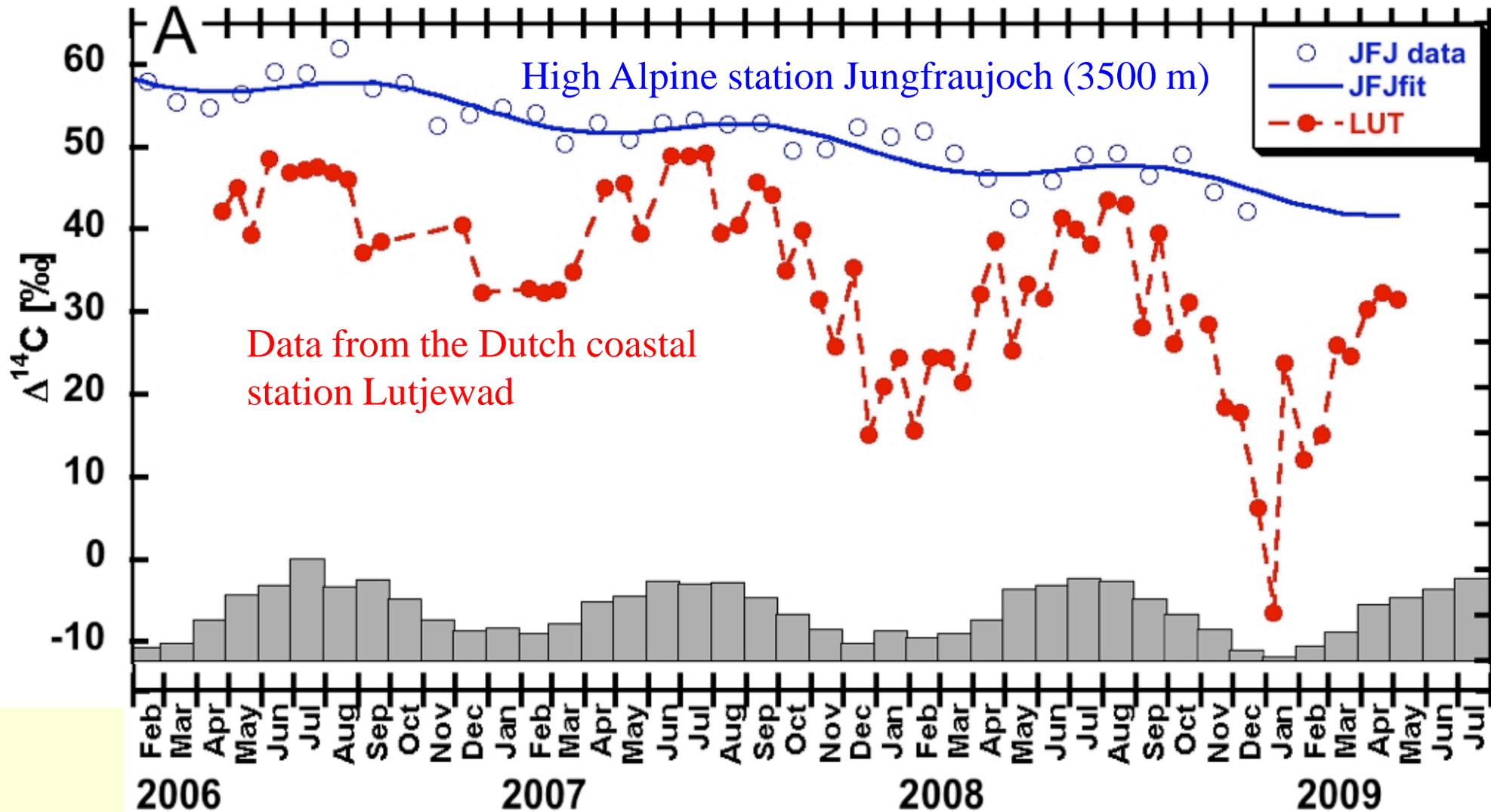
Calculation of regional CO_2 -ff excess (CO_2 -ffx) in ppm:



1 ‰ precision in ^{14}C corresponds to 0.4 ppm CO_2 -ffx



$^{14}\text{CO}_2$ in The Netherlands compared to European background



Van der Laan et al.,
Tellus (2010), 62B, 389–402

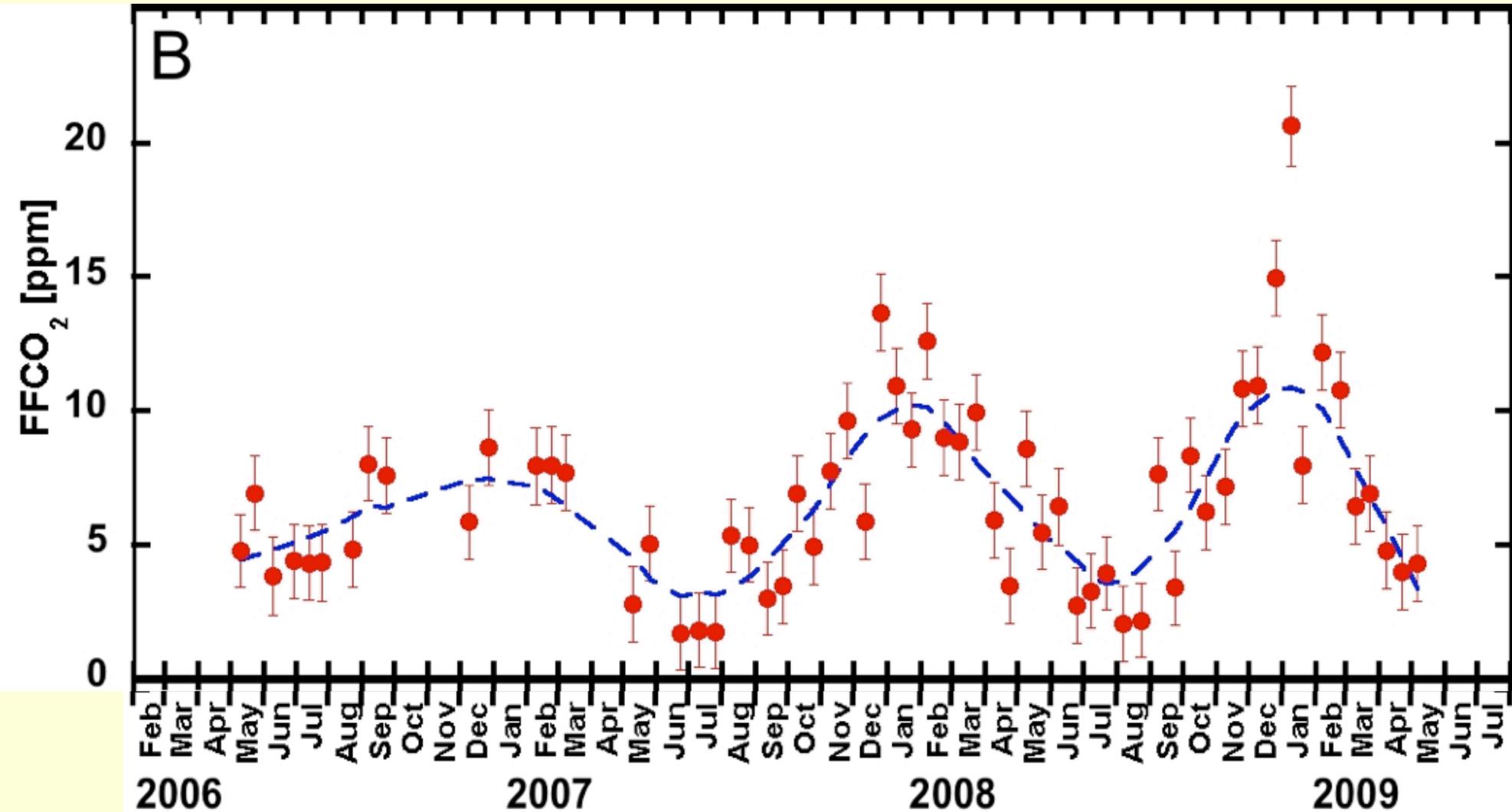


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Measurements of the fossil fuel CO₂ concentration for the Netherlands



^{14}C measurements are expensive and labor-intensive

Samples need to be taken individually (either “grab samples” or integrated ones)

Need to be transported to an AMS facility

Need extensive pretreatment: Extraction of CO_2 , graphitization, target preparation

Require a complicated and expensive facility:



AMS installation CIO Groningen University



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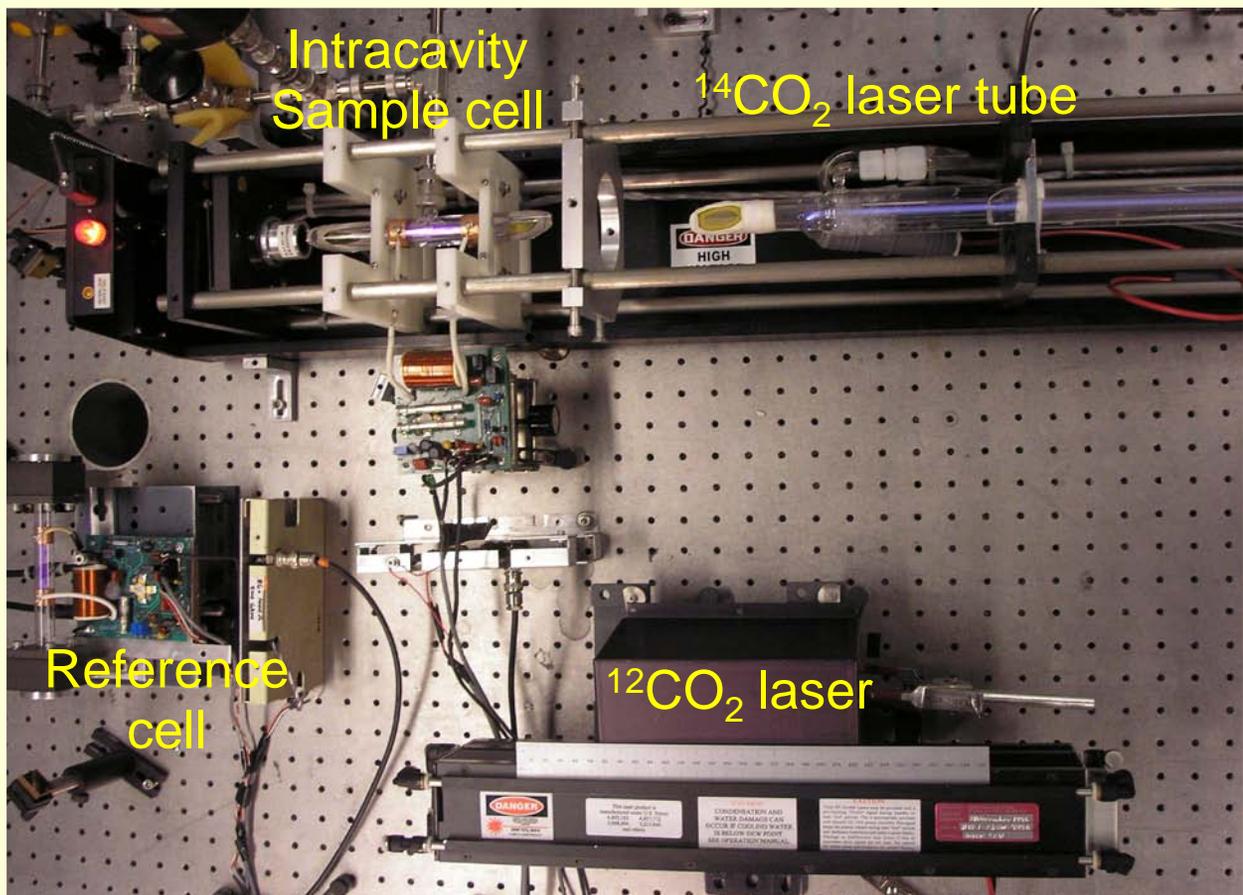
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The alternative: ICOGS

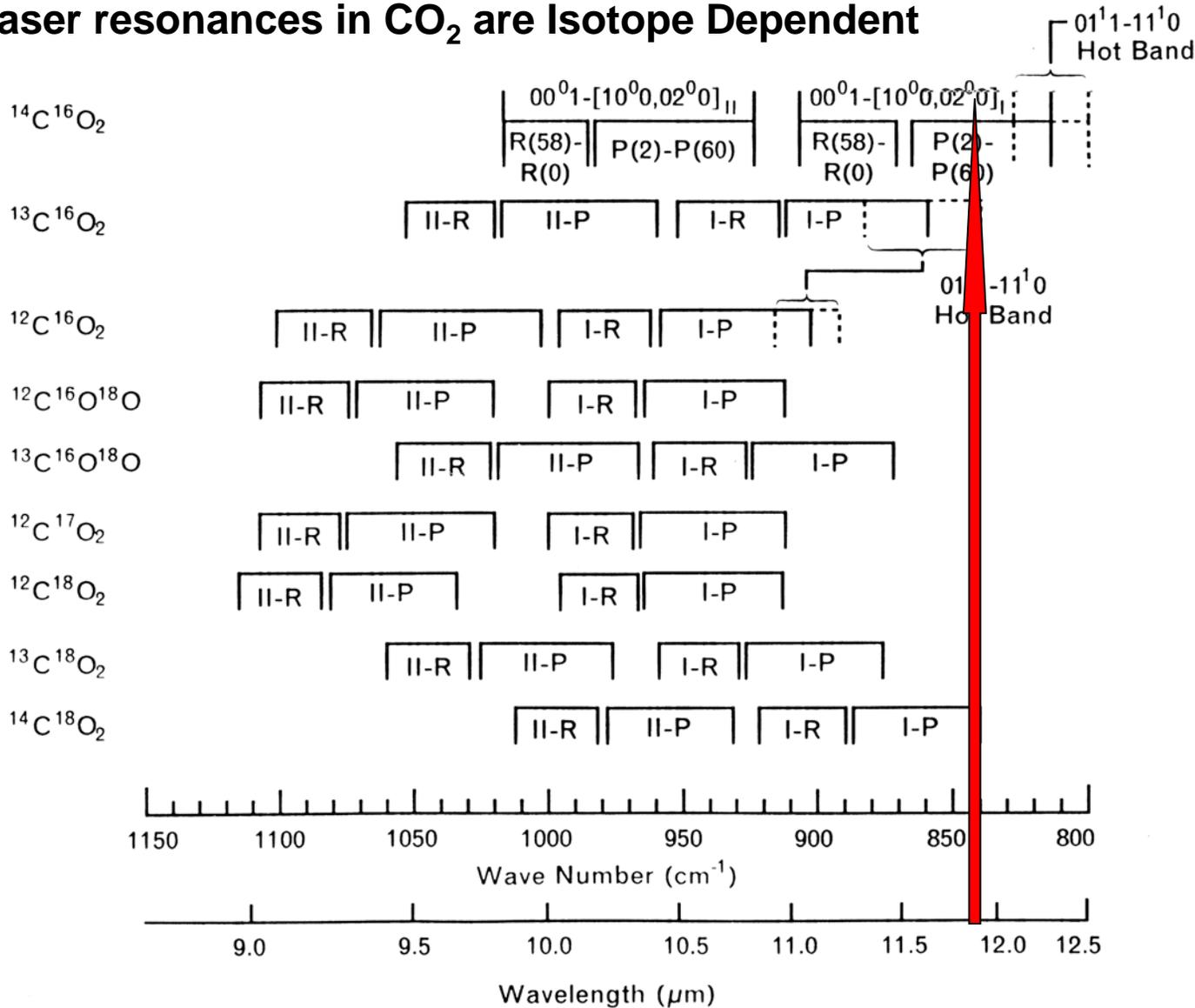
Intra Cavity Opto Galvanic Spectroscopy

Potential for continuous
in situ $^{14}\text{CO}_2$
measurements

Daniel E. Murnick et al.,
Analytical Chemistry 2008, 4820-
4824



Laser resonances in CO₂ are Isotope Dependent

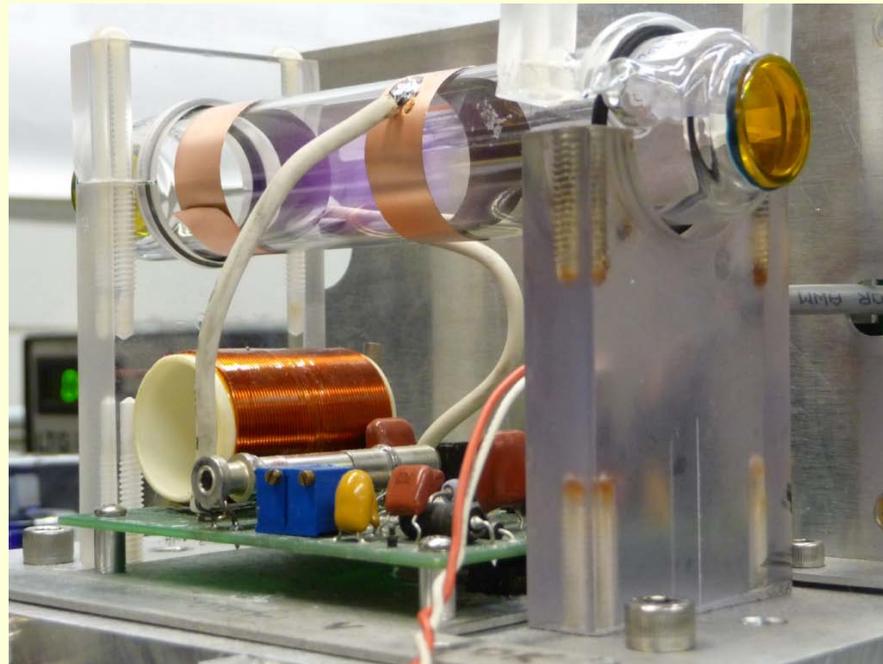


SELECTIVITY

¹⁴CO₂ laser transition
 At 11.8 μm

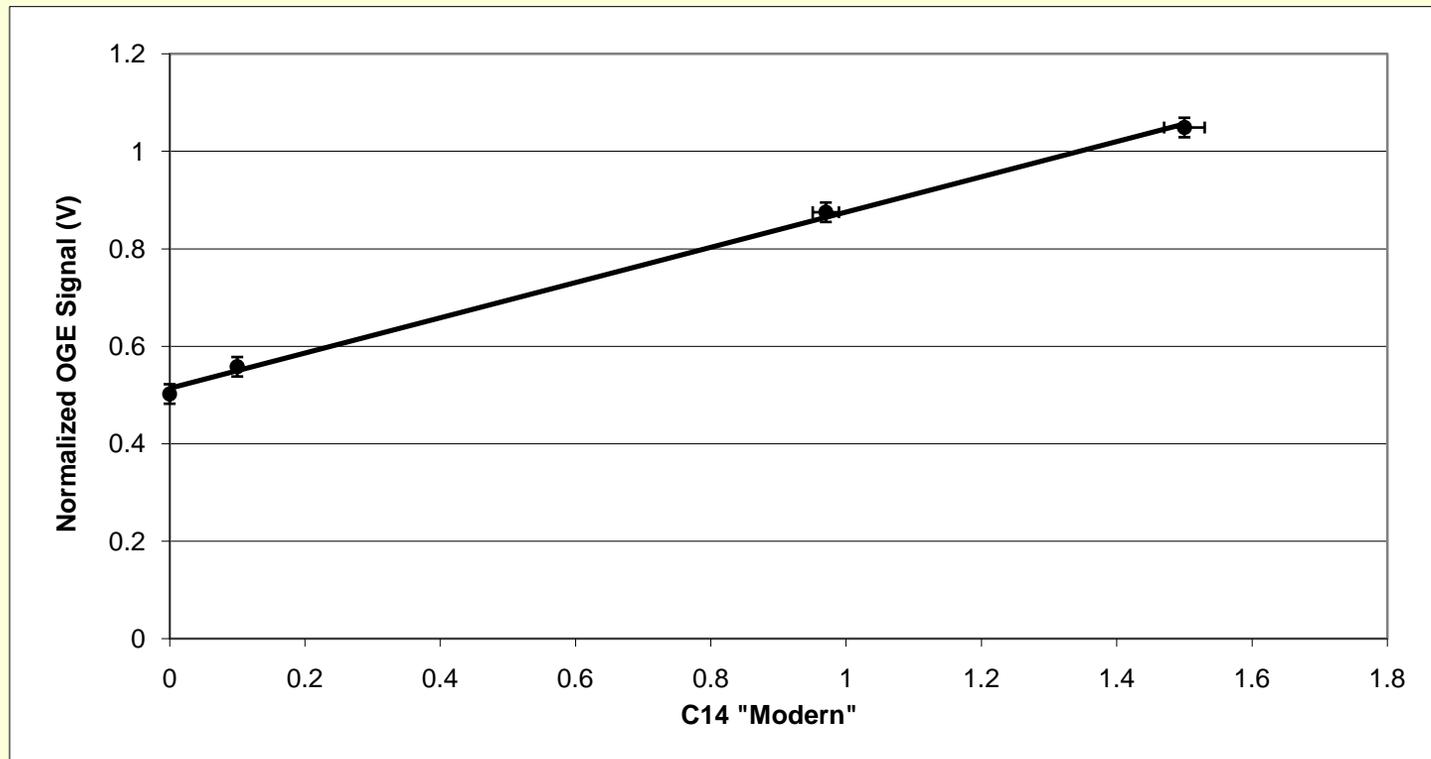
SENSITIVITY achieved through THE OPTOGALVANIC EFFECT (OGE) and high (intra-cavity) laser power

Laser radiation changes distribution of various species within an electrical discharge which changes the electron energy distribution function. This leads to an easily measurable impedance change of the system .

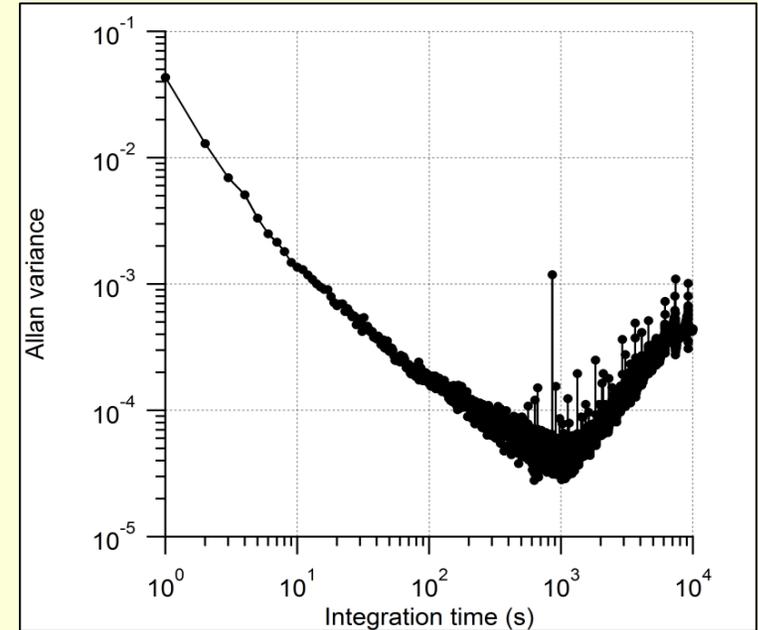
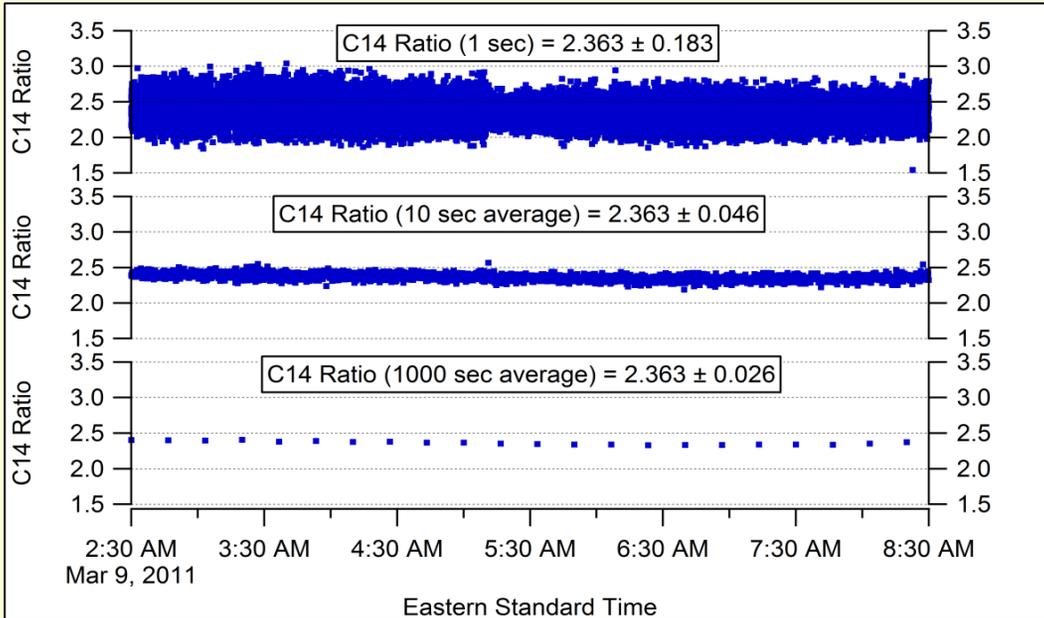


ICOGS, similar to IRMS and AMS, produces a Double Ratio Signal:

$$\text{“DR”} = \frac{{}^{14}\text{C}_{\text{sample}}/{}^{12}\text{C}_{\text{sample}}}{{}^{14}\text{C}_{\text{ref}}/{}^{12}\text{C}_{\text{ref}}}$$



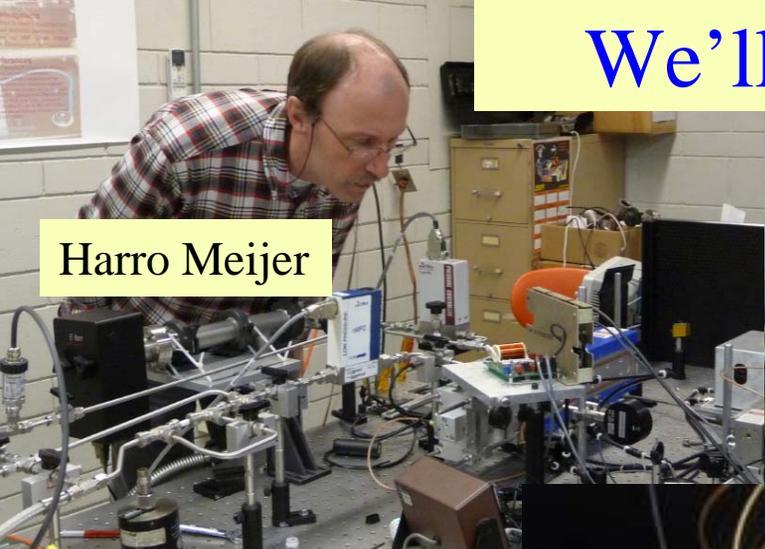
High Potential: signal precision corresponds to $<1\text{‰}$



Items to be (re)solved:

- non-linearity*
- Drift of reference cell*
- P and T dependence*
- Electrical Noise*
- ^{13}C dependence*

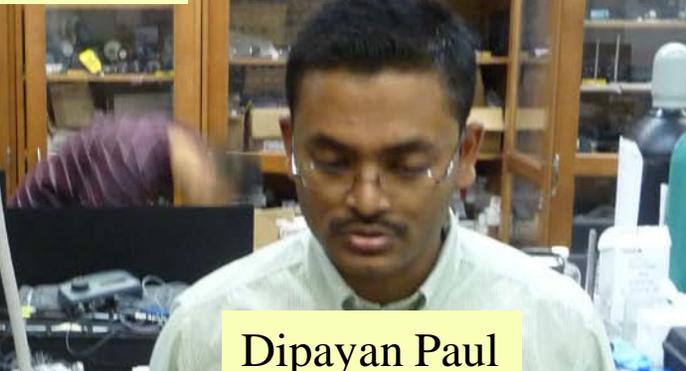
We'll keep you posted!



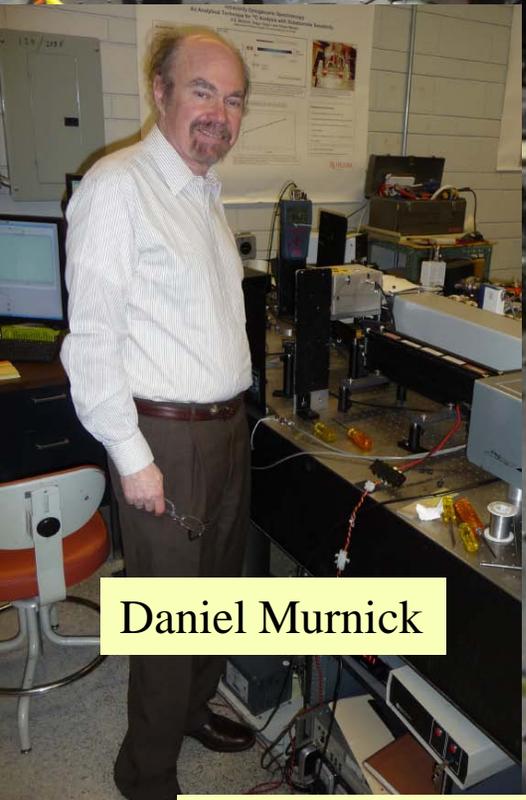
Harro Meijer



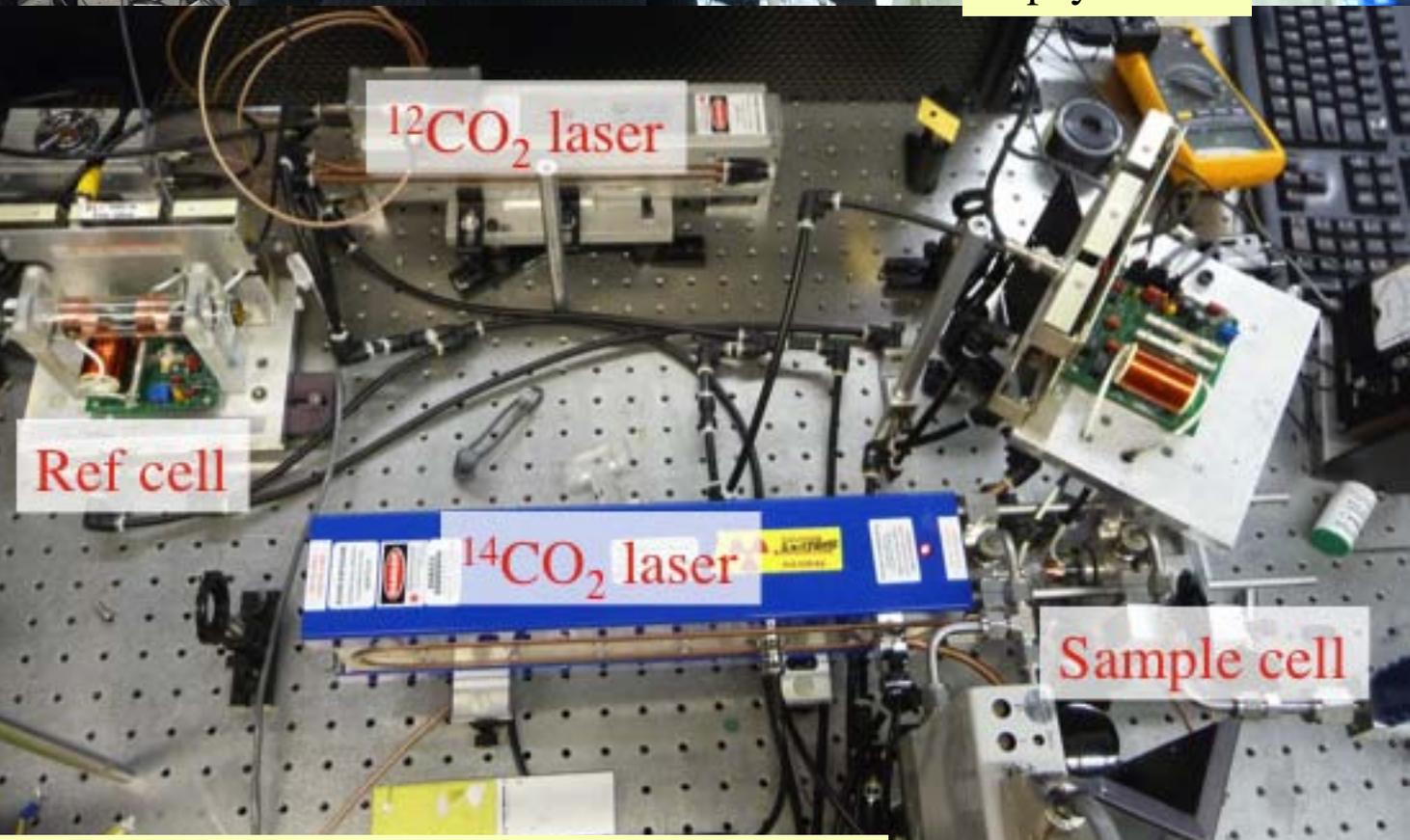
Erhan Ilkmen



Dipayan Paul



Daniel Murnick



Ref cell

$^{12}\text{CO}_2$ laser

$^{14}\text{CO}_2$ laser

Sample cell

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