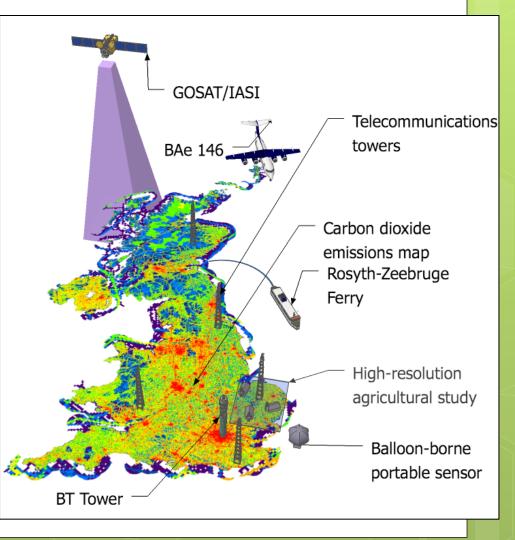
The importance of reference standards in atmospheric GHG monitoring networks

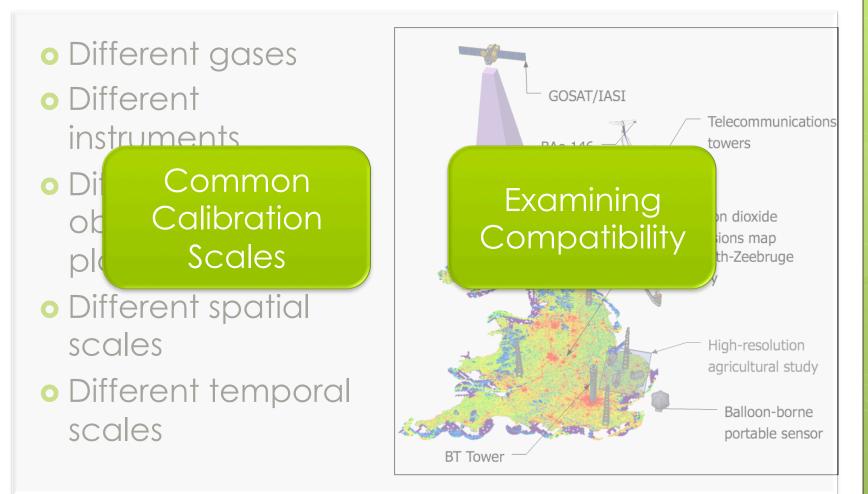
Ann Stavert & many others University of Bristol

GAUGE Project

- To quantify the UK GHG budget → Emission reduction policies.
- Put the UK GHG budget into a global context.
- Integrating multi-platform and multi-scale (temporal and spatial) data sources.
- Include new sensor technology
- Interpret this new data set using inverse modelling.



Combining data



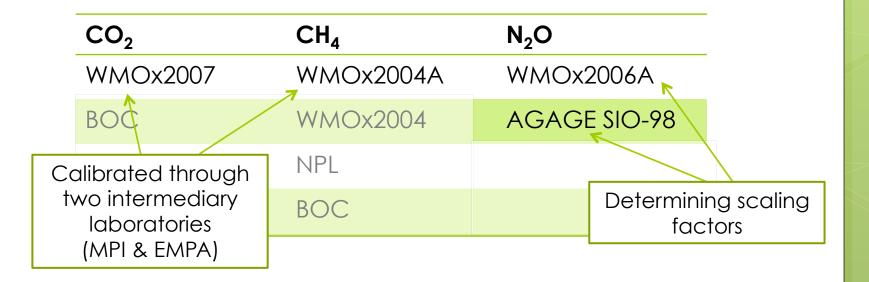
Calibration scales

| Laboratory | Sites (WDCGG Site Index) | Reported Standard Scale | Most Recent Calibration | WMO Round Robin |
|------------|--|-------------------------|-------------------------|---------------------|
| CSIRO | CGR540S0, CSIRO Flask Network** | WMO | 2001-11 at CMDL | 91/92, 95/97, 99/00 |
| NIWA | BAR541S0 | SIO 1995 | 1995-11 at SIO | 91/92, 95/97, 99/00 |
| CAMS | WLG236N0 | X93 | 1994-01 at SIO | 95/97, 99/00 |
| METRI/SNU | KSN233N0 | X97 | SIO | 95/97 |
| JMA | NMN224N0, RYO239N0, YON224N0, ALG99990, EOM99990, RYF99990 | WMO | 1999-03 at CMDL | 91/92, 95/97, 99/00 |
| MRI | TKB236N0, INS9999A, HKH99990, KIY99990, NTU99990, RFM99990, WLT99990 | MRI 1997 | | 91/92, 95/97, 99/00 |
| NIES | COI243N0, HAT224N0 | NIES 95 | | 95/97, 99/00 |
| Tohoku | SYO769S0 | Tohoku | İ | 91/92, 95/97, 99/00 |
| Shizuoka | HMM234N0 | | Nippon Sanso | |
| Aichi | MKW234N0 | WMO | JMA | |
| Saitama | DDR236N0, URW235N0 | WMO | JMA | |
| CMDL | BRW471N0, MLO519N0, SPO789S0, SMO514S0, CMDL flask network* | WMO | 2001-01 at CMDL | 91/92, 95/97, 99/00 |
| NIST | | NIST | | 91/92, 95/97, 99/00 |
| SIO | | SIO | | 91/92, 95/97, 99/00 |
| MSC | ALT482N0, CSJ451N0, SBL443N0 | SIO 1991 | 2000-03 at CMDL | 91/92, 95/97, 99/00 |
| IGP | HUA312S0 | X81 | | |
| MGO | BER255N0, KOT276N0, KYZ240N0, STC652N0, TER669N0 | X97 | 1991 at SIO | |
| KSNU | ISK242N0 | | MGO | |
| INM | IZA128N0 | X87, X93 | 1997-01 at CMDL | 91/92, 95/97, 99/00 |
| LSCE | AMS137S0, MCH653N0 | X93 | 1998-08 at CMDL | 91/92, 95/97, 99/00 |
| IMS | CMN644N0 | X93 | 1998-10 at CMDL | 91/92, 95/97 |
| ENEA | LMP635N0 | X93 | 2000-08 at CMDL | 91/92, 95/97, 99/00 |
| CNR | JBN762S0 | WMO | ENEA | |
| CESI | PLR645N00 | X85 | 1997-07 at CMDL | 99/00 |
| UBA | BRT648N0, DEU649N0, NGL653N0, SSL647N0, LGB652N0, WST654N0, ZGT654N0, ZGP647N0 | WMO | 1998-10 at CMDL | 91/92, 95/97, 99/00 |
| Heidelberg | | WMO | 1998-10 at CMDL | 95/97, 99/00 |
| IFU | WNK647N0, ZSP647N00 | SIO 1974 | | 99/00 |
| ZAMG | SNB647N00 | WMO | UBA | |
| RIVM | KMW653N0 | NIST | | |
| MISU/NILU | ZEP678N0 | X93 | 1996-07 at CMDL | 95/97, 99/00 |
| HMS | KPS646N0 | WMO 1985 | 2000-03 at CMDL | 91/92, 95/97, 99/00 |
| NIMH | FDT645N20 | | SIAD SpA, Italy | |
| SAWS | CPO134S0 | WMO | 1997-06 at CMDL | 99/00 |

Calibration scales

Fixed set of reference standards to which the measurements can be traced

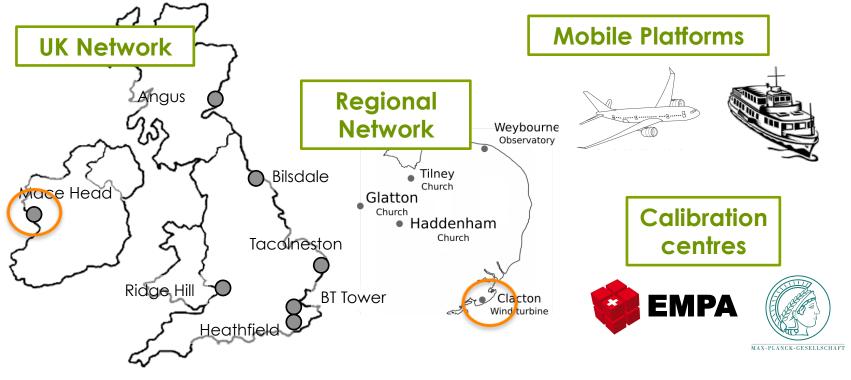
Typically manometrically or gravimetrically produced



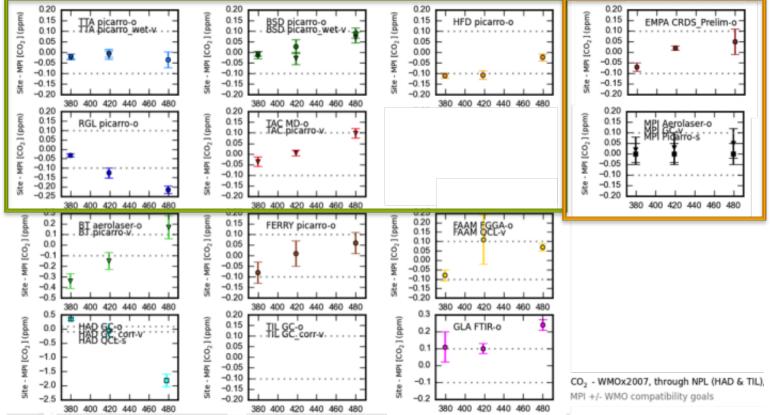
Examining compatibility

Intercomparison program (ICP)

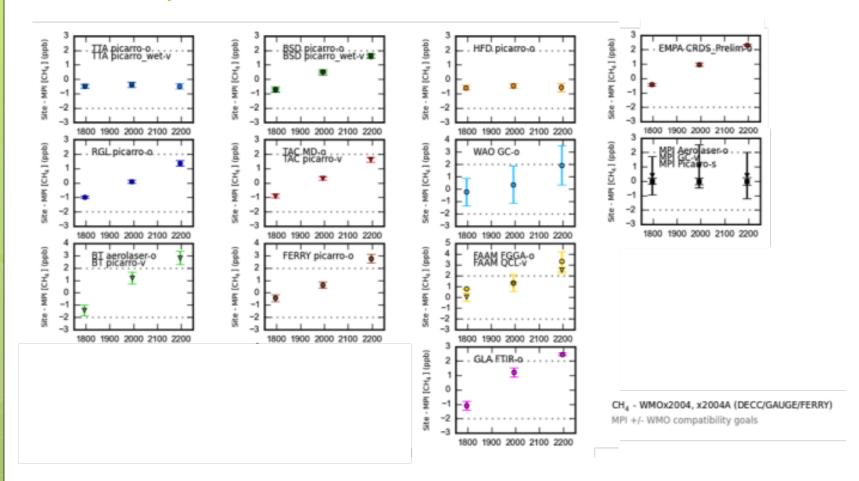
- Three cylinders
- Concentration range
- Measured at each location
- Same tubing and regulators
- Quantifying instrumental & calibration differences



CO₂ - Compatibility



CH₄ - Compatibility

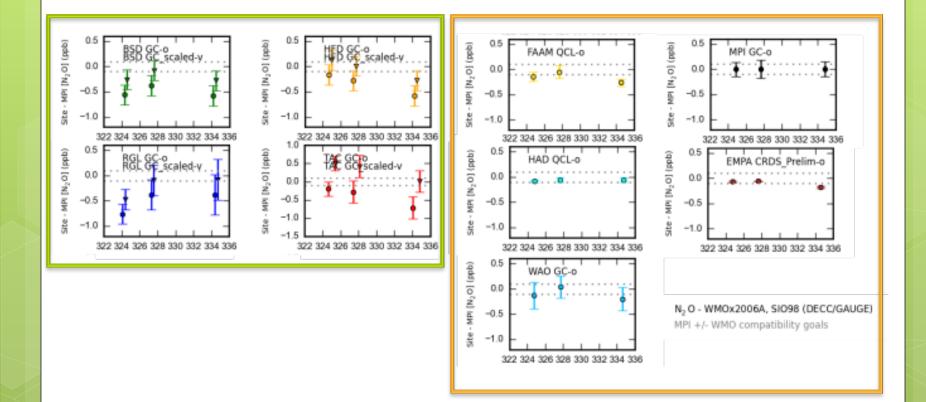


MPI & EMPA divergence?

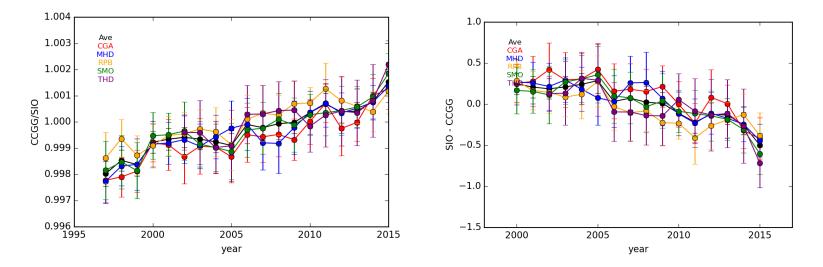
| Site | Trend | Via | Instrument | Year |
|----------|-------------|-------------|------------|------|
| TTA | No | MPI | CRDS | 2014 |
| | | | | |
| RGL | Yes | MPI | CRDS | 2011 |
| TAC | Yes | MPI | CRDS | 2011 |
| BSD | Yes, strong | EMPA | CRDS | 2015 |
| BT | Yes, strong | EMPA | CRDS | 2014 |
| Ferry | Yes, strong | EMPA | CRDS | 2014 |
| FAAM | Yes, strong | EMPA | CRDS | 2014 |
| GLA | Yes, strong | EMPA | CRDS | 2014 |
| WAO NCAS | Yes, strong | NOAA direct | NDIR | - |

| ICP's | - | MPI | CRDS | 2013 |
|-------|---|-----|------|------|
| | | | | |

N₂O - Compatibility

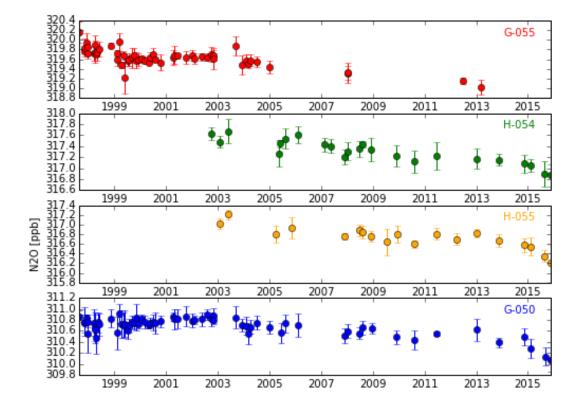


N₂O – Compatibility Scaling factors

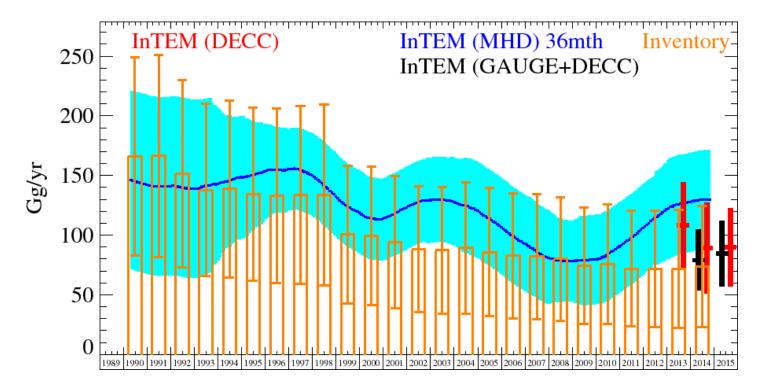


- Fixed annual factor based on flask/in situ comparison at co-located AGAGE (SIO) and CCGG (WMO) sites.
- CCGG measurements only collected in "baseline" periods so typically only looking at concentrations near ambient and the concentration is increasing over time.

N₂O – Compatibility Scaling factors



Importance of reliable reference standards



Standard requirements Gases & Analytical Techniques

- Bulk gases matched to natural air particularly important for optical techniques
- Useful concentration ranges e.g. NMHC currently only 6 ppb in N₂ available need 0.5 to 6 ppb in natural air
- Isotopic composition matched to sample
- Calibration/recalibration needs to be quick!

Standard requirements

Practicalities and Multiplatform networks

- Space
 - Multispecies standards not just CO_2 , CH_4 and N_2O also CO, SF_6 , HFC's CFC's...
- Cylinder size
 - Small for Ferry/Church/Aircraft
 - Large for long term trend observations at fixed sites
- Cost
 - Typically need at least 4 cylinders (up to 7 for some approaches) per site
 - Recalibrated multiple times within the life of the cylinder
- Networks
 - Known scaling factors or comparisons to link with other scales

Acknowledgments



