In-situ measurements of CO_2

Calibration, error estimates, role of in-situ chemical measurements, quantification of fossil fuel emissions

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Requirements for our greenhouse gas measurements

Goals of GHG observing system in today's environment:

1. Provide independent assessment of emissions reductions
2. Monitor & understand the carbon cycle, improve prognoses

Measurements should be accepted as fully trustworthy, implying complete and prompt disclosure of all results, including data flagged as "bad"

⟶ *Disclosure is not an afterthought. It takes people and resources*

All measurements have to be proven to be comparable

All reported measurements should be accompanied by defensible uncertainty estimates.

⟶ *Defensible uncertainty estimates require a considerable amount of duplication*

⟶ *Uncertainty includes systematic errors that vary in time and are poorly understood*

Requirements for our greenhouse gas measurements

Some definitions in metrology:

Measurement: Process of experimentally obtaining a quantity value that can reasonably attributed to a quantity
Note: Any measurement is a comparison with a measurement standard

Measurand: Quantity *intended* to be measured (mole fraction in dry air)
Note: A measurement includes the collection of a sample and its pretreatment, such as drying.

Measurement result: Set of quantity values attributed to a measurand, together with any other available relevant information
Note: In most cases a measurement result has to include an estimate of its uncertainty, taking into account all known contributions, not just a statistical estimate of repeatability.

Measurement error: Measured quantity value minus a reference quantity value

Measurement precision: Closeness of agreement of replicate measurements under specified conditions:

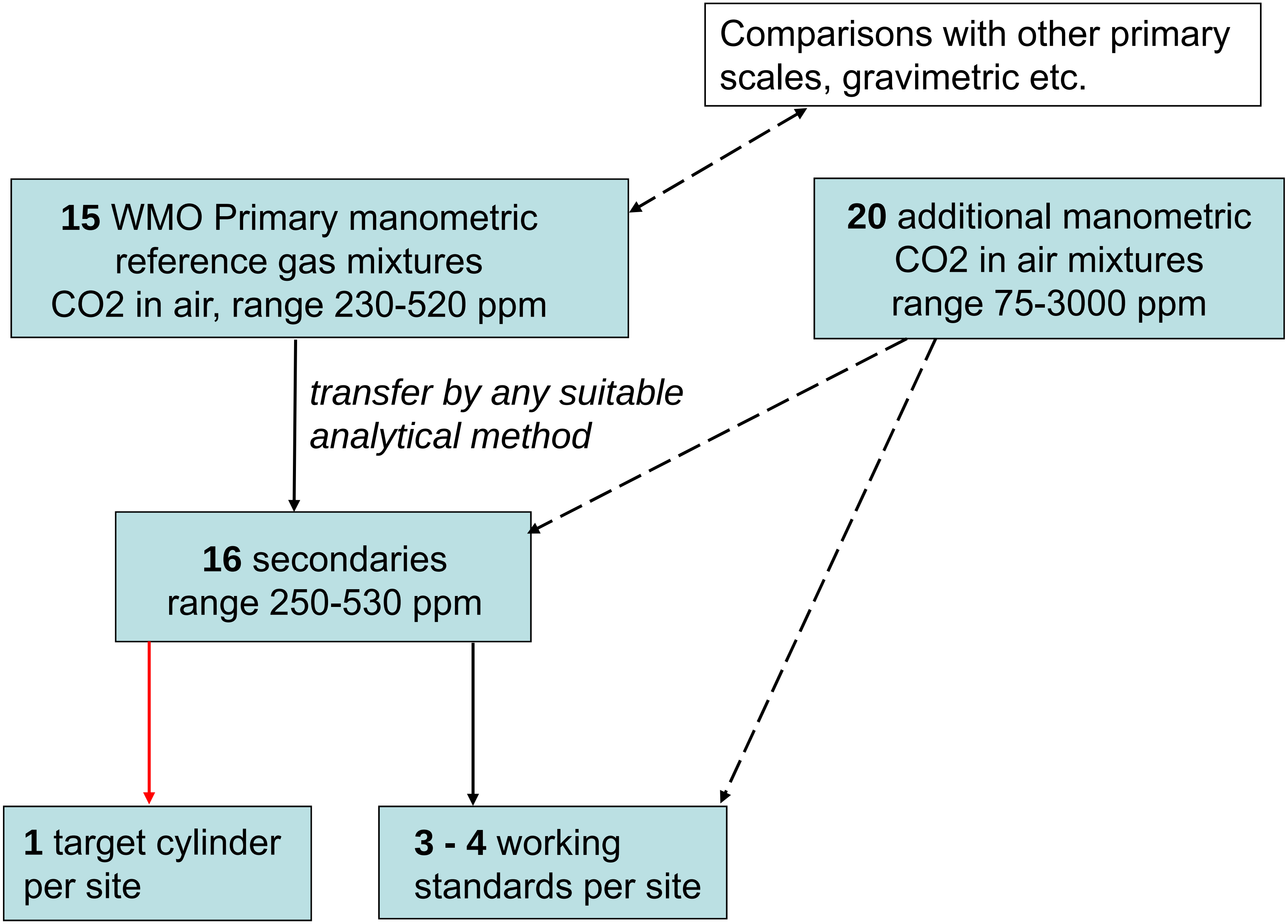
1. repeatability: same operators, same equipment and procedure, same location, same conditions, over relatively short time
2. reproducibility: different operators, equipment, procedure, location, conditions, and over extended time period.

Comparability: Measurement results are comparable if they are metrologically traceable to the same reference

Traceability: result is related to a reference through a documented *unbroken chain of calibrations*

Sources: VIM3 (2008); De Bièvre, Metrologia, 2008

WMO Mole Fraction Scale for CO2 (X2007)



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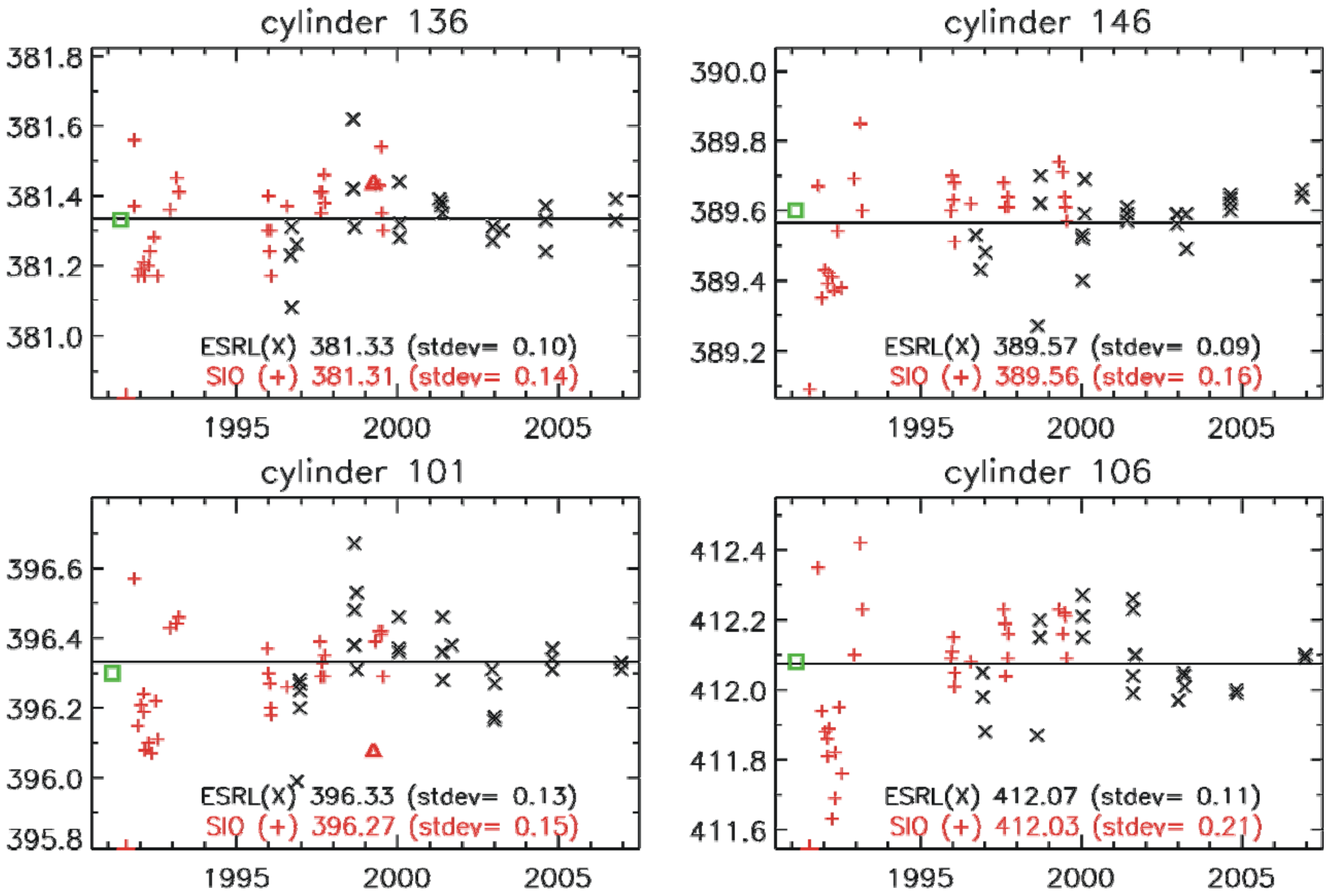

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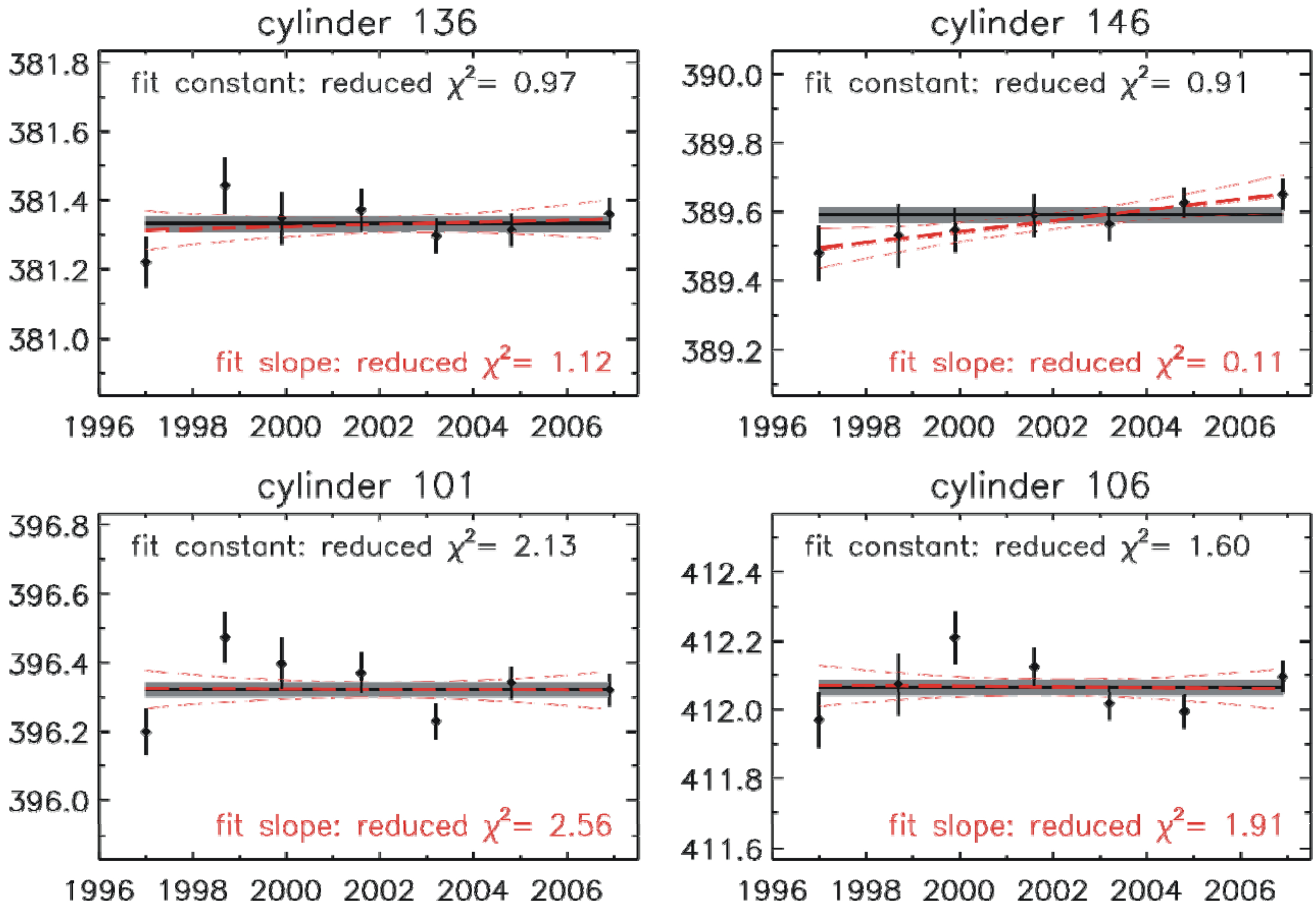

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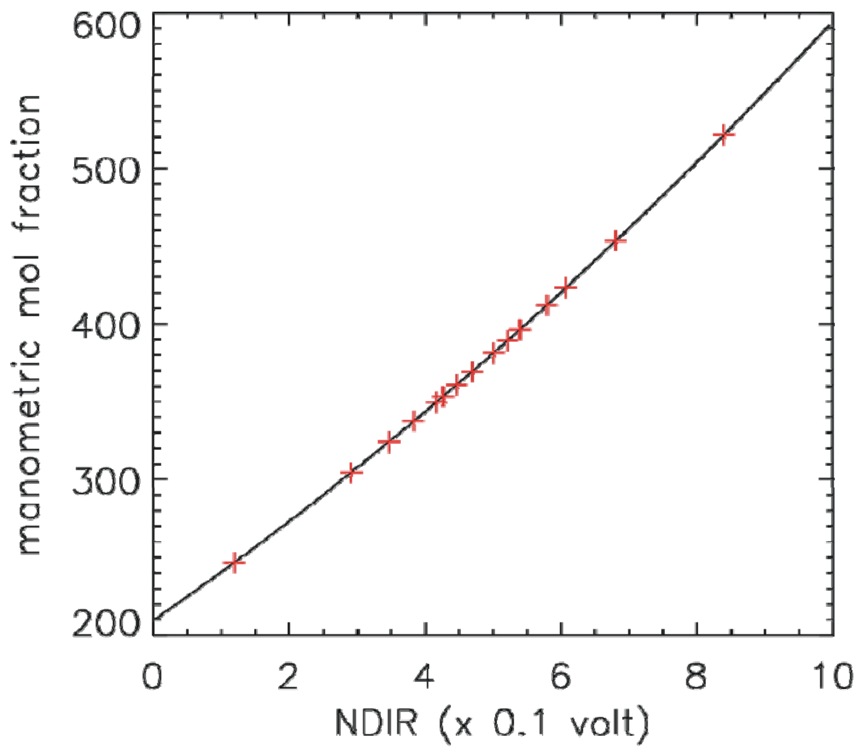
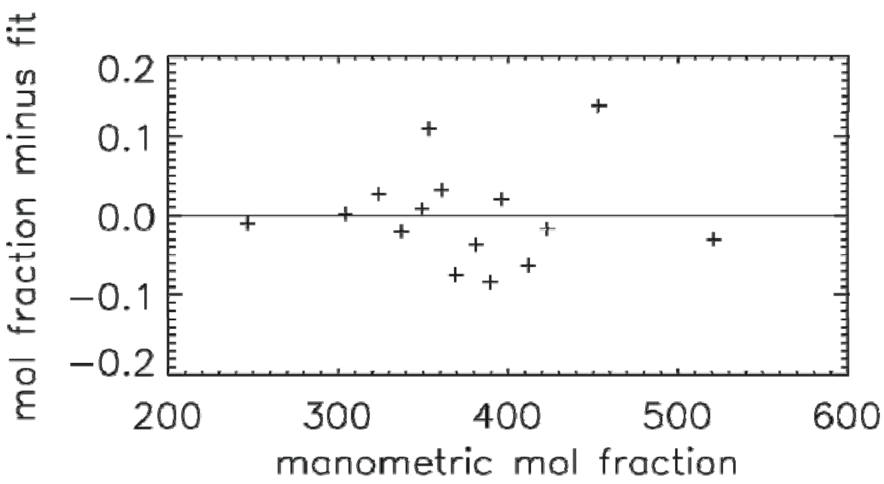
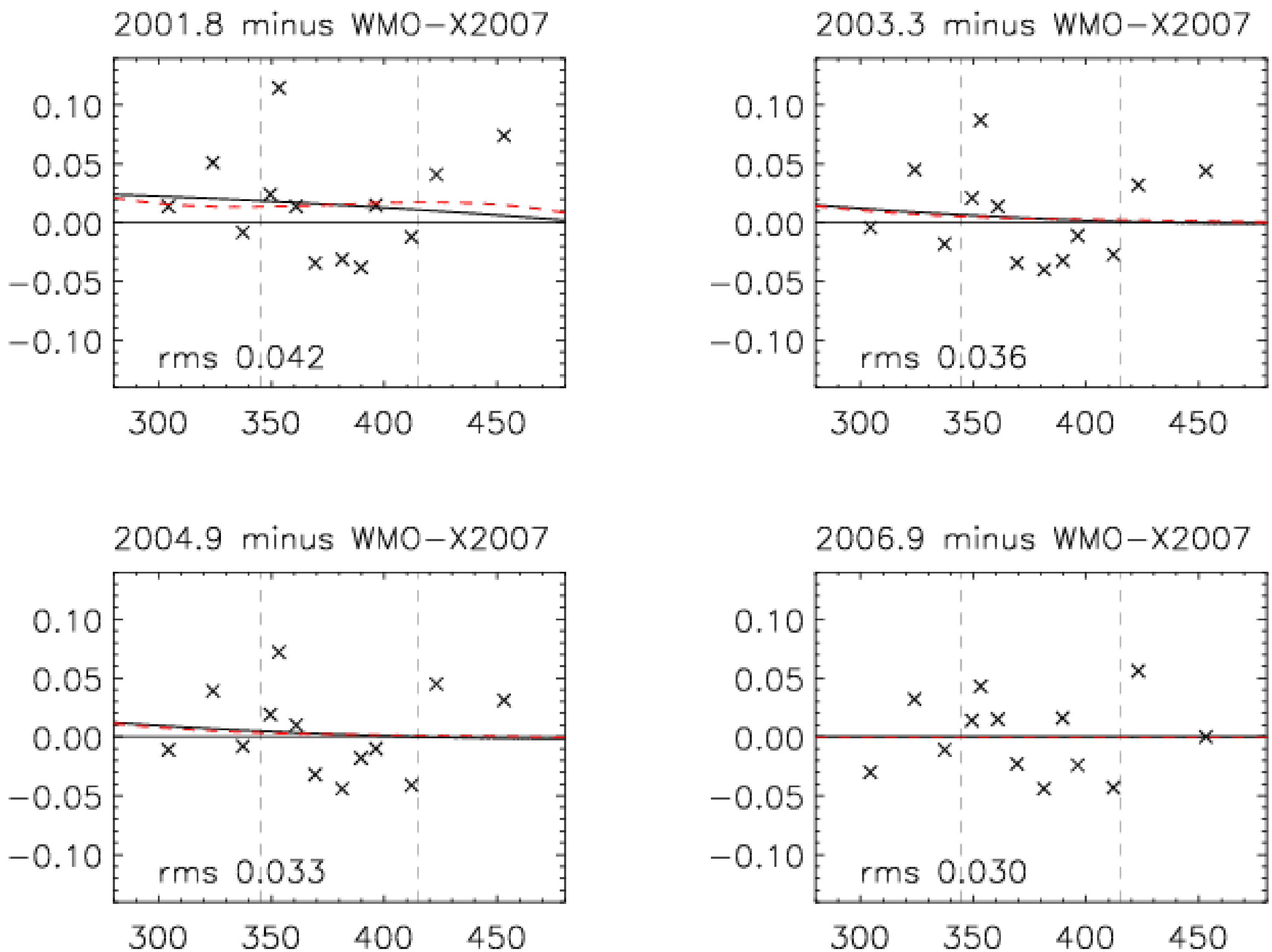




Internal consistency of the scale, X2001

WMO Mole Fraction Scale for CO_2 (X2007)

recent history of the WMO scale



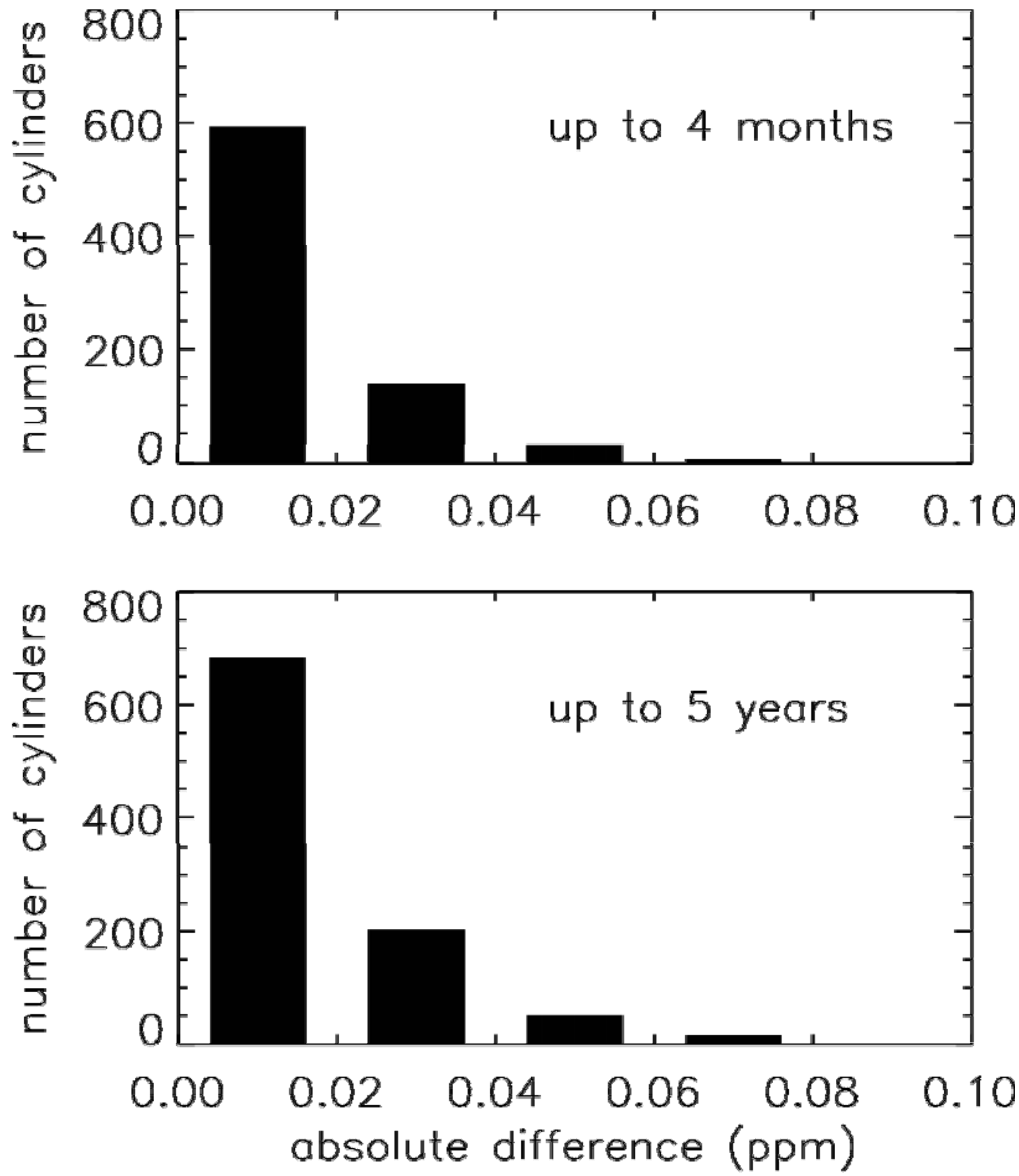
WMO Mole Fraction Scale for CO_2 (X2007)

Comparison of NIES gravimetric standards with WMO-X2005

Cylinder	NIES	ESRL NDIR May 05 July 06	ESRL mano July 06
30089	350.14	350.21	350.15
30091	350.02	350.03	350.03
30092	390.11	390.09	390.10
30093	390.11	390.09	390.15
30094	389.03	389.02	389.02

NIES data courtesy of Yasunori Tohjima

WMO Mole Fraction Scale for CO_2 (X2007)

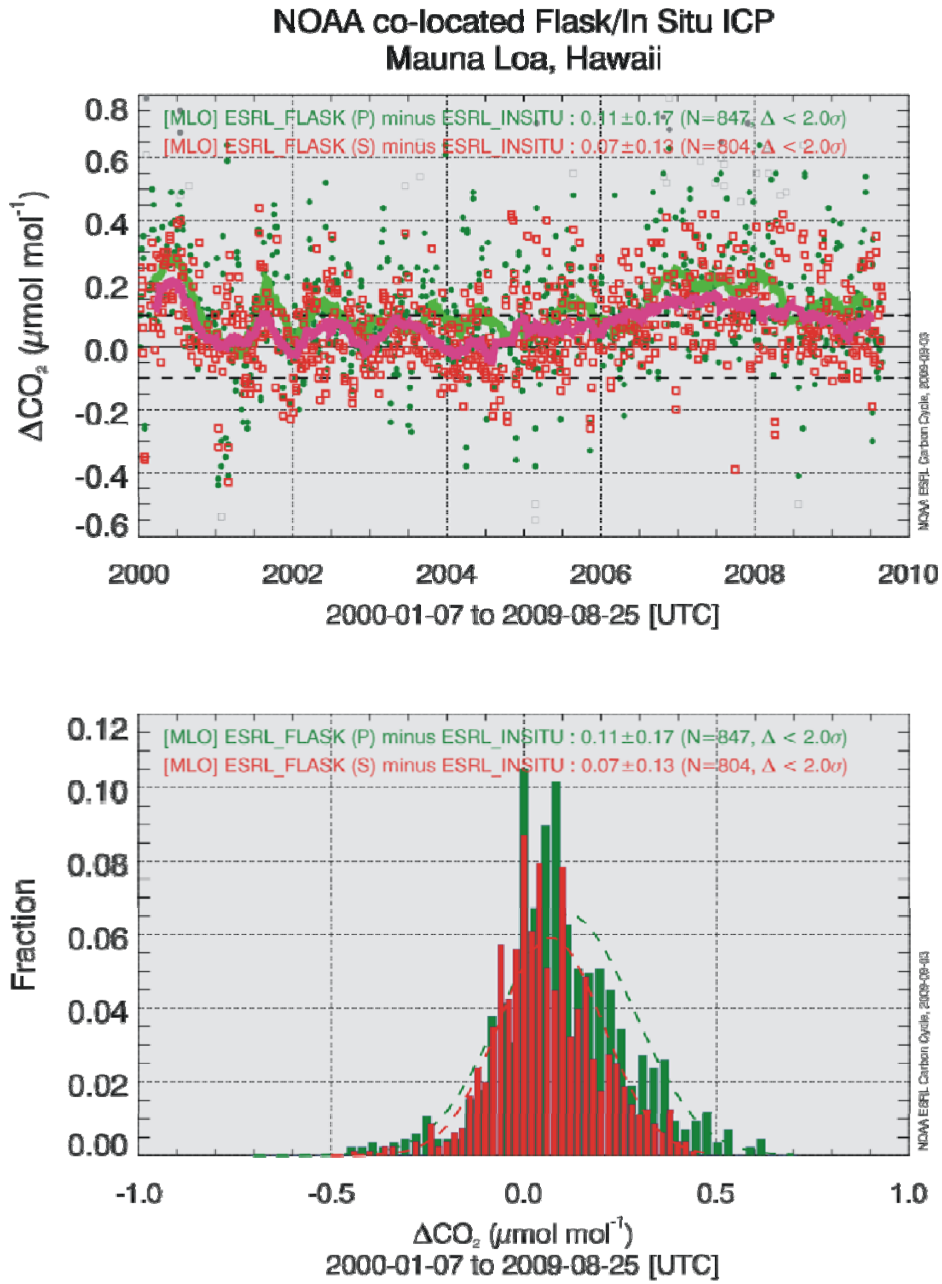


771 comparisons
mean absolute difference
0.015 ppm

950 comparisons
mean absolute difference
0.016 ppm

Duane Kitzis (ESRL), statistics since 2004

Uncertainty estimates of in-situ measurements



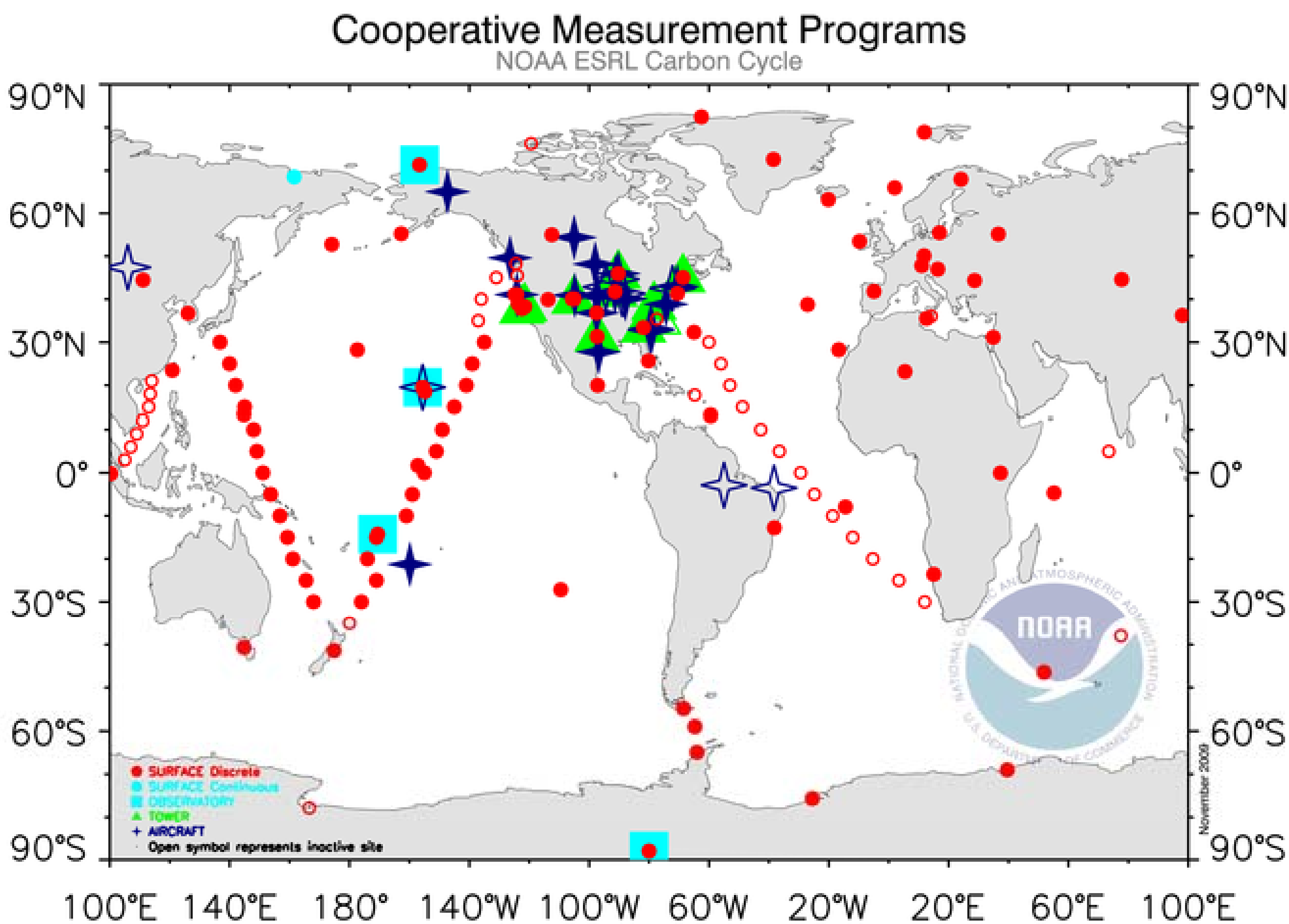
Conclusions:

Uncertainty estimate of WMO X2007 scale is 0.14 ppm (2 sigma), which is consistent with independent scales.

Uncertainty of the *propagation* of the scale is 0.04 ppm (2 sigma)

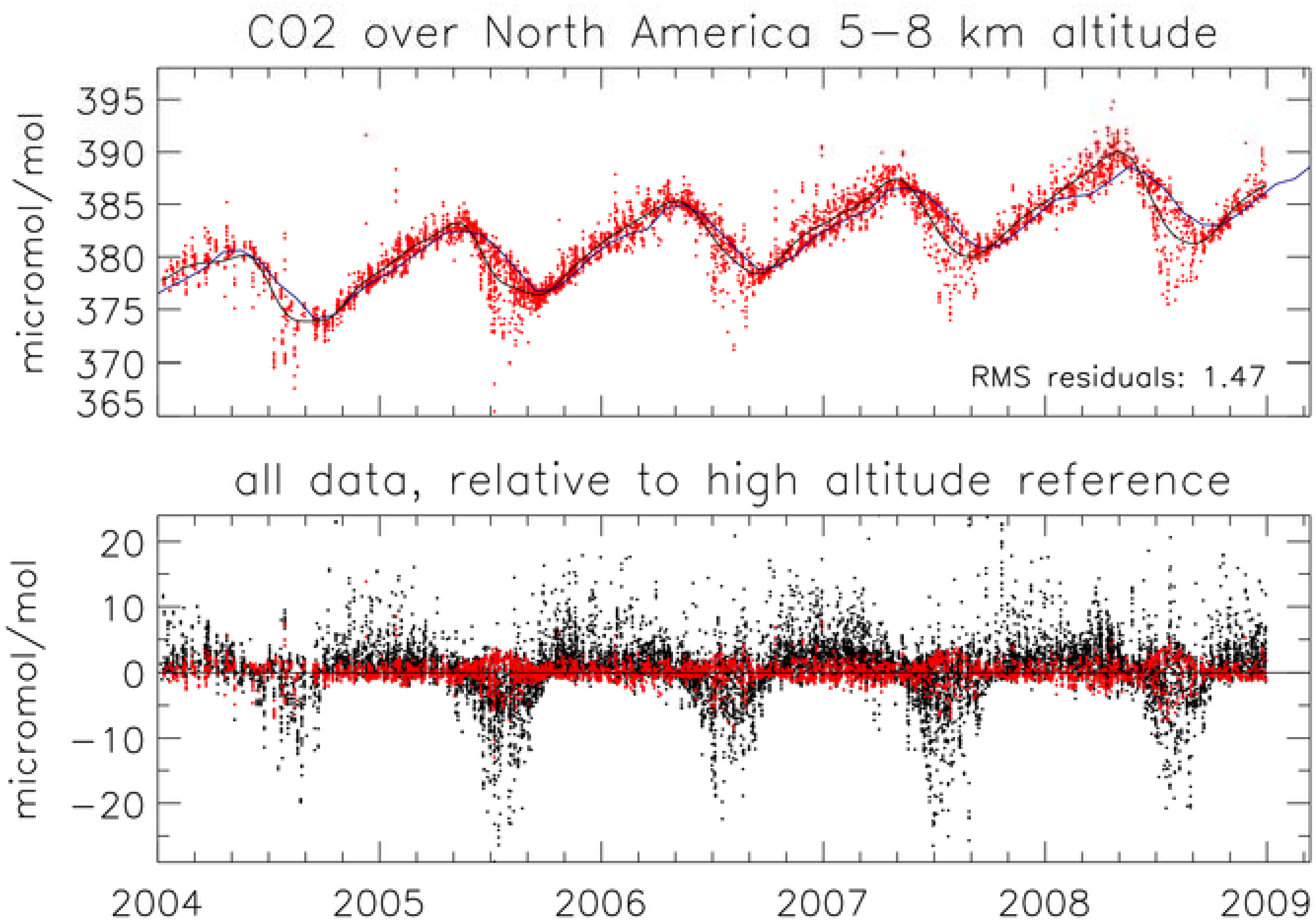
Full uncertainty of air measurements: Slowly varying biases mostly related to air handling (often not understood) <0.3 ppm (2 sigma)

Role of in-situ measurements



NOAA ESRL Carbon Cycle operates 4 measurement programs. Semi-continuous measurements are made at 4 baseline observatories, a few surface sites and from tall towers. Discrete surface and aircraft samples are measured in Boulder, CO. Presently, atmospheric carbon dioxide, methane, carbon monoxide, hydrogen, nitrous oxide, sulfur hexafluoride, the stable isotopes of carbon dioxide and methane, and halocarbon and volatile organic compounds are measured. Contact: Dr. Pieter Tans, NOAA ESRL Carbon Cycle, Boulder, Colorado, (303) 497-6678, pieter.tans@noaa.gov, http://www.esrl.noaa.gov/gmd/ccgg/.

Role of in-situ measurements



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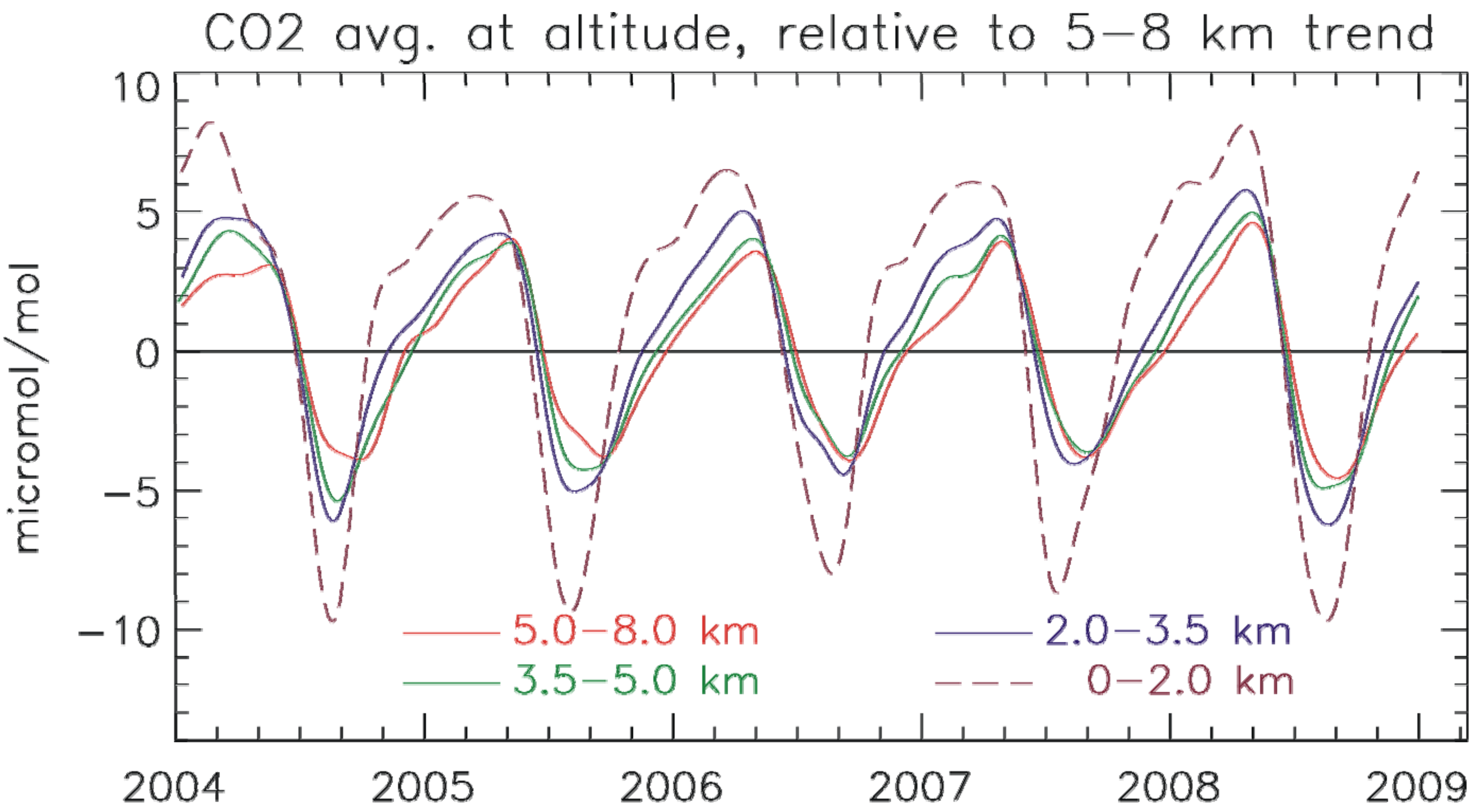
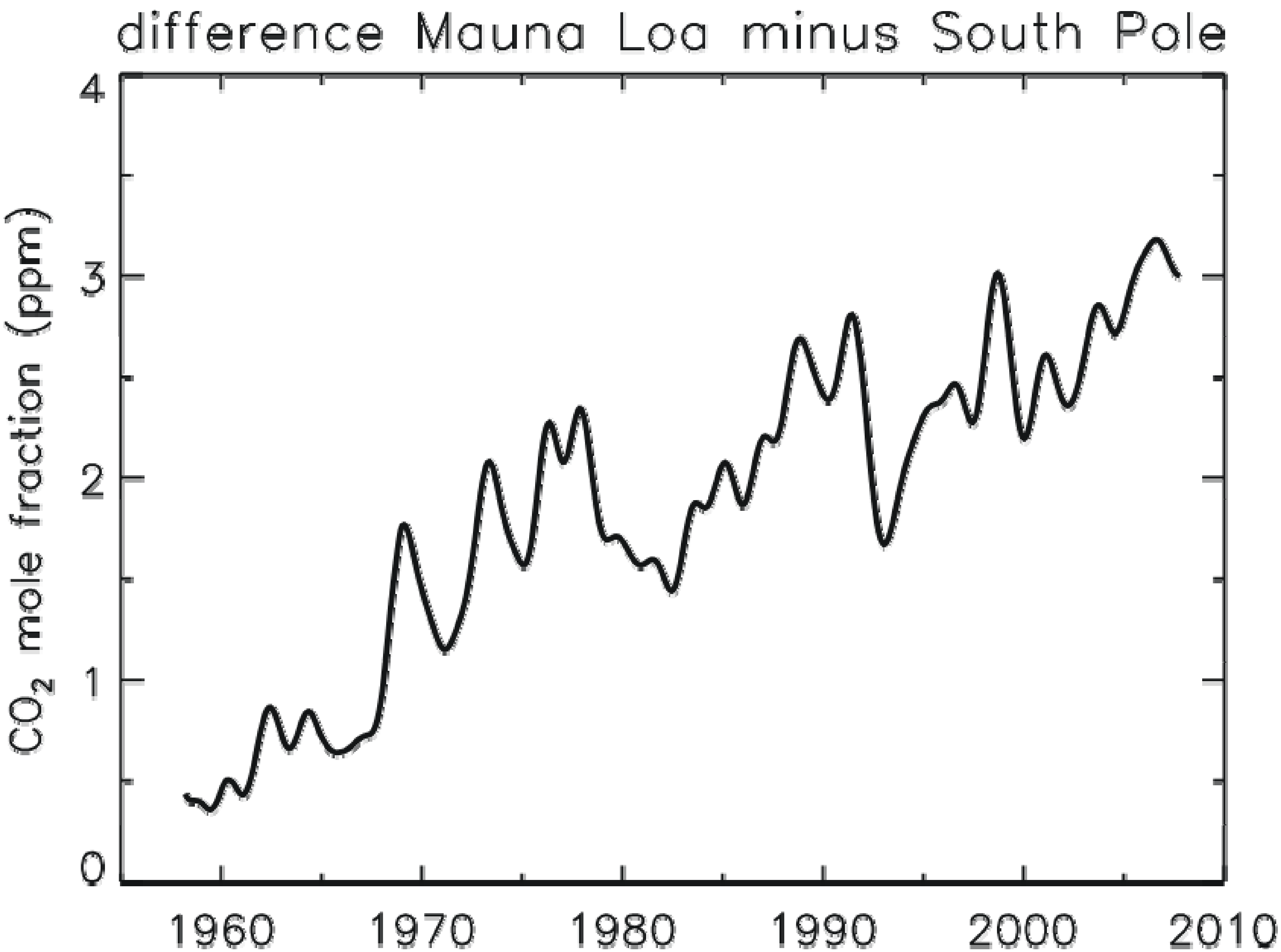
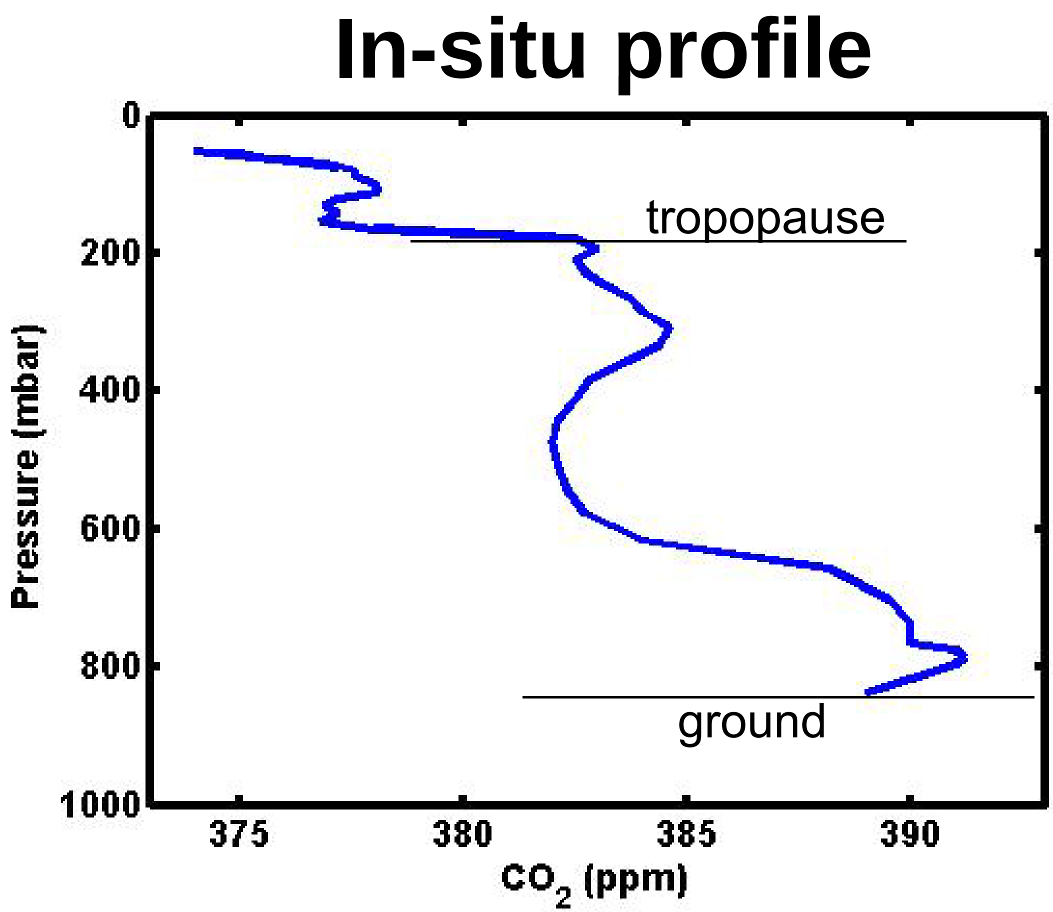


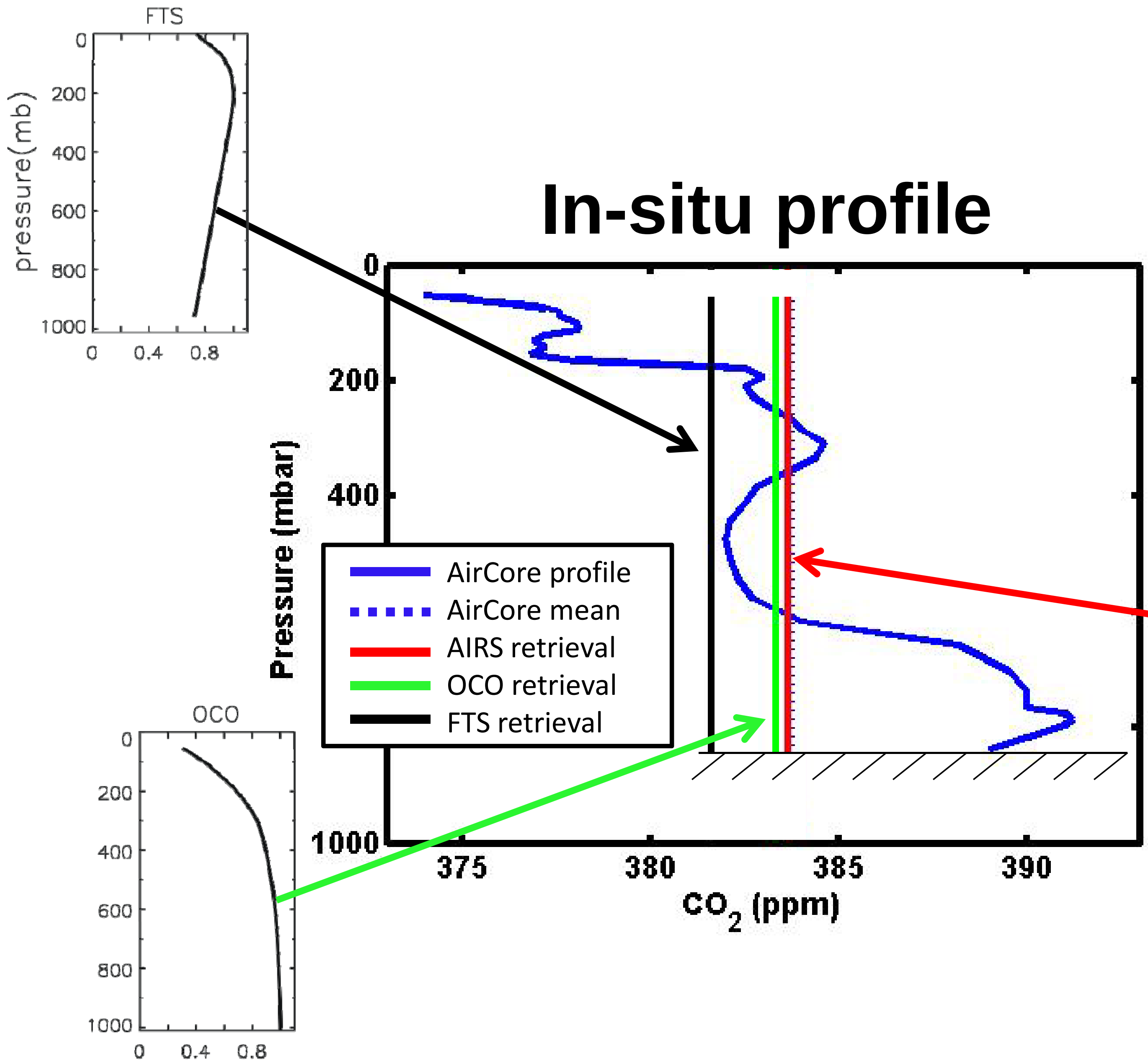
Role of in-situ measurements




In-situ profile
0
200
400
600
800
1000
Pressure (mbar)
375
380
385
390
CO2 (ppm)
tropopause
ground

AirCore

Role of in-situ measurements



Conclusions:

Chemically stable in the atmosphere, CO_2 is an excellent tracer for atmospheric transport.

Independent methods (measurements, models) are necessary to provide a more realistic estimate of uncertainty of source/sink estimates.

In-situ full profile measurements are needed on an ongoing basis to discover and diagnose biases of remote sensing, so that retrieval algorithms can be improved.

Verification of emissions

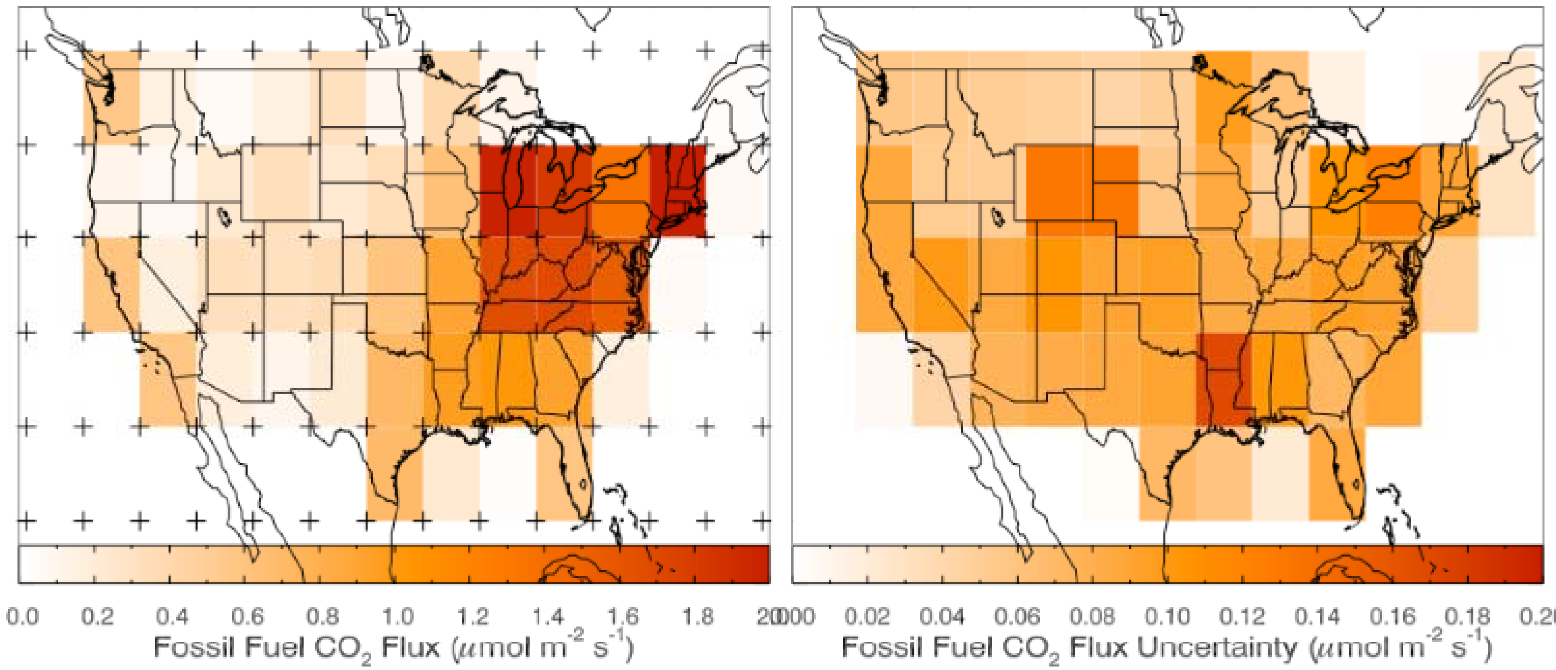
$$\Delta X = \frac{E\,(mol/s)}{area} \times \frac{fetch\,(\sqrt{area})}{w\,(m/s)} \times \frac{1}{column\,(mol/m^2)}$$

Estimates of typical CO2 increases (ΔX) due to fossil fuel combustion:
(average, downwind side of area, 5 m s-1 wind, BL height 1 km)

U.S.	0.8 ppm (column)	3 ppm (BL 2 km)
Germany	0.6	5
Indonesia	0.1	1
S. Korea	0.6	5
Houston	0.7	6
Beijing	1.1	9
Shanghai	1.8	15

Observing system simulation experiment:

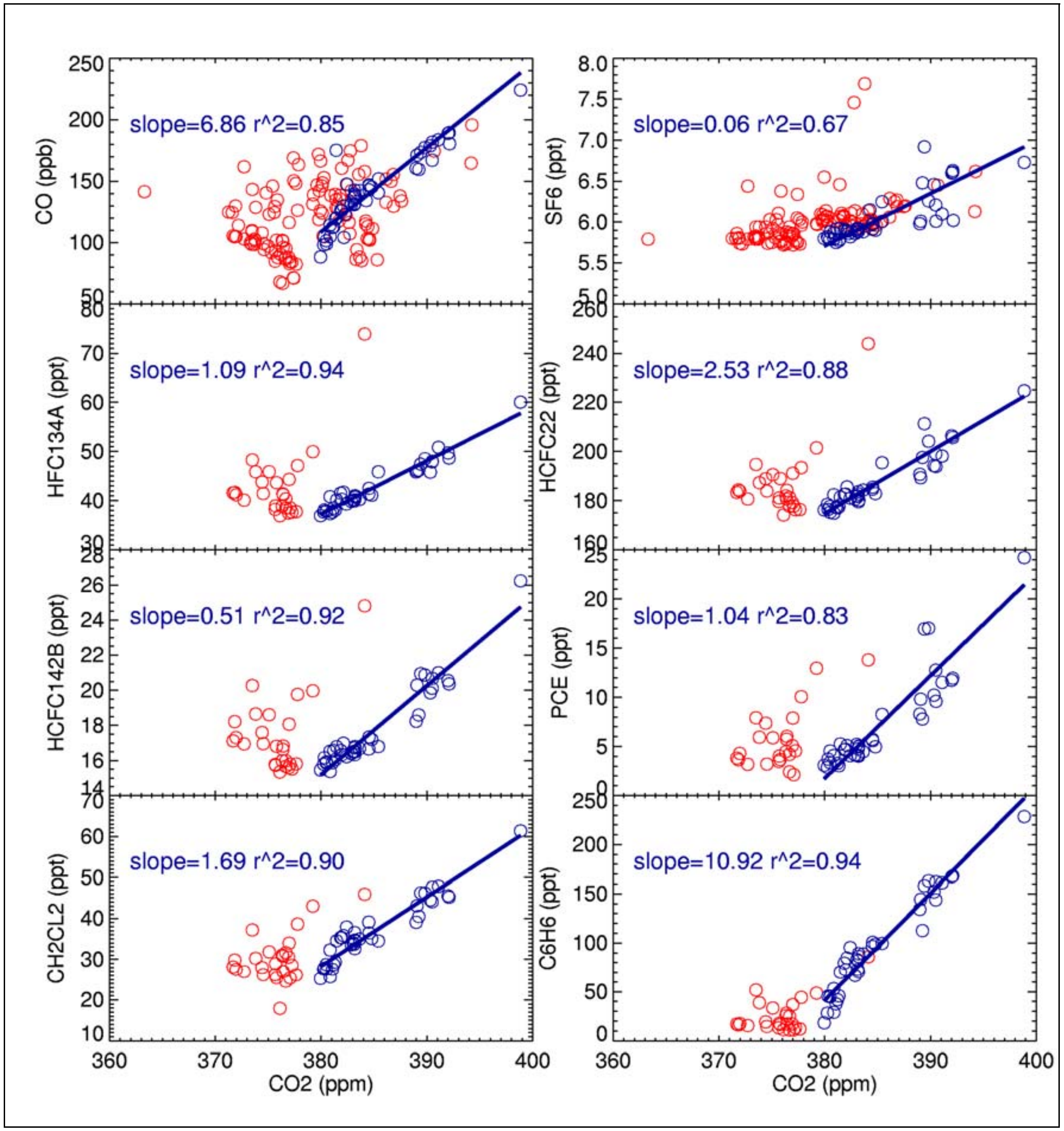
10,000 $^{14}CO_2$ samples/year, one every 3 days in every grid point below, Lagrangian back-trajectories, measurement error 2 permil or 0.7 ppm of recent fossil fuel CO2.



John Miller (ESRL)

Verification of emissions

CO2 vs. anthropogenic gases

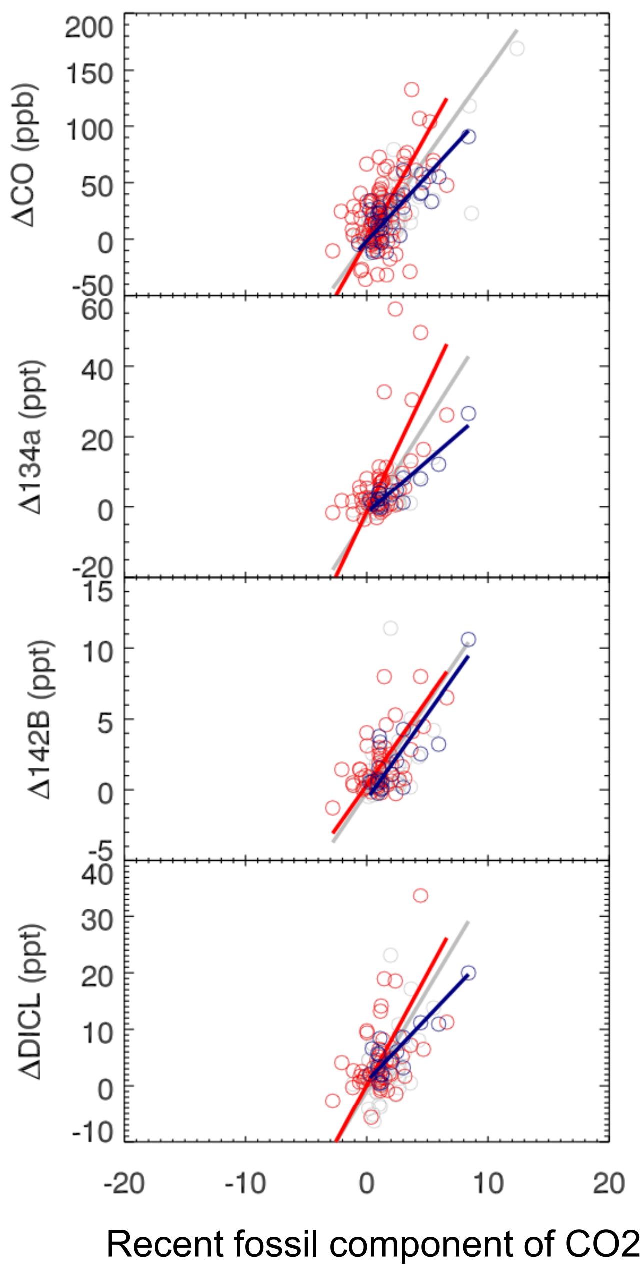


blue: winter

red: summer

John Miller, ESRL

Verification of emissions



Observed
emissions ratios:

m=19 ppb/ppm
m=12 ppb/ppm

m=7.2 ppt/ppm
m=3.0 ppt/ppm

m=1.2 ppt/ppm
m=1.2 ppt/ppm

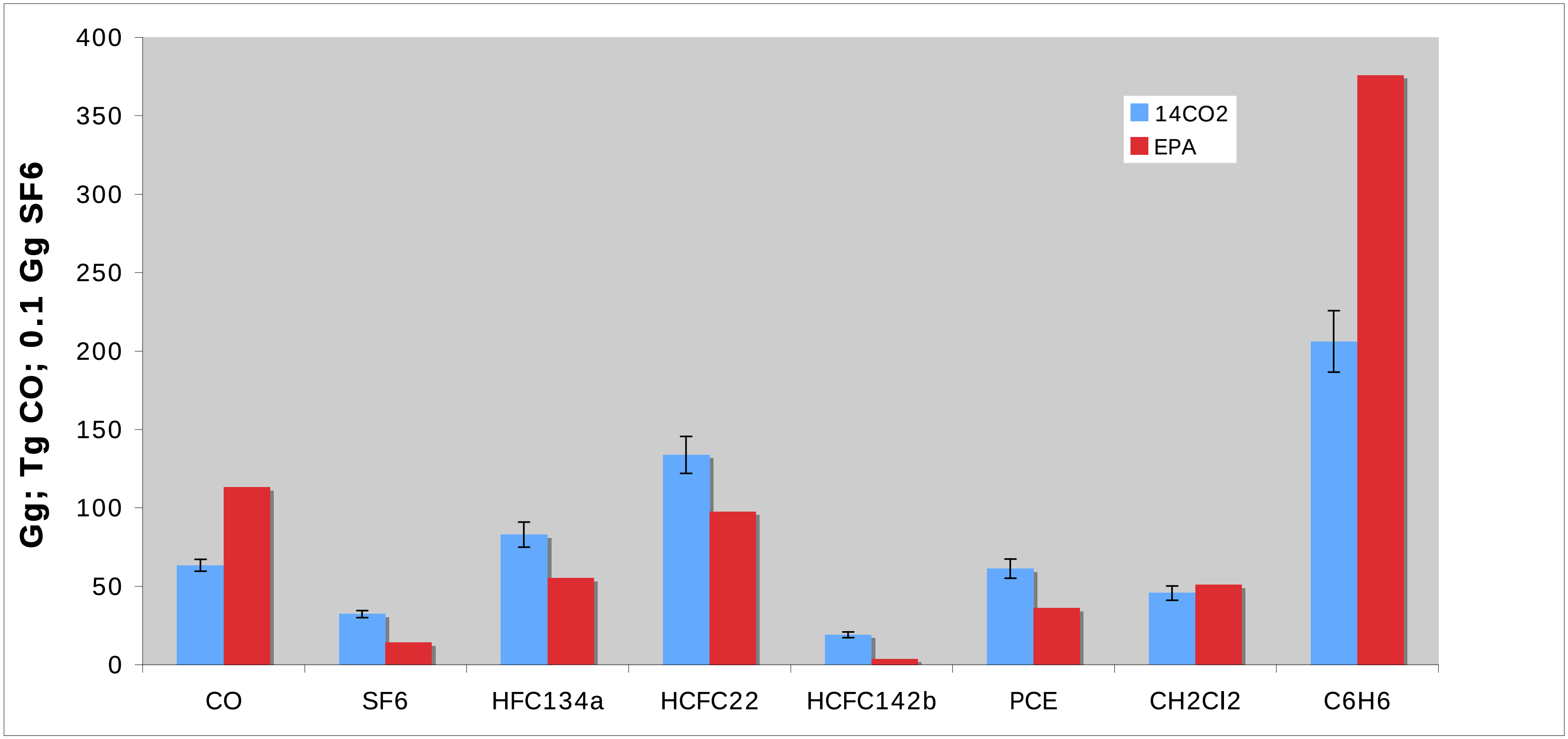
m=4.0 ppb/ppm
m=2.3 ppb/ppm

$$m_{gas} \times E_{ff} = E_{gas}$$

Red=Summer
Blue=Winter

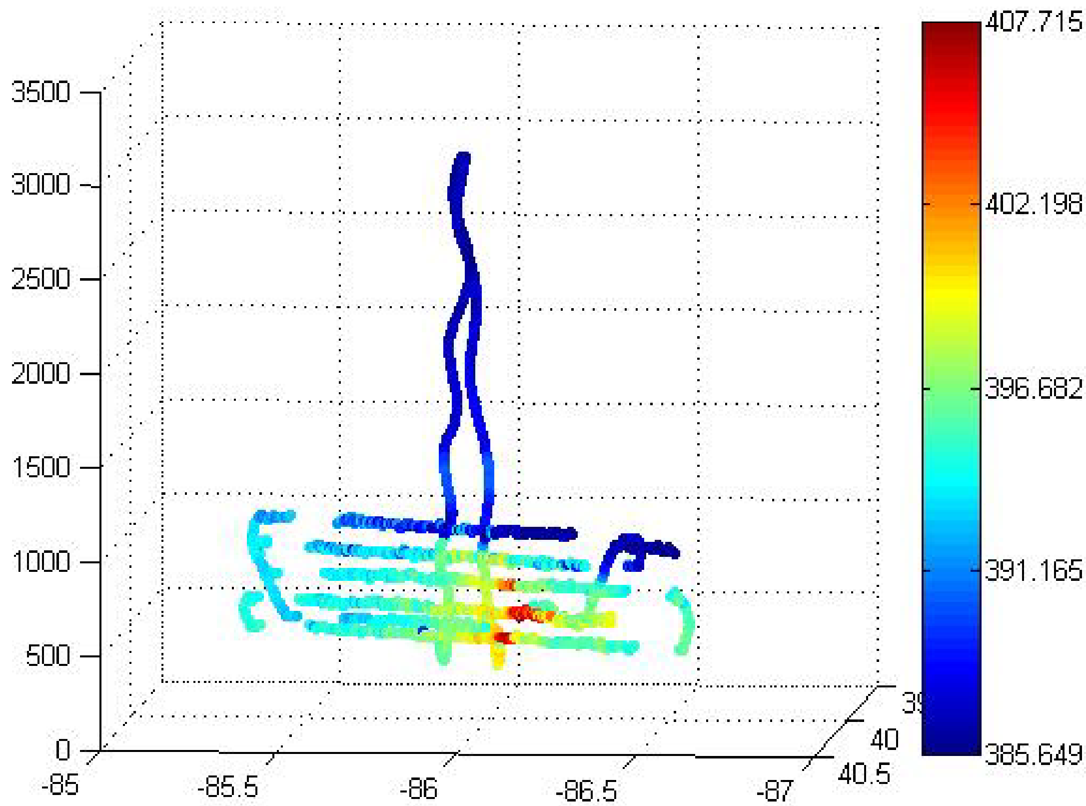
John Miller, ESRL

USA Emission Estimates



John Miller, ESRL

Down wind of Indianapolis, November 2008



Paul Shepson, Purdue

Conclusions:

$^{14}CO_2$ measurements separate CO_2 from recent fossil fuel burning from natural sources/sinks, making ^{14}C a clean tracer for fossil fuels.

5000 ^{14}C samples per year would quantify regional fossil fuel CO_2 to ~10% on regional scales, if there is no transport error.

Initially use ^{14}C tracer to improve transport – as long as we can trust inventories.

Correlate $^{14}CO_2$ depletion with other species, to quantify emissions from other species. They in turn can help fossil fuel quantification in fairly remote areas where $^{14}CO_2$ depletion is very dilute.

$^{14}CO_2$ measurements extract a clean seasonal cycle signal from terrestrial ecosystems