Monitoring Trends and Spatial Distributions of Carbon Cycle Greenhouse Gases and Related Tracers

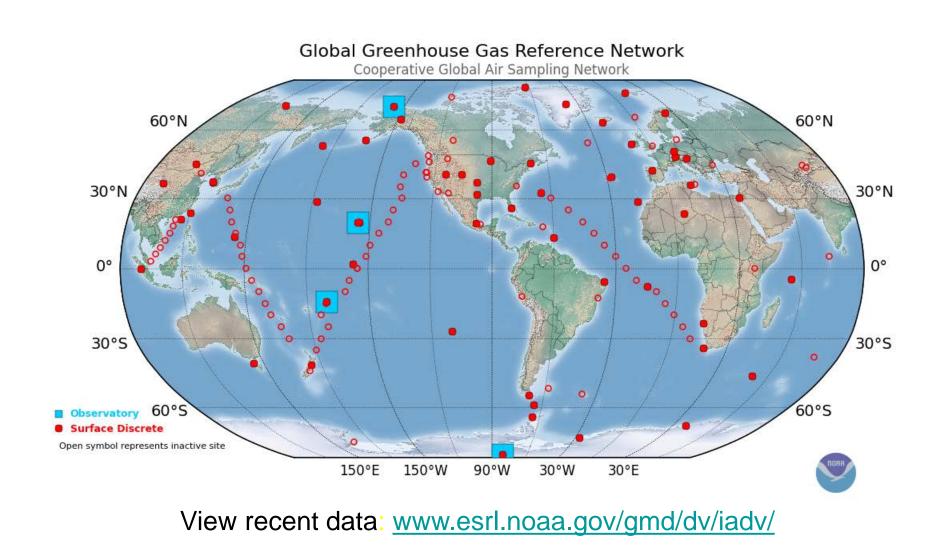
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Acknowledgement: GMD Administrative Staff

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Cooperative Global Air Sampling Network - unique in its coverage Weekly samples collected with portable sampler Sites selected to sample well-mixed air

Scientific Motivation

- Determine budgets and how they change with time
 - Quantify emissions and sinks of LLGHGs at global to large regional spatial scales
 - Determine impacts of climate change on LLGHG budgets
 - Long-term continuity and consistency of observations are important

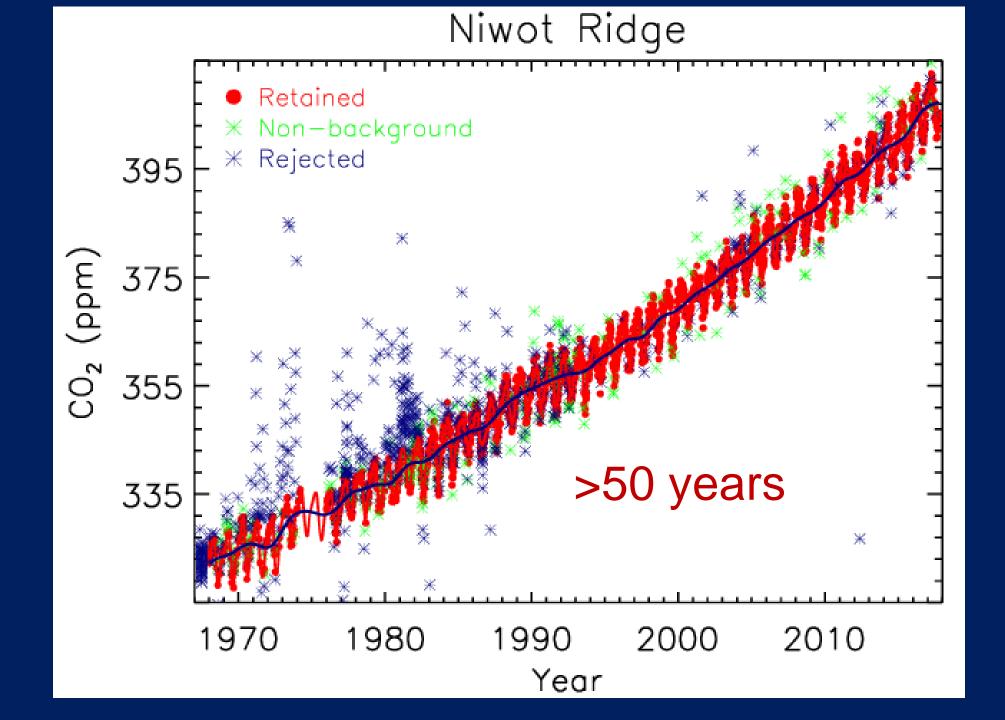
Approach

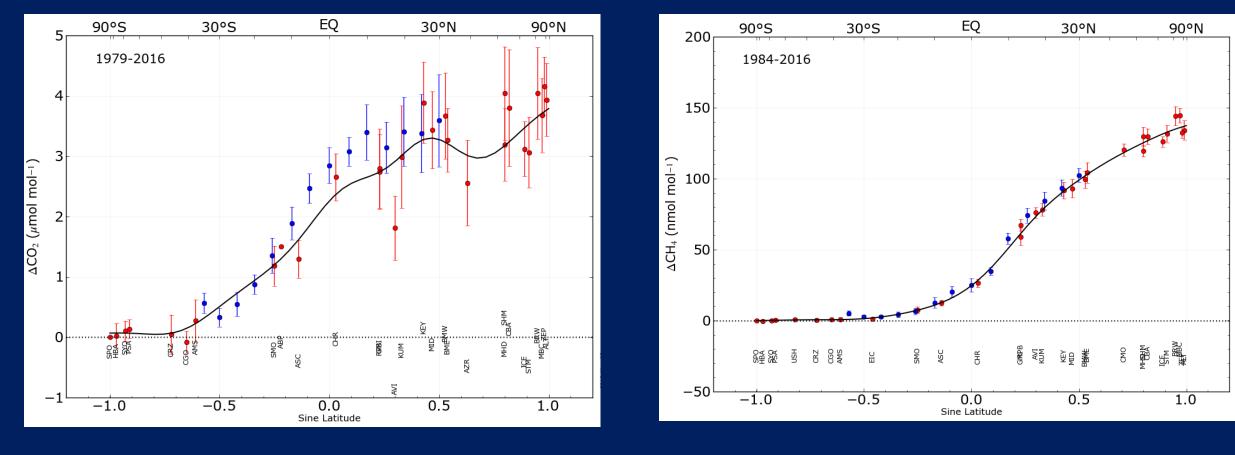
- Accurately, precisely measure spatial, temporal distributions of LLGHGs and related tracers
 - Meaningful temporal and spatial gradients
 - Ensure long-term consistency with QA scheme
 - Developed by Dave Keeling in 1950s

Analytical Capabilities

(All flask-air samples)

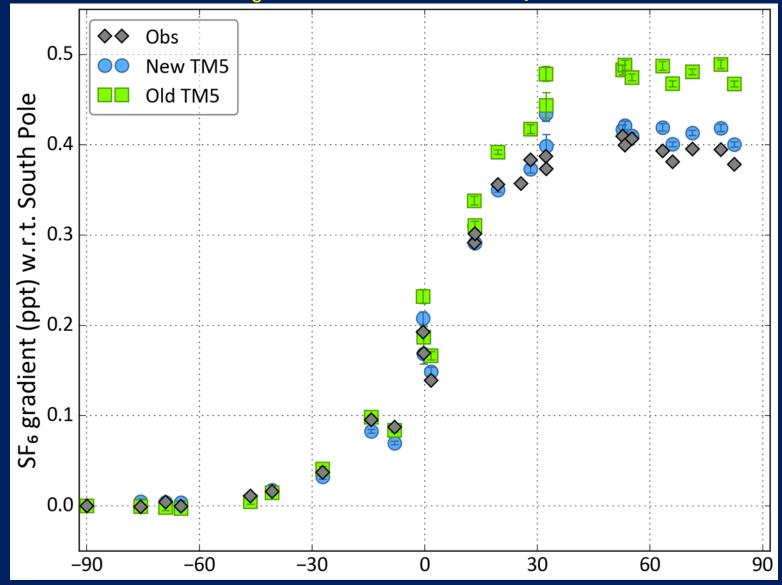
Uncertainty (68% CI) Technique Gas 0.08 µmol mol⁻¹ $NDIR \rightarrow CRDS$ CO_2 CH_{4} $0.9 \text{ nmol mol}^{-1}$ $GC/FID \rightarrow CRDS$ $VUV-RF \rightarrow TILDAS$ CO 1.7 nmol mol⁻¹ **GC/PD-HeID** H_2 *0.5 nmol mol⁻¹ $GC/ECD \rightarrow TILDAS$ N_2O 0.26 nmol mol⁻¹ SF₆ 0.04 pmol mol⁻¹ GC/ECD $\delta^{13}CO_2$ **DI-IRMS** *0.01‰ δ¹³CH₄ **GC/CF-IRMS** *0.04‰ C₂-C₇ NMHC †<15% **GC/FID** *Repeatability; †Median pair difference



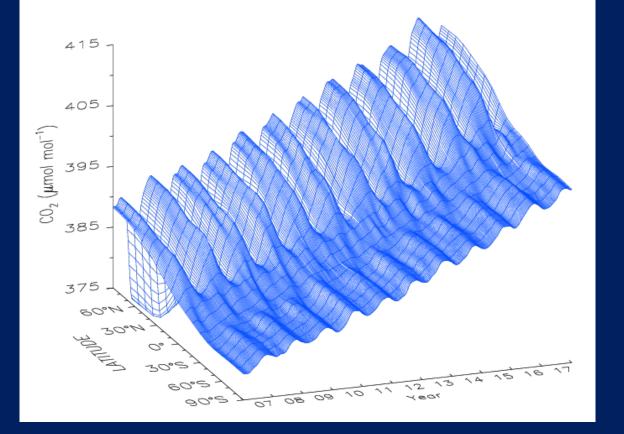


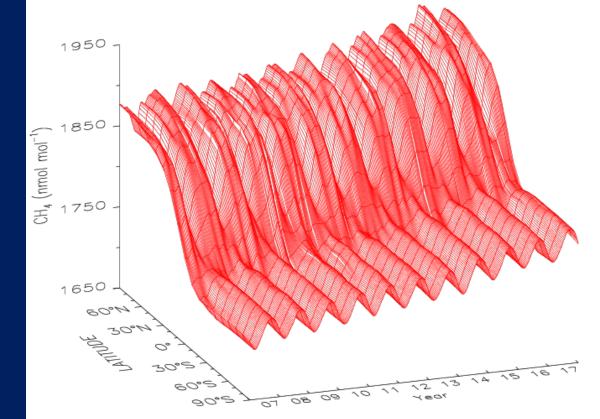
Latitude gradient constrains budgets of emissions and sinks: Tans et al., 1990: NH terrestrial carbon sink Fung et al., 1991: Less HNH, greater tropical CH₄ emissions

SF₆: Test Model Transport



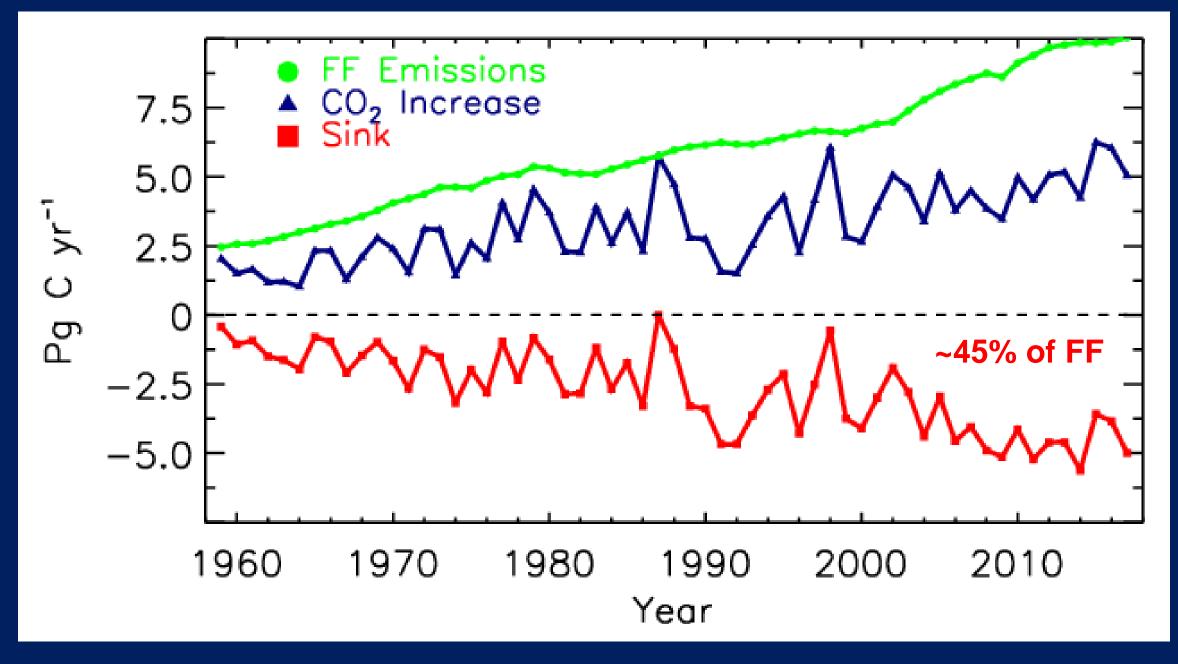
Peters et al., JGR, 2004; Basu et al., ACP, 2016.



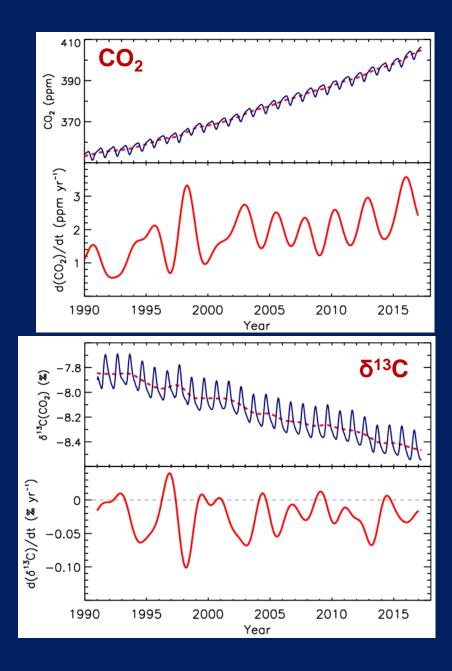


Calculation of global and zonal surface means:

NOAA global trends web pages (Organizations, e.g., 2° Institute) Assessments (e.g., IPCC) AGGI (Radiative forcing) Peer-reviewed global GHG budget analyses



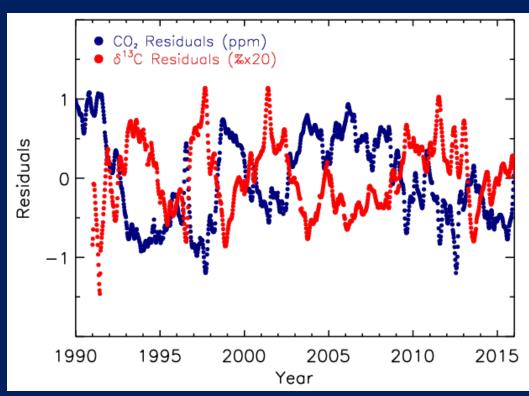
Based on update of Ballantyne et al., Nature, 2012.

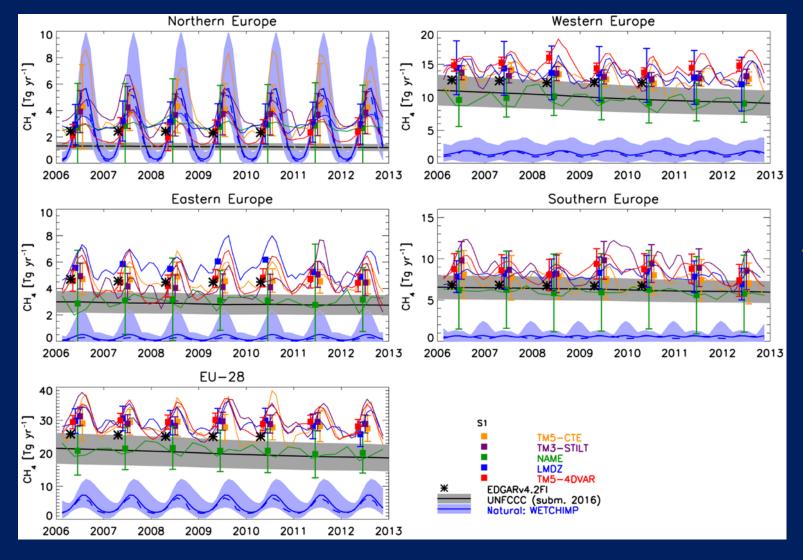


δ^{13} C as process indicator

-Differentiate ocean/terrestrial biosphere fluxes -Biosphere: ~0.045‰ ppm⁻¹ -Ocean: ~0.005‰ ppm⁻¹

δ^{13} C scaled to match CO₂ residuals:





Use of observations in atm inversion products to study global budgets: $CT (CO_2 \text{ and } CH_4)$ $CAMS (CO_2, CH_4, \text{ and } N_2O)$ $GCP (CO_2 \text{ and } CH_4)$ Research studies Also used in regional-scale studies: Bergamaschi et al., 2018

Summary

- CCG network is unique in its spatial coverage
- Continually evolving to meet scientific needs
- Delivers internally-consistent, calibrated observations of known quality over long time scales
 - Detailed QA/QC system
- Great scientific benefit at relatively small cost
 - Fundamental constraints on GHG budgets and CTMs

Uncertainties

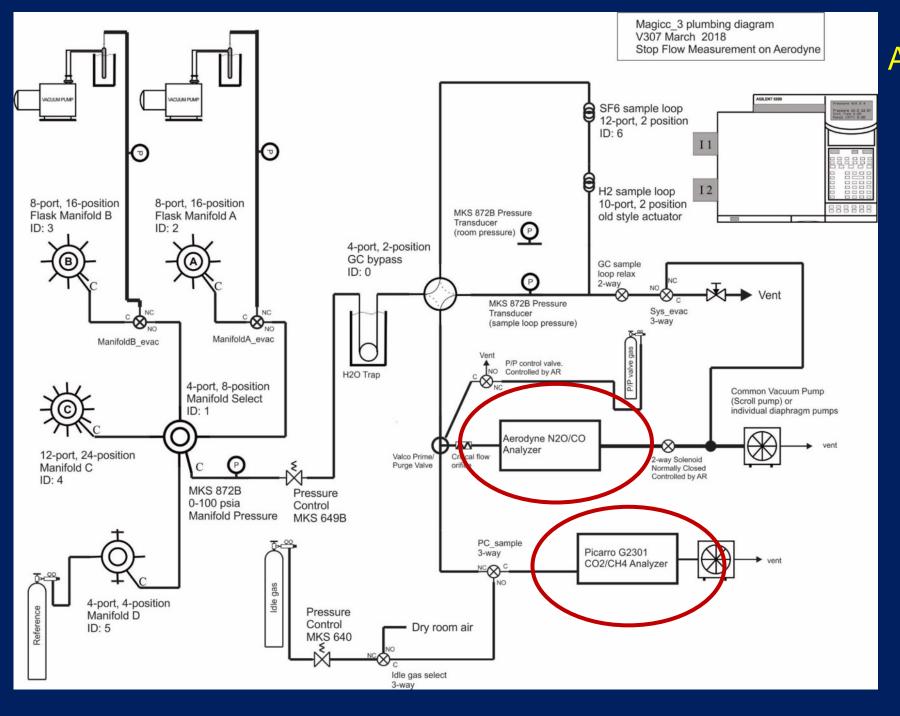
- Uncertainties on measurements from flask-air
 - Assessing major components of uncertainty (u_i)
 - Other terms, when required

$$-u^{2} = u_{st}^{2} + u_{lt}^{2} + u_{sp}^{2} + \dots$$

- Uncertainties on zonal means
 - Network contribution (bootstrap random sampling)
 - Potential bias contribution (Monte Carlo random modifications)

Future of Network

- Enhance spatial coverage
 - Increase sampling from ships (restart POC; add new basins)
 - Add tropical sites (Taiping Is.; Reunion Is.)
 - Improve existing sampling methods
- Improve quality of measurements
 - Testing new flask-air analysis system
- Increase efficiency (w/o sacrificing quality)



Analysis Upgrade: Same time/sample Less Sample Used Improved Precision Standard Cal Scheme Improved User Interface Increased Efficiency

Ensuring Quality of Data

• Quality Assurance

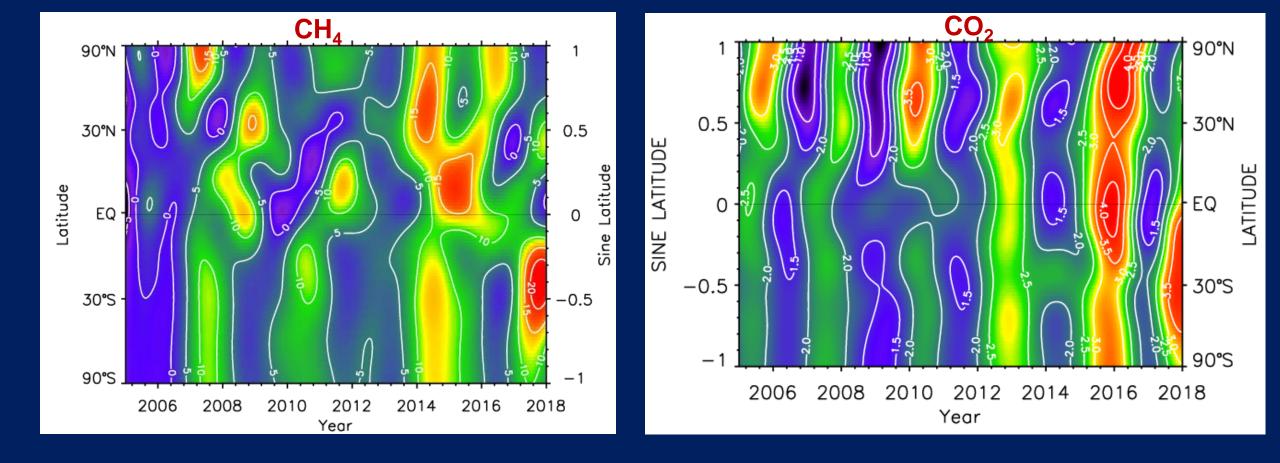
- Daily test flasks and surveillance cylinders
- Testing portable air samplers
- Quality Control
 - Inspection of "data" for sampling and analysis problems
 - Comparisons with independent measurements

QA/QC

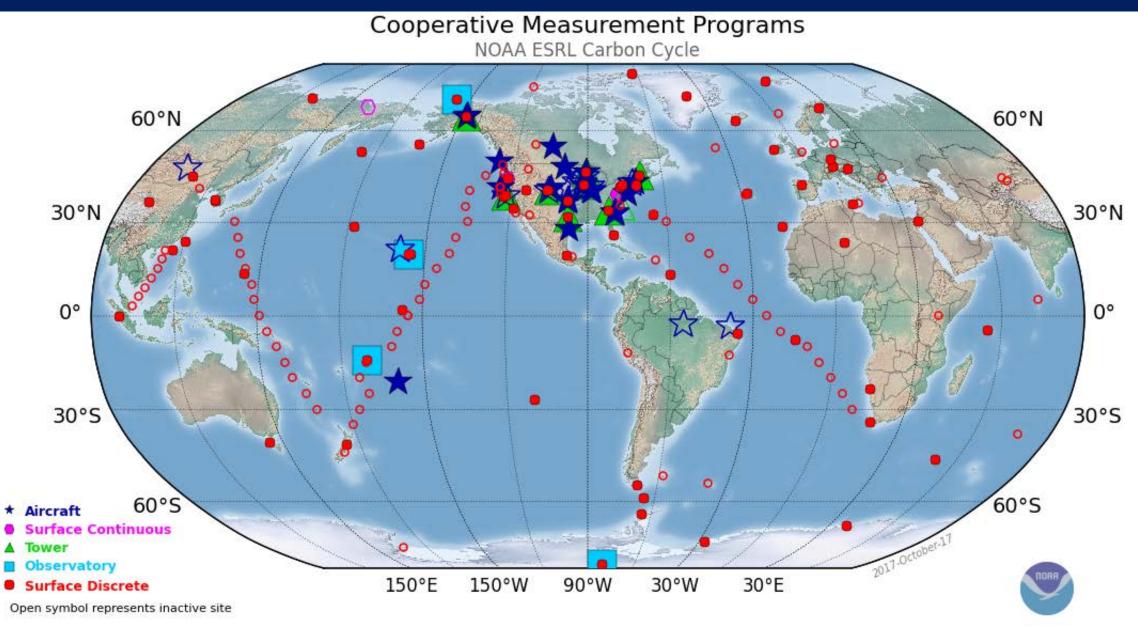
- Test flasks
 - Pair filled from cylinder of calibrated air run daily
- Target cylinders
 - Short-term (close to ambient) run monthly
 - Long-term (wide range in X) run few times/year
- Flask/in situ comparisons at observatories
- Comparisons with GAW partners + others
 - Same air
 - Co-located

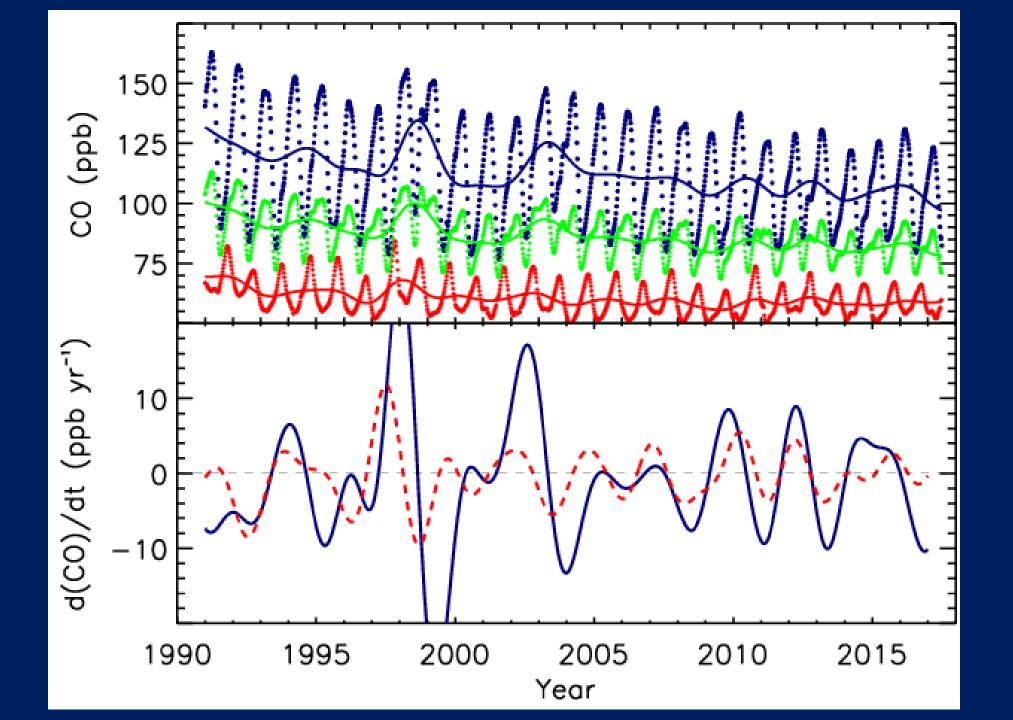
Remote Sensing

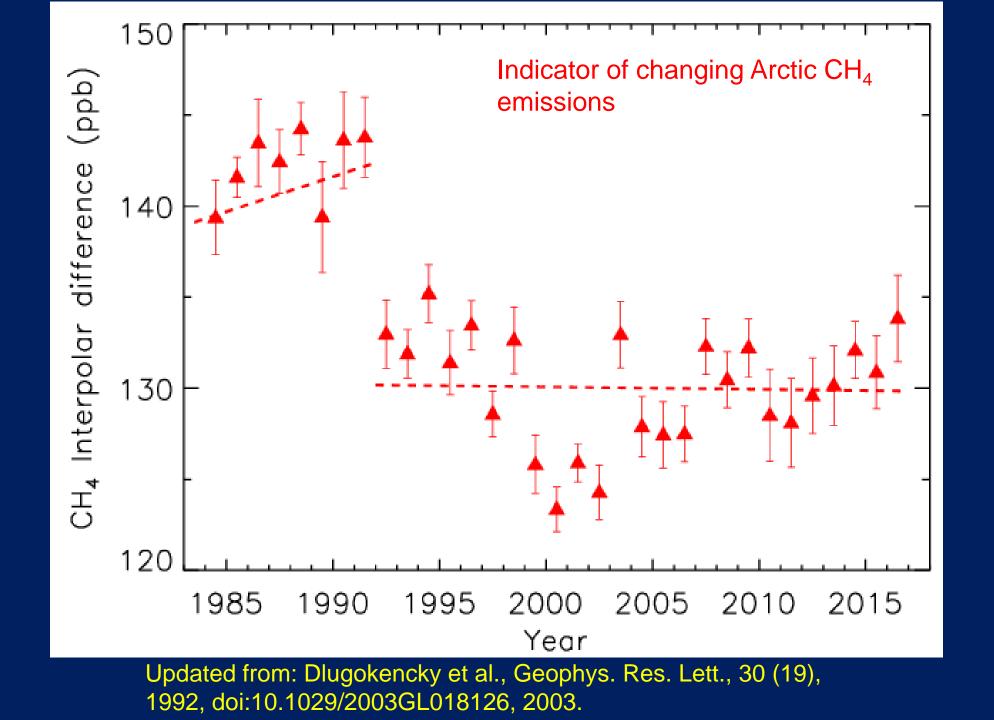
- Never calibrated, only evaluated
 - -e.g., with vertical profiles; Aircore
- Sensor degradation over time
- Potential biases (e.g., land vs ocean)
- "Short" deployment for satellites
- Retrieve total column; strongest signals at surface
- Different retrieval versions give very different results – e.g., in CO₂ inversions

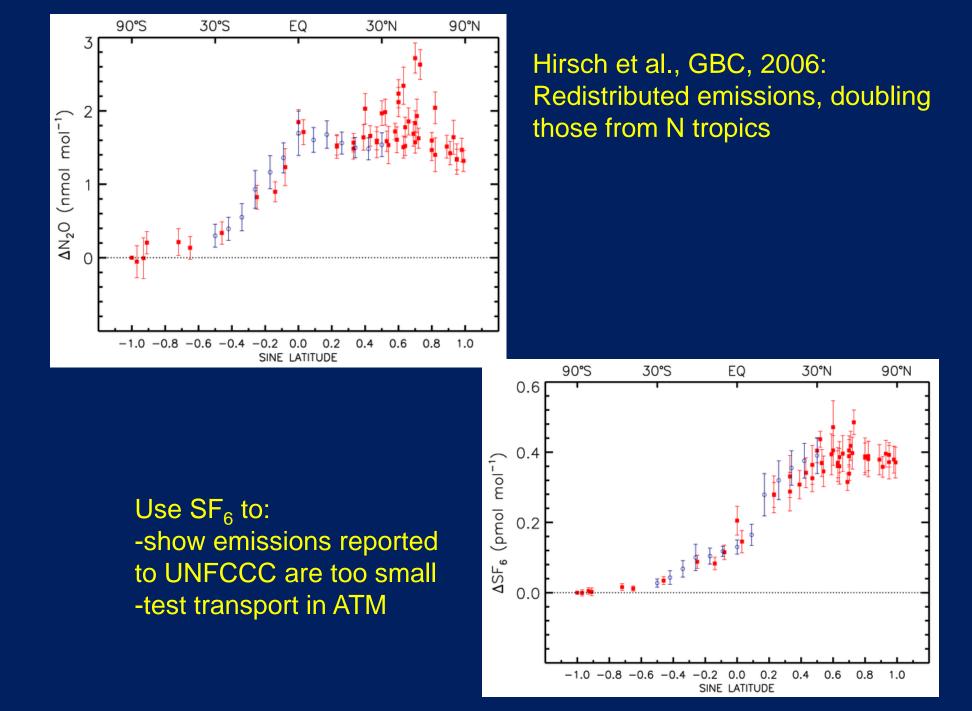


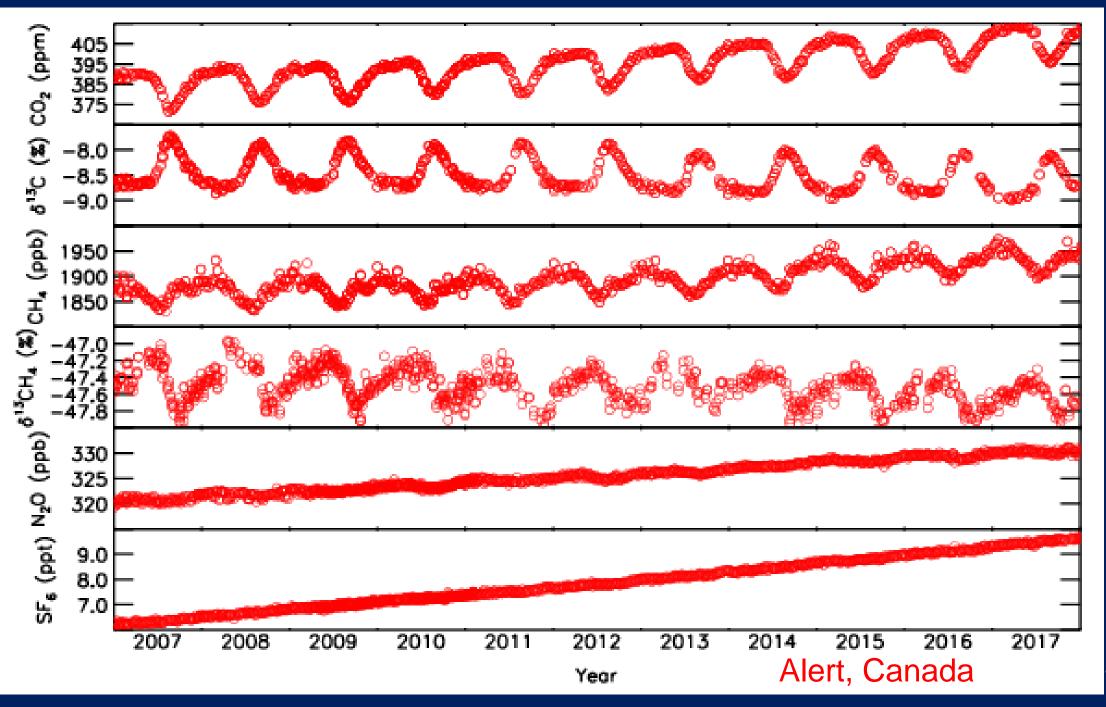
Calibration: Calibration links the measured response of an analyzer, under controlled conditions, to known values of measurement standards (with known uncertainties). That response is used to assign values and uncertainties to other samples. Standards must be linked to fundamental SI units in a single, unbroken, hierarchical chain of traceability.

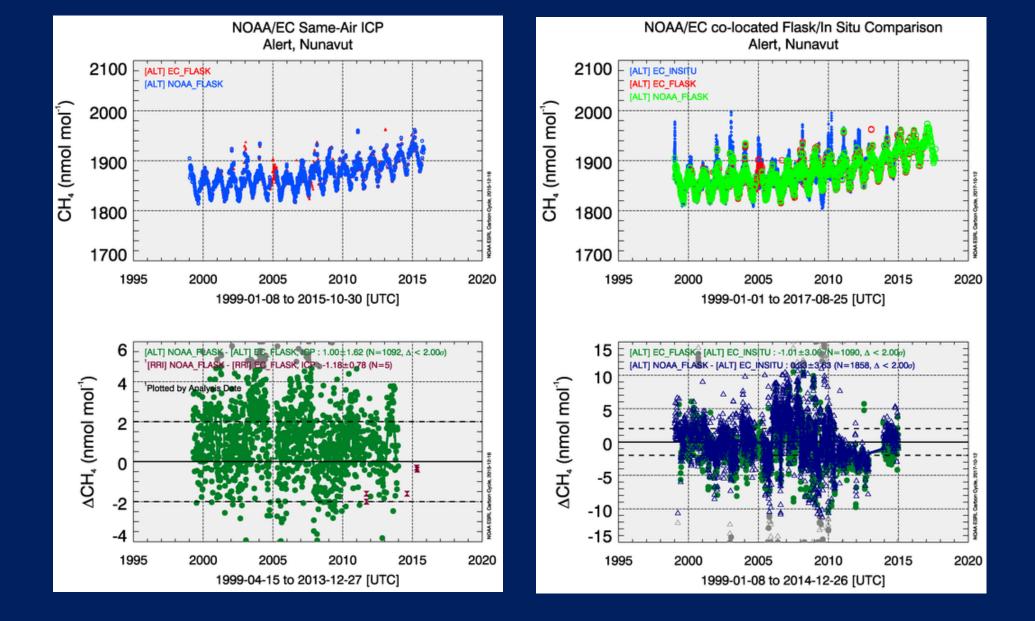






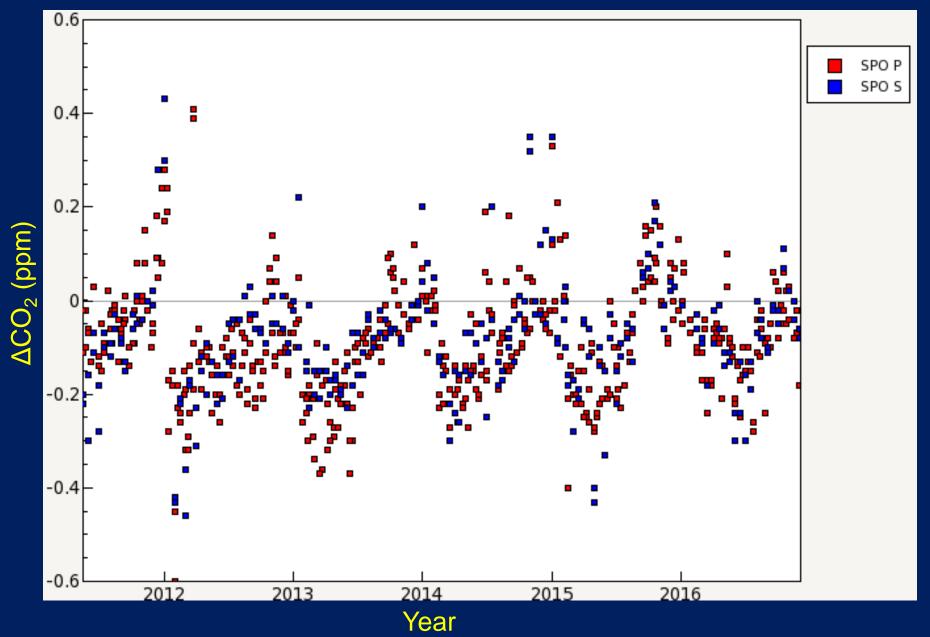


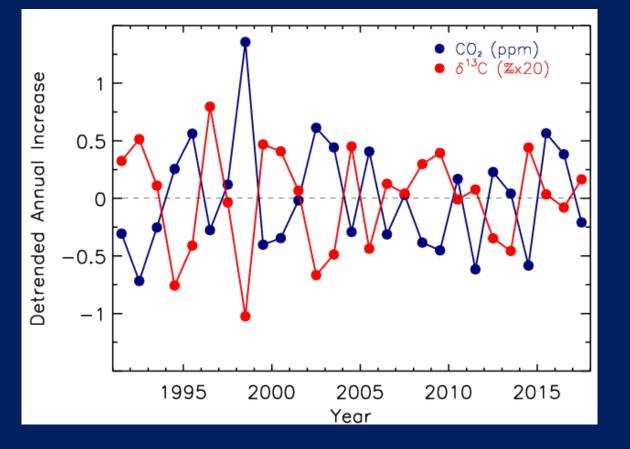


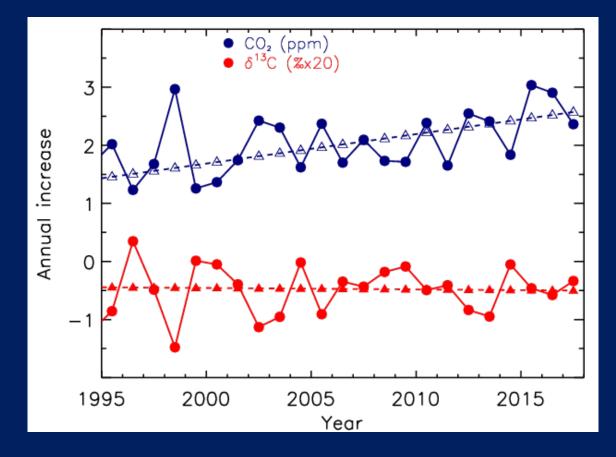


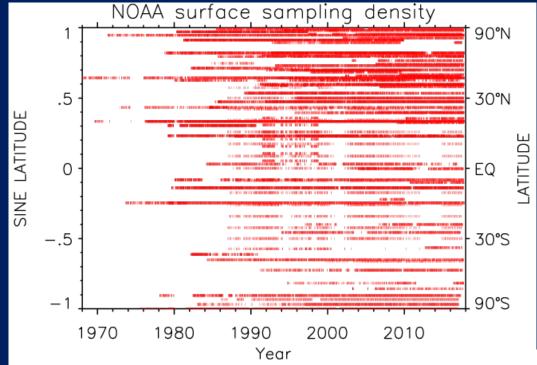
Quality Control

Using *in situ* measurements for CO₂ quality assurance: SPO



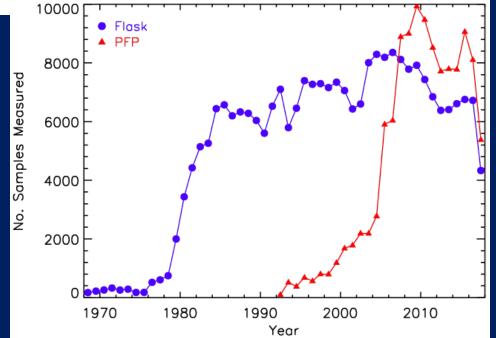




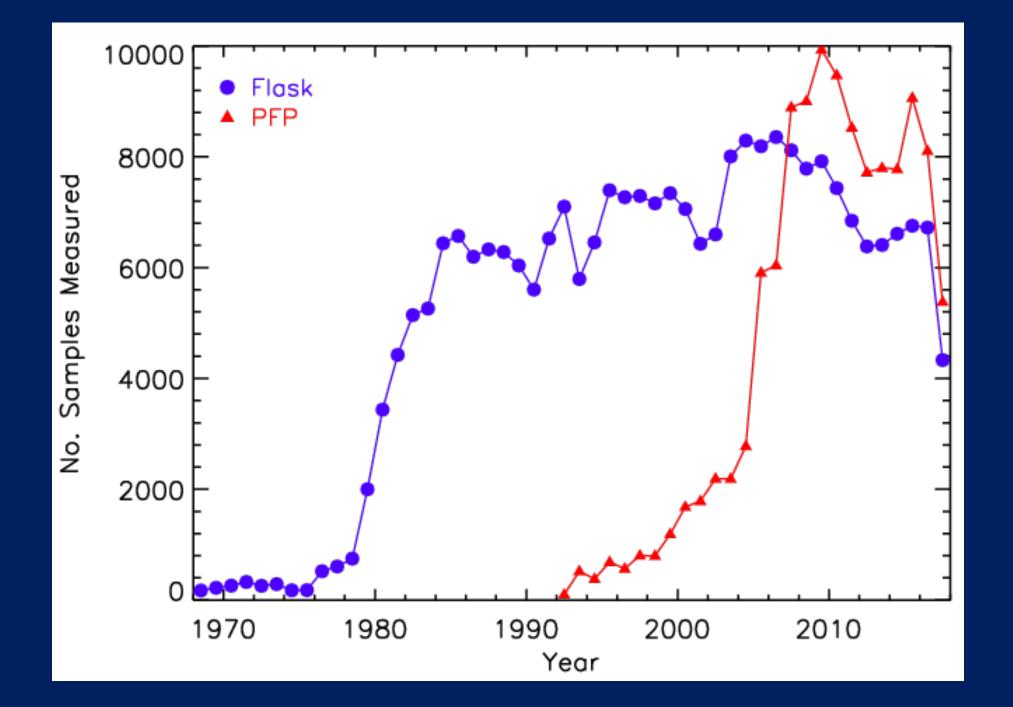


-Measurement load increased with expansion of network and addition of NA projects

-Added CO₂ at obs. in early-1970s -Expansion through 1980s -Increasing # species measured -Addition of N.A. focus (PFPs)



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A Dynamic Program

- 1967 began CO₂ measurements
- 1983 began CH₄ measurements
- 1988 began CO/H₂ measurements
- 1990 began $\delta^{13}CO_2$ measurements
- 1997 began N₂O/SF₆ measurements
- 1998 began $\delta^{13}CH_4$ measurements
- 2004 began halo-compound measurements
- 2005 began NMHC measurements