NOAA Global Monitoring Annual Conference
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Keeping Up the Standards: Building and Maintaining a Global Atmospheric Measurement Network

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Station Locations and Custom Instrumentation

What problem(s) are you trying to solve?

Advanced Global Atmospheric Gases Experiment (AGAGE)

Mace Head 52°N

Trinidad Head 41°N

“Legacy”
ALE/GAGE/AGAGE
Station Locations

Ragged Point 13°N

Cape Matatula 14°S

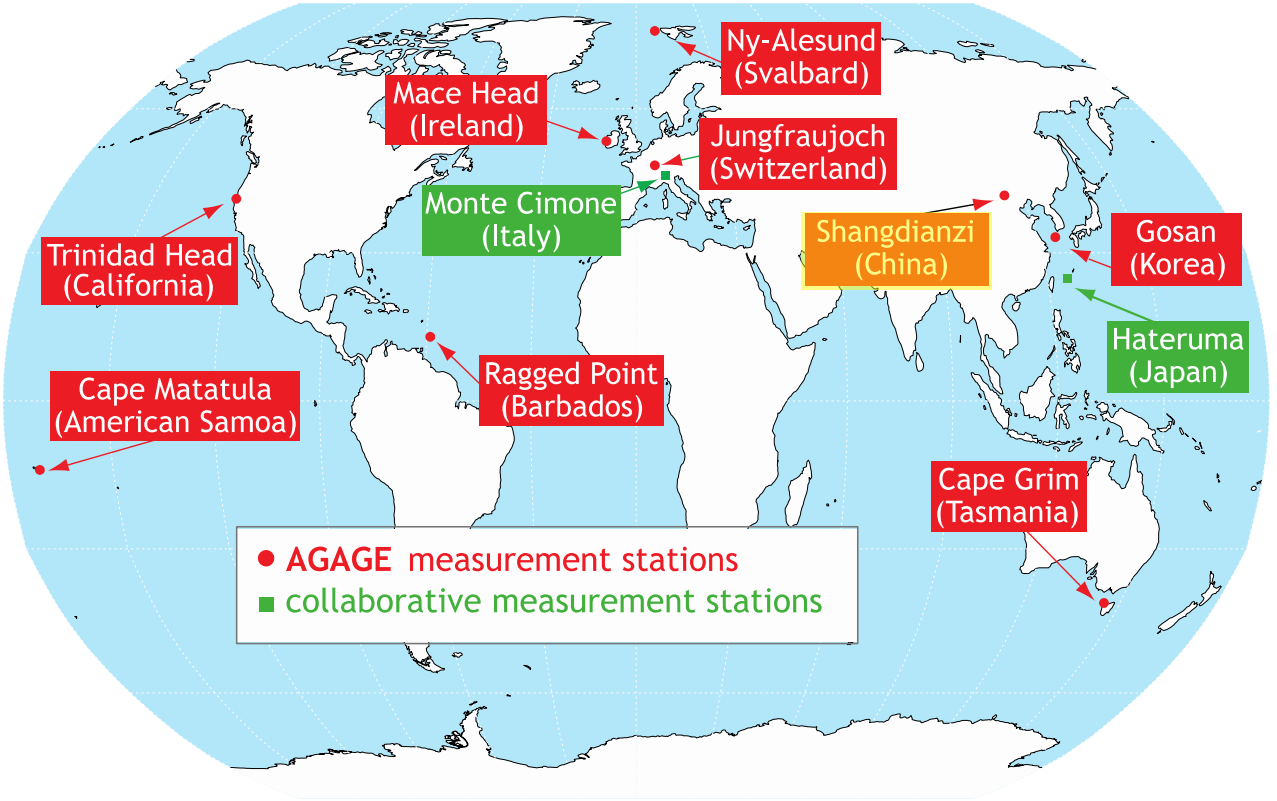
Cape Grim 41°S

AGAGE

Advanced Global Atmospheric Gases Experiment (AGAGE)

AGAGE and its predecessors ALE and GAGE have been measuring changes in the composition of the global atmosphere since 1978.

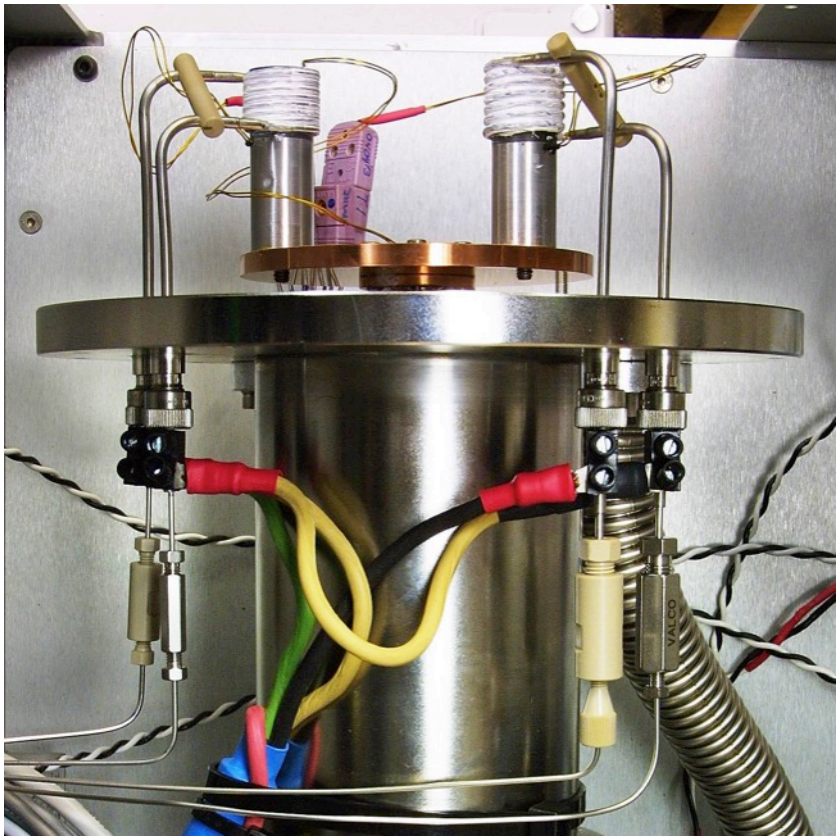
AGAGE measures at high frequency over the globe almost all of the important species regulated by the Montreal Protocol to protect the stratospheric ozone layer, and almost all of the significant non-CO_2 gases in the Kyoto Protocol to mitigate climate change.

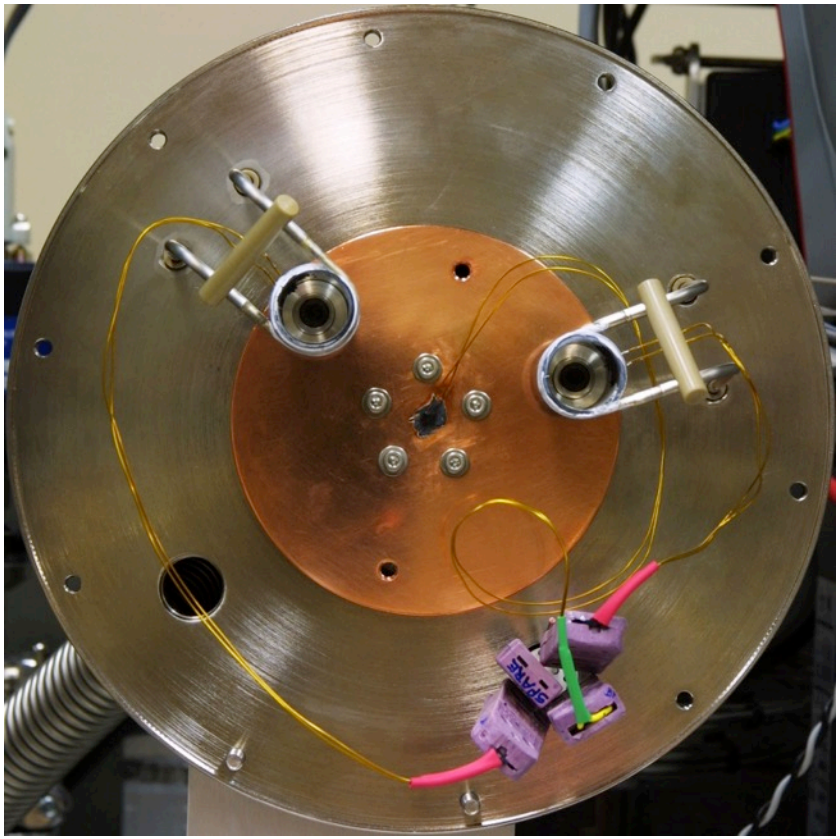


AGAGE stations occupy coastal & mountain sites around the world chosen to provide accurate measurements in clean and polluted air of trace gases whose lifetimes are long compared to atmospheric transport times.

AGAGE *Medusa* Cryotrapping GC-MS (left) and GC-Multidetector (right) Instruments at Trinidad Head, California

Medusa Cryotraps (top view)





Medusa Cryotraps (front view)

AGAGE measured species. Medusa in Blue; GC-MD: Green; Both: Red.

AGAGE currently measures over 50 environmentally active atmospheric trace gases in clean & polluted air using custom automated gas chromatographic and mass-spectrometric instrumentation.

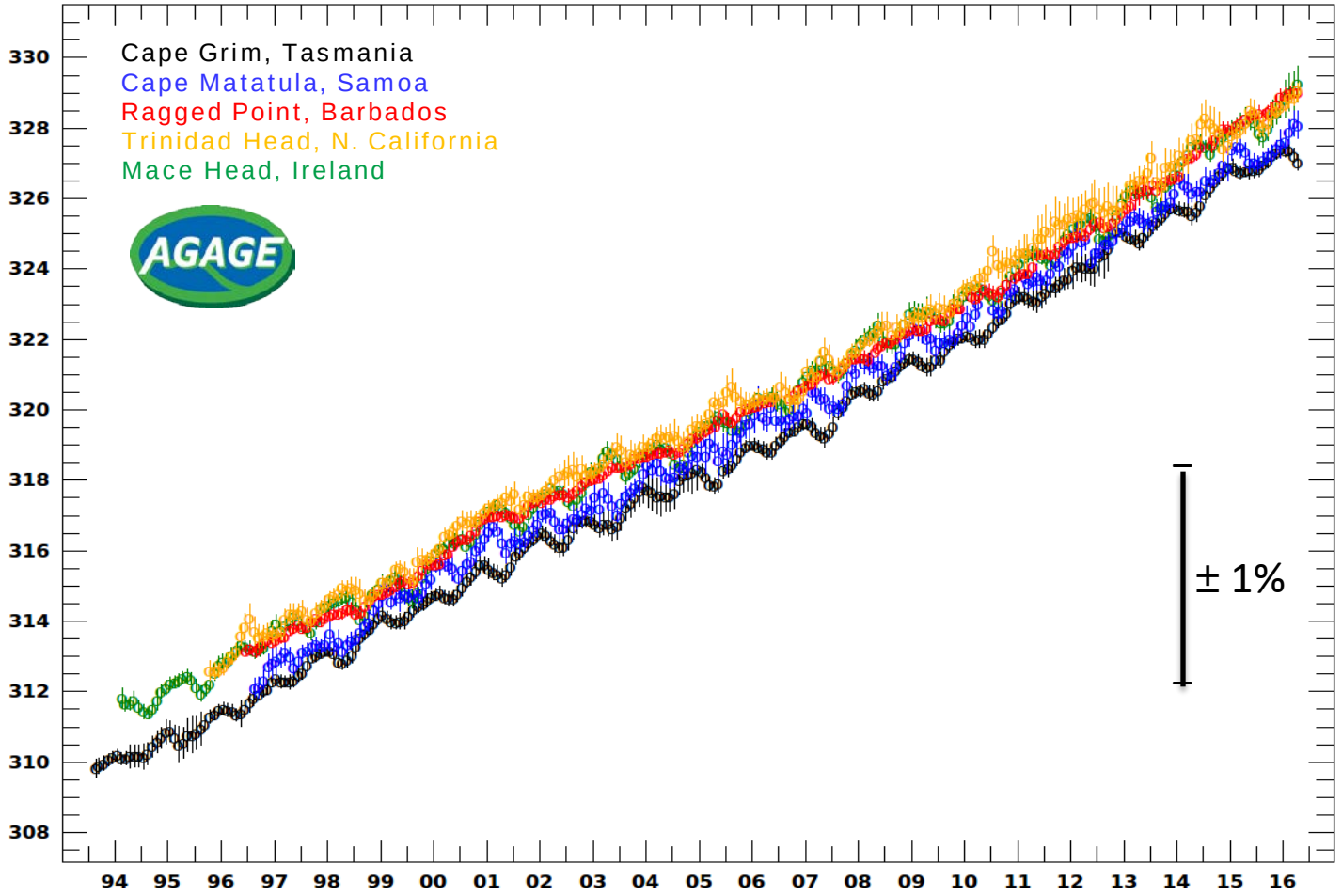
Public Data Archive at:
http://cdiac.ornl.gov/ndps/alegage.html

* CO 80-140

Calibration and Calibration Scales

Independence, Traceability, Reproducibility, Timeliness

Structuring the calibration problem to maximize the scientific value of long-term measurements of trace gases in the global atmosphere:



Background Nitrous Oxide Dry Air Mole Fractions in ppb on the SIO-98 Primary Calibration Scale: Monthly Means and Standard Deviations: 36 Measurements/Day at 5 AGAGE Stations

Important Considerations When Measurement Precision Exceeds Primary Standard Preparation Accuracy

- **Accuracy *vs.* precision: The importance of a rigorously defined calibration scale at near-ambient atmospheric levels.**
- **Real gases and well-defined units: The dry air mole fraction.**
- **Defining the problem in a workable way: Going stepwise from ppm to ppb to ppt using the "bootstrap" method.**
- **Measuring concentration ratios and determining the precision of primary standard preparation in the presence of instrumental nonlinearity: Creating a calibration scale.**
- **Confirming long-term stability and traceability: Making and measuring new primary standards over time.**

The "Bootstrap" Method

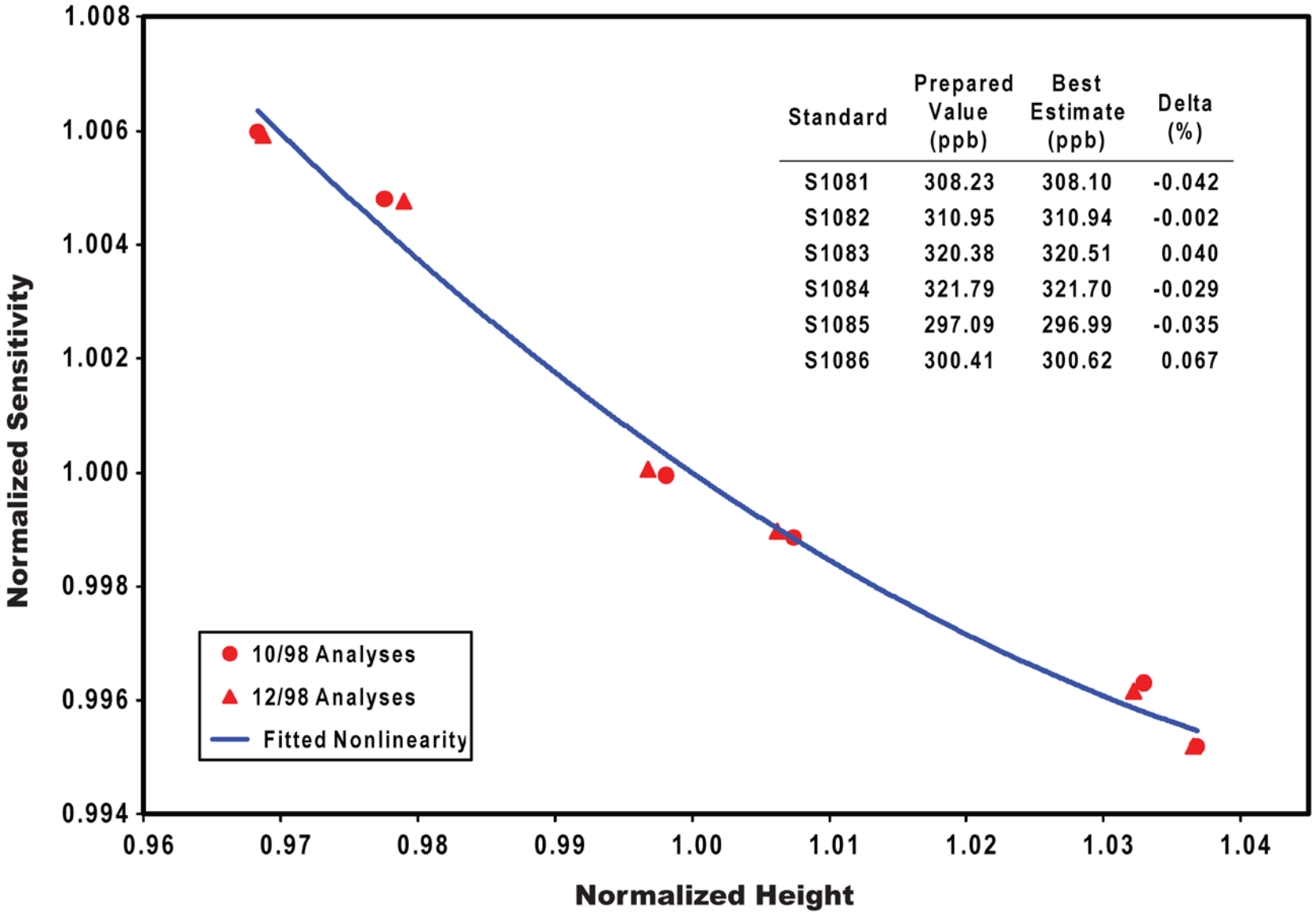
A Stepwise Ratio Approach of Cascading Precisions and Accuracies:

Step 0: The SIO (Keeling) Manometric Carbon Dioxide (CO_2) ppm Ambient Atmospheric Calibration Scale – CO_2 in Dry Air.

Step 1: Calibration of the Nitrous Oxide (N_2O) at ppb Ambient Atmospheric Levels

- Prepare gravimetric and volumetric mixtures with N_2O/CO_2 ambient mole ratios using large quantities of gas to minimize errors.
- Dilute aliquots of these mixtures to ambient levels (~2500-fold) using N_2O- and CO_2-free artificial "zero air" (~400 L in 15 L silica-coated SS high-pressure canisters)
- Measure CO_2 and calculate N_2O from the mole ratios of the diluted mixtures.
- Prepare multiple primary standards and precisely measure their N_2O concentrations against each other to establish an N_2O calibration scale and to quantify the precision of the primary standardization process.

Nitrous Oxide Primary Standards: SIO-98 Calibration Scale
(297-321 ppb, σ = 0.045%, n = 6)



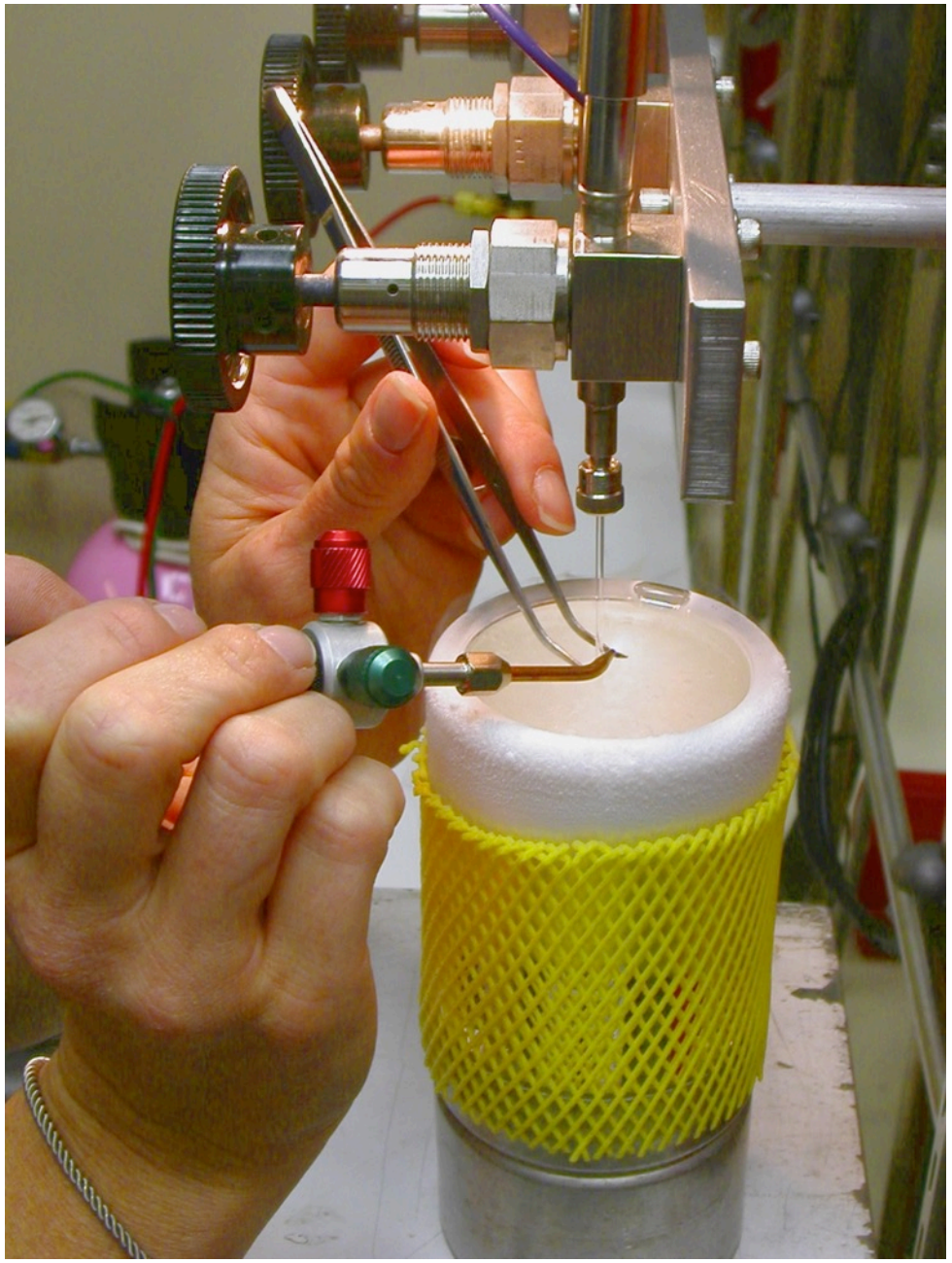
Standard	Prepared Value (ppb)	Best Estimate (ppb)	Delta (%)
S1081	308.23	308.10	-0.042
S1082	310.95	310.94	-0.002
S1083	320.38	320.51	0.040
S1084	321.79	321.70	-0.029
S1085	297.09	296.99	-0.035
S1086	300.41	300.62	0.067

Step 2: **Calibration of Halocarbons and Other Trace Gases at ppt Ambient Atmospheric Levels (~600 ppt to ~1 ppt)**

- **Prepare gravimetric mixtures with trace gas/N_2O ambient mole ratios of ~2×10^{-3} to ~4×10^{-6} using large quantities of gas to minimize errors.**
- **Dilute aliquots of these mixtures to ambient levels (~3×10^6 -fold) using trace gas- and N_2O-free artificial "zero air" (1500-2100 L in 35 L electropolished SS high-pressure canisters).**
- **Measure N_2O dry gas mole fraction and calculate dry mole fractions of trace gases from the mole ratios of the diluted mixtures.**
- **Prepare multiple primary standards and precisely measure their trace gas concentrations against each other to establish a trace gas calibration scale and to quantify the precision of the primary standardization process.**

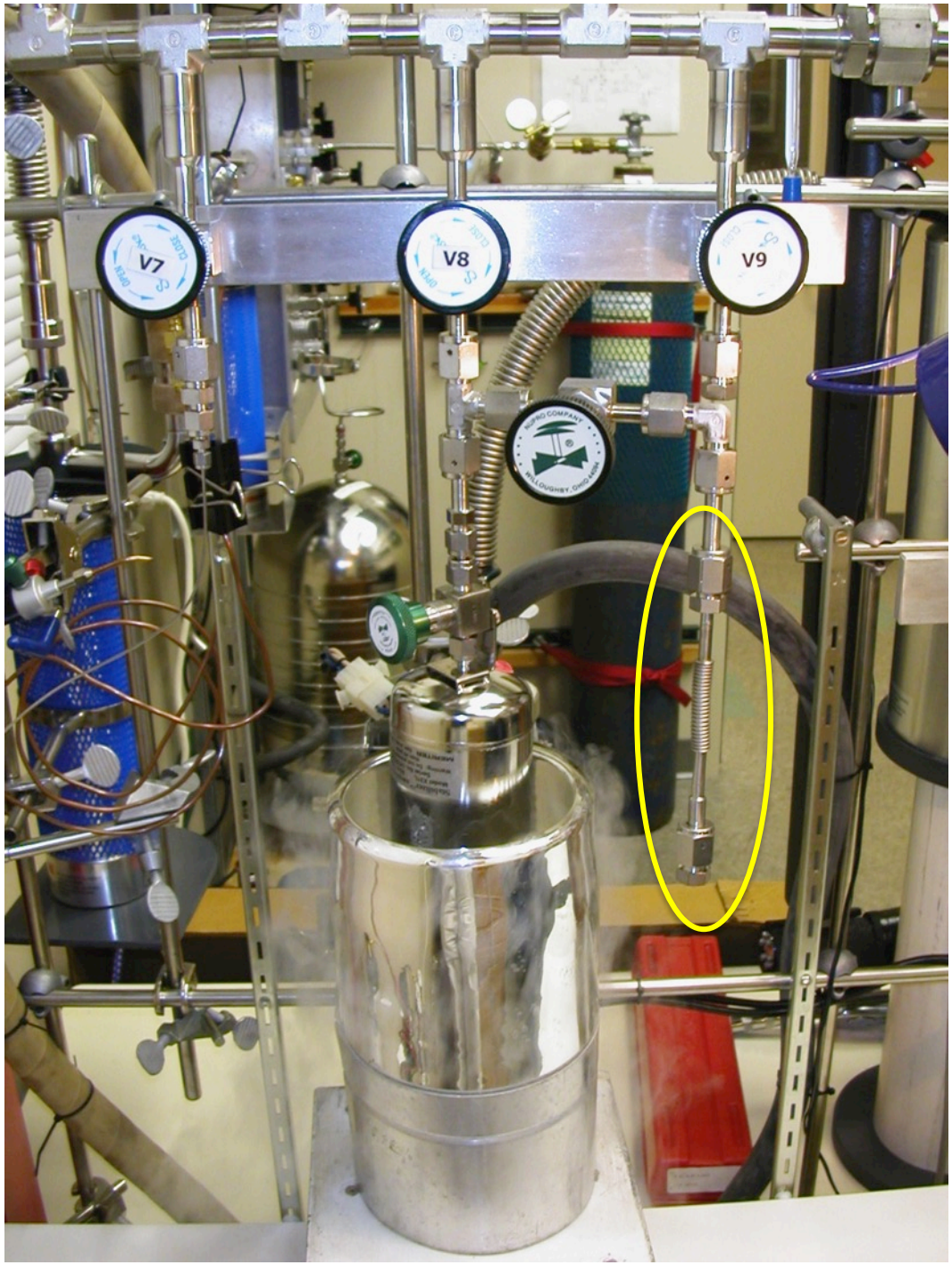
Standards
High-Vacuum
Line
(front view)

Micro-Capillary Sealing



Mixture Canister and Capillary Breaker

(~mg (±1µg) of each halocarbon in ~40 g (±1mg) N_2O)

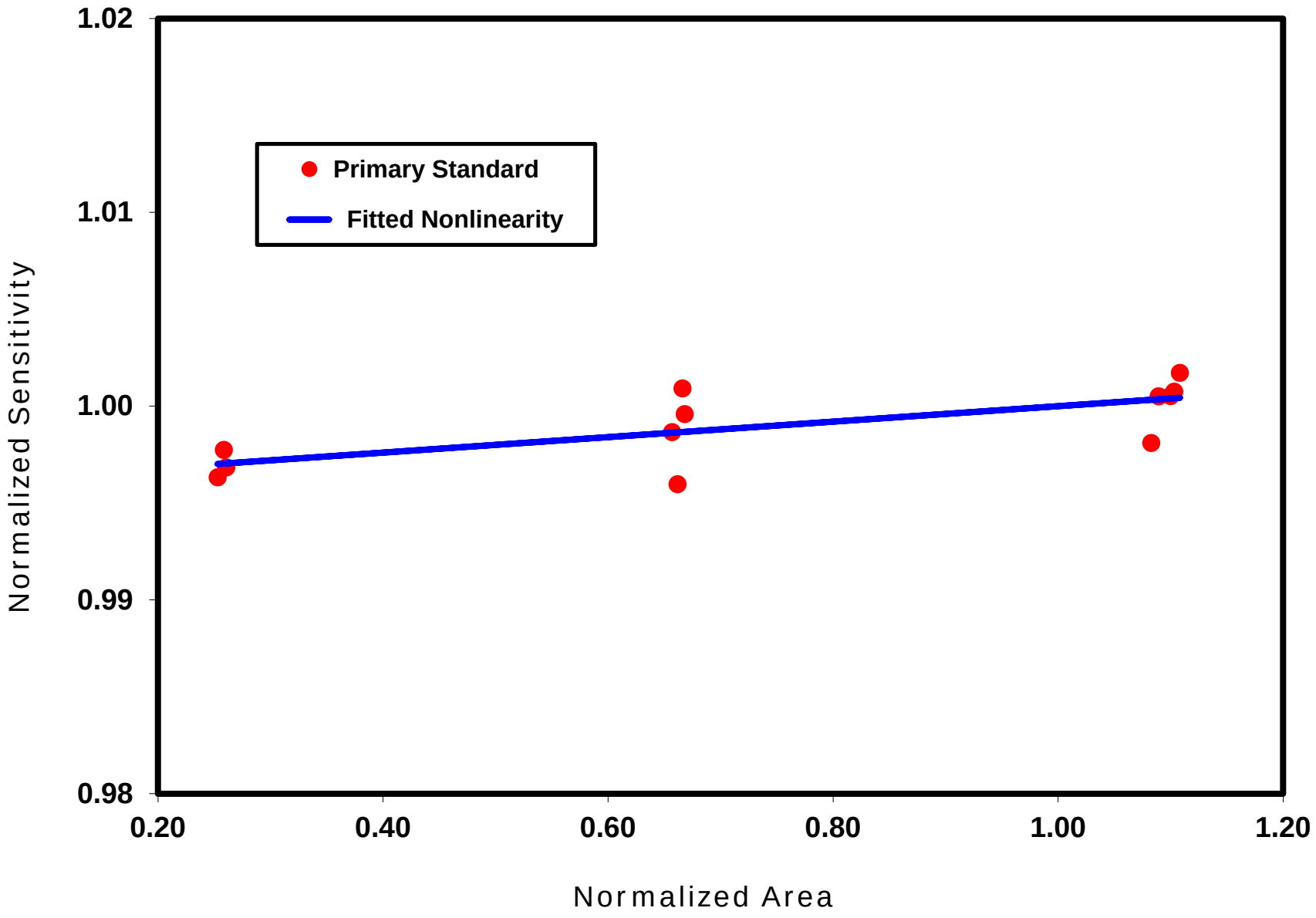


Standards High-Vacuum Line (rear view)

(~35 liter thermostated N_2O volume)

Spiking System

(~0.45 ml of halocarbon-N_2O mixture in ~1400 liters of purified "zero air")


HCFC-141b Primary Standards: SIO-2005 Calibration Scale
(5-20 ppt, σ = 0.14%, n = 12)
Primary Standard
Fitted Nonlinearity
Normalized Sensitivity
1.02
1.01
1.00
0.99
0.98
0.20
0.40
0.60
0.80
1.00
1.20
Normalized Area

The "R1" Relative Calibration Scale

Transferring Calibrations to Real Air Measurements:

- Compress ~2100 L of clean real air into 35 L electropolished SS high-pressure canisters, with ~20 torr water vapor for stability, for use as "gold tank" secondary standards.
- Measure these against each other for all trace gases measured by AGAGE, and arbitrarily designate one of them as the "R1" relative calibration gas.
- Calibrate "R1" concentrations for all trace gases for which we have a primary calibration scale by measuring them against our artificial air primary standards. "R1" values can also be determined against any other calibration scale (e.g. NOAA, NIES, etc.)
- All ambient air measurements in the AGAGE network are initially calculated relative to the "R1" scale, which is propagated to field stations using tertiary real air transfer standards.
- Calibration factors are then applied to obtain atmospheric concentrations. Calibrations can be refined, or made retrospectively, for any trace gas measured on the "R1" relative calibration scale.

SIO Primary Standard Preparations for 45 AGAGE Species: R1 Values and Precisions

Nitrous Oxide, Fluorinated S and N Gases, PFCs, CFCs, and HCFCs

Species	Scale	R1 Value	Number of Standards	Approximate Concentrations	Relative Standard Deviation
N_2O	SIO-98	318.15 ppb	6	300 - 320 ppb	0.05%
NF_3	SIO-12	0.9591 ppt	4	8 ppt	0.51%
SF_5CF_3	SIO-14	0.165 ppt	4	1.3 ppt	2.3%
SF_6	SIO-05	5.34 ppt	4	5 ppt	0.41%
SO_2F_2	SIO-07	1.288 ppt	5	3.5 ppt	0.76%
CF_4	SIO-05	74.01 ppt	4	84 ppt	0.23%
PFC-116 (C_2F_6)	SIO-07	3.58 ppt	5	4 ppt	0.29%
PFC-218 (C_3F_8)	SIO-07	0.409 ppt	5	2 ppt	0.49%
PFC-318 (c-C_4F_8)	SIO-14	1.266 ppt	4	1.3 ppt	0.23%
C_4F_{10}	SIO-12	0.1718 ppt	4	1.4 ppt	1.13%
C_5F_{12}	SIO-12	0.1237 ppt	4	1.4 ppt	0.50%
C_6F_{14}	SIO-12	0.2694 ppt	4	2.7 ppt	0.77%
C_7F_{16}	SIO-12	0.1178 ppt	4	1.4 ppt	2.21%
C_8F_{18}	SIO-12	0.0869 ppt	4	1.4 ppt	1.90%
CFC-11	SIO-05	255.54 ppt	23	230 - 290 ppt	0.29%
CFC-12	SIO-05	546.31 ppt	27	500 - 550ppt	0.25%
CFC-113	SIO-05	80.15 ppt	17	75 - 85 ppt	0.21%
CFC-114	SIO-05	16.63 ppt	13	16 - 20 ppt	0.14%
CFC-115	SIO-05	8.32 ppt	13	8 - 10 ppt	0.47%
HCFC-22	SIO-05	167.01 ppt	20	100 - 200 ppt	0.27%
HCFC-141b	SIO-05	18.64 ppt	12	5 - 20 ppt	0.14%
HCFC-142b	SIO-05	15.37 ppt	13	7 - 21 ppt	0.21%

SIO Primary Standard Preparations for 45 AGAGE Species: R1 Values and Precisions

HFCs, Halons, Methyl and Cyclic Halides

Species	Scale	R1 Value	Number of Standards	Approximate Concentrations	Relative Standard Deviation
HFC-23	SIO-07	20.63 ppt	3	15 ppt	0.39%
HFC-32	SIO-07	0.663 ppt	5	5 ppt	0.49%
HFC-125	SIO-14	3.12 ppt	4	15	0.20%
HFC-134a	SIO-05	28.53 ppt	13	5 - 35 ppt	0.28%
HFC-143a	SIO-07	4.56 ppt	5	6 ppt	0.56%
HFC-152a	SIO-05	4.17 ppt	13	2 - 6 ppt	0.56%
HFC-227ea	SIO-14	0.654 ppt	4	1.3 ppt	0.74%
HFC-236fa	SIO-14	0.0929 ppt	4	1.3 ppt	0.72%
HFC-245fa	SIO-14	1.337 ppt	4	1.5 ppt	3.51%
HFC-365mfc	SIO-14	0.606 ppt	3	1.2 ppt	0.51%
HFC-4310mee	SIO-14	0.180 ppt	3	1.4 ppt	1.71%
Halon-1211	SIO-05	4.47 ppt	13	4 - 6 ppt	0.52%
Halon-1301	SIO-05	3.06 ppt	13	3 - 5 ppt	0.55%
Halon-2402	SIO-14	0.502 ppt	3	1.2 ppt	0.98%
CH_3Br	SIO-05	10.15 ppt	12	15 ppt	0.57%
CH_3Cl	SIO-05	568.00 ppt	4	620 ppt	0.15%
CH_2Cl_2	SIO-14	36.27 ppt	4	39 ppt	1.64%
$CHCl_3$	SIO-98	10.29 ppt	9	5 - 30 ppt	0.71%
CCl_4	SIO-05	94.74 ppt	20	90 - 105 ppt	0.61%
CH_2BrCl	SIO-10p	0.177 ppt	1	10 ppt	n/a
$CHBrCl_2$	SIO-10p	0.290 ppt	1	10 ppt	n/a
CH_3CCl_3	SIO-05	27.97 ppt	27	12 - 140 ppt	0.59%
$n\text{-}C_3H_7Br$	SIO-10p	0.197 ppt	1	10 ppt	n/a

Propagating Calibrations to Field Measurements

- To track changes in atmospheric composition, a new set of "gold tank" secondary real air standards is compressed each year during at the Scripps pier during "background" conditions. These are calibrated against our growing suite of existing "gold tank" secondary standards maintained in the laboratory.
- The new "gold tanks" are used to calibrate tertiary real air standards compressed at the same time, and these are sent to the field. Most non-linearity analytical concerns are thus addressed in the central calibration laboratory rather than in the field.
- In the field, standards and samples are measured alternately to maximize drift correction for highest precision species. Due to its high gas consumption rates, quaternary standards are also used for the Medusa. These are calibrated against tertiary standards in the field.
- Tertiary standards are returned to the laboratory for re-calibration after about 9 months in the field, and are also compared to new tertiary standards in the field before they are returned.

Data Processing, Station Support and Data Review

Interactive and Evolving Custom Software,
Shared Diagnostics and Maintenance,
Shared Data Access and Review,
World Data Center Reporting

Procedural Overview

- Instruments are fully automated and controlled by custom software running under Linux OS and updated over the Internet. All raw data are collected, stored and distributed over the Internet. Instruments can be monitored remotely in real time, and can be controlled remotely.
- Diagnostic tools protect standards and instruments using a host of alarm protocols that can send alarm e-mails and/or shut down instruments when malfunctions are detected. Data are preprocessed on-site, so that station operators and remote laboratories can see the same results. Voice and video Skype are used to support maintenance and repair work.
- Operating procedures are uniform and transparent across the network, with all PI's having access to all station data. Collaborations and exchanges with other networks (e.g. NOAA, NIES, UK DECC, Empa, KNU, CAMS, NILU…) are strong and growing.
- Data are reviewed across the network twice a year at on-line data meetings, and then at biannual AGAGE meetings, using some of the software tools described in the following figures. Quality-controlled data are released to the CDIAC world data center twice a year.

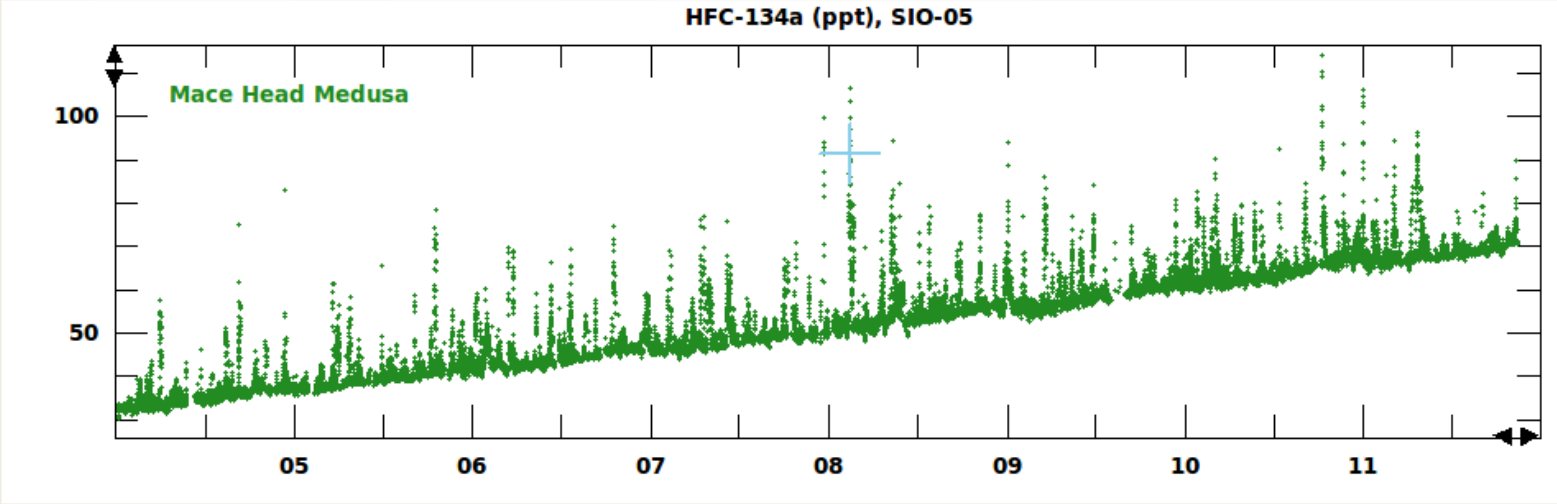
GCcompare (/agage/summary/agageplot-gcms) (on gaslab)

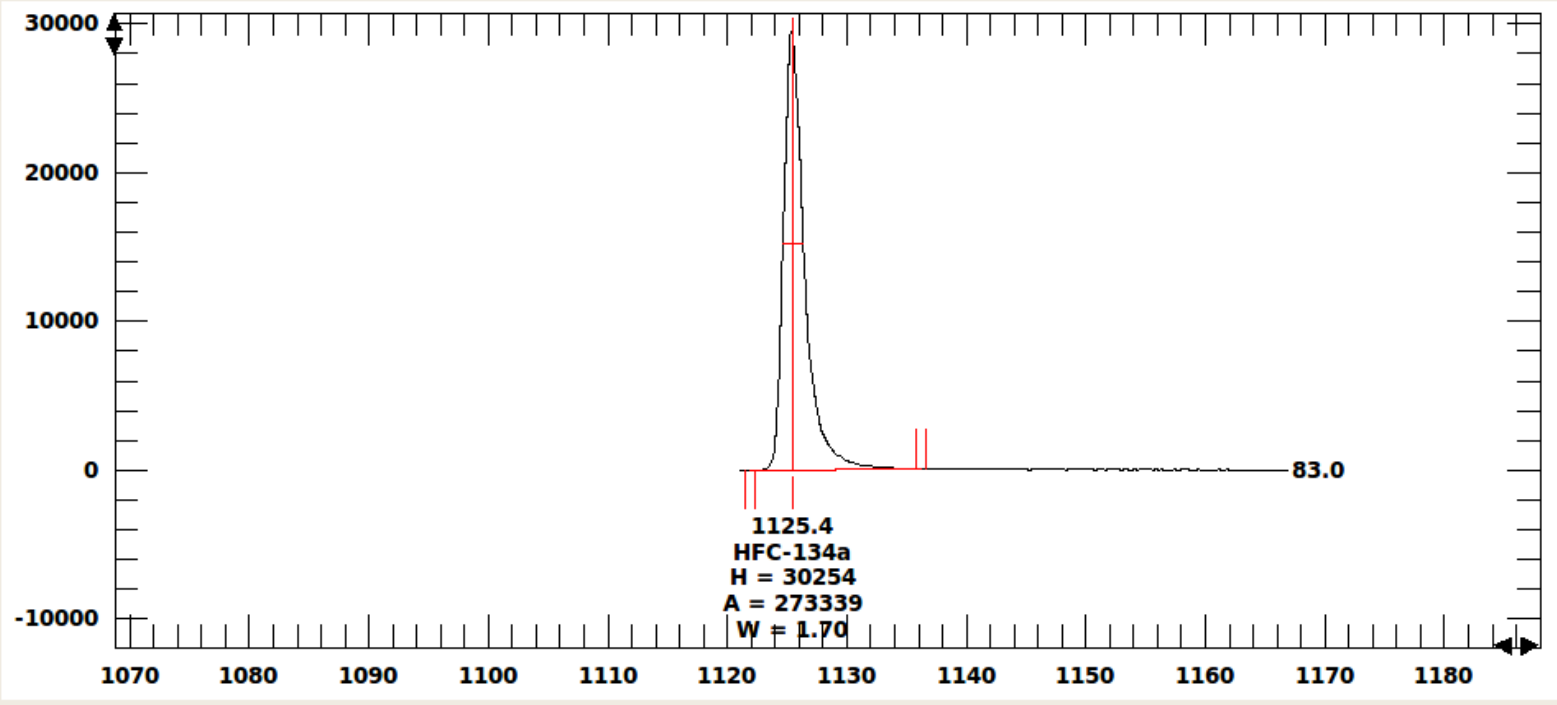
File Options View Help

Gas: HFC-134a Runtype: air Xaxis: time Yaxis: C (reported)

- Cape Grim Medusa
- Cape Matatula Medusa
- Ragged Point Medusa
- [x] Mace Head Medusa
- Trinidad Head Medusa
- La Jolla Medusa
- La Jolla Medusa7
- Aspendale Medusa
- Gosan Medusa
- Jungfraujoch Medusa
- Zeppelin Medusa
- Shangdianzi Medusa
- Shangdianzi sogeA-MD
- Zeppelin ADS
- Mte Cimone ADS
- Aspendale ADS
- Jungfraujoch ADS
- Cape Grim ADS
- Mace Head ADS
- Cape Grim SF6 ECD

- (•) show multiple sites
- ( ) show single site
- [ ] show monthly means





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File Options View Help

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- [x] Mace Head Medusa
- Trinidad Head Medusa
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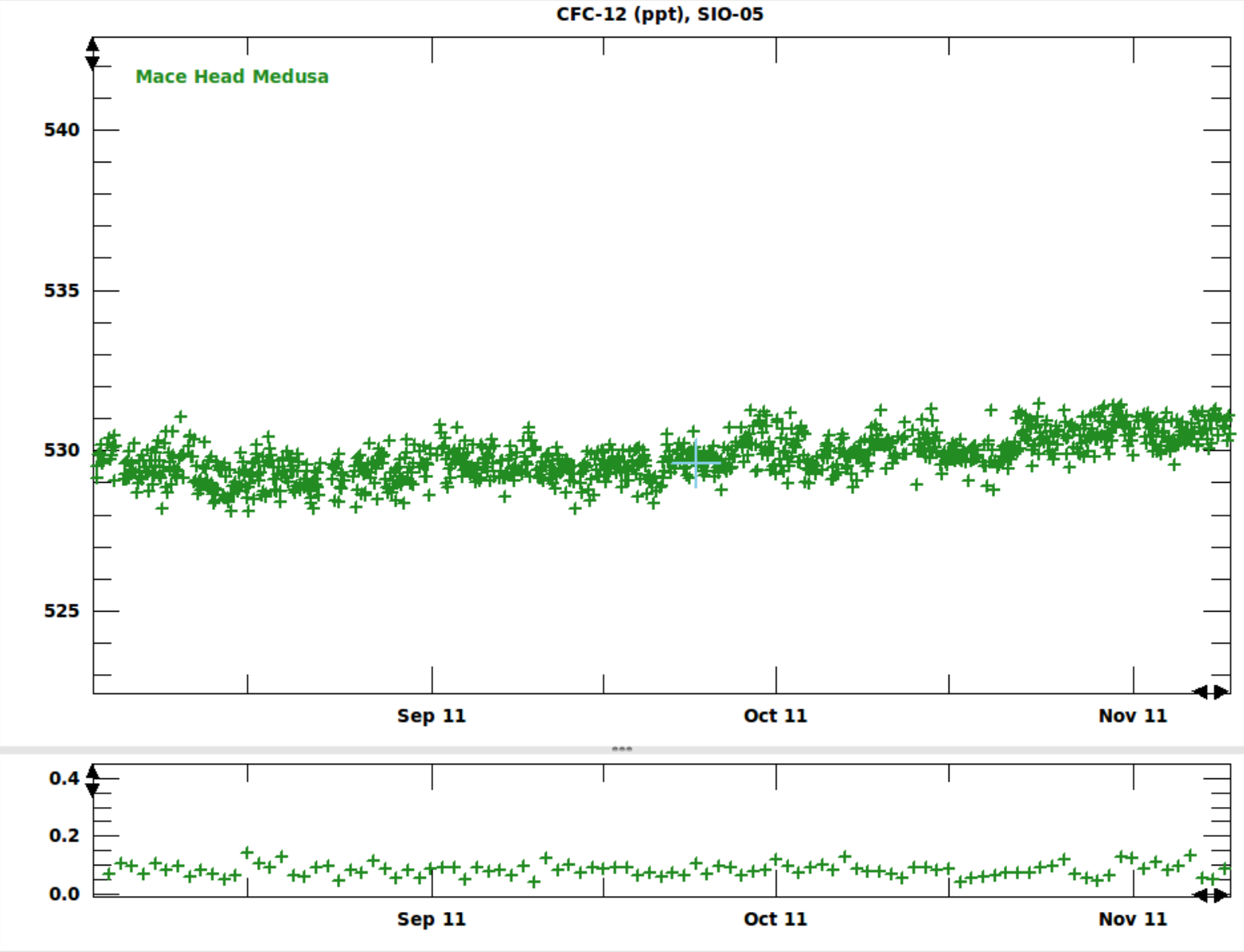
- Mace Head ADS
- Cape Grim SF6 ECD



- (•) show multiple sites
- ( ) show single site
- [ ] show monthly means

macehead-medusa 110924.0248.air.1

GCWerks-compare (/agage/summary/agageplot-gcms) (on gaslab)

File Options View

Gas: HFC-134a Runtype: air Period: 2004 - 2010 Xaxis: time Yaxis: C (reported)

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- Cape Matatula Medusa
- Ragged Point Medusa
- Trinidad Head Medusa
- Mace Head Medusa
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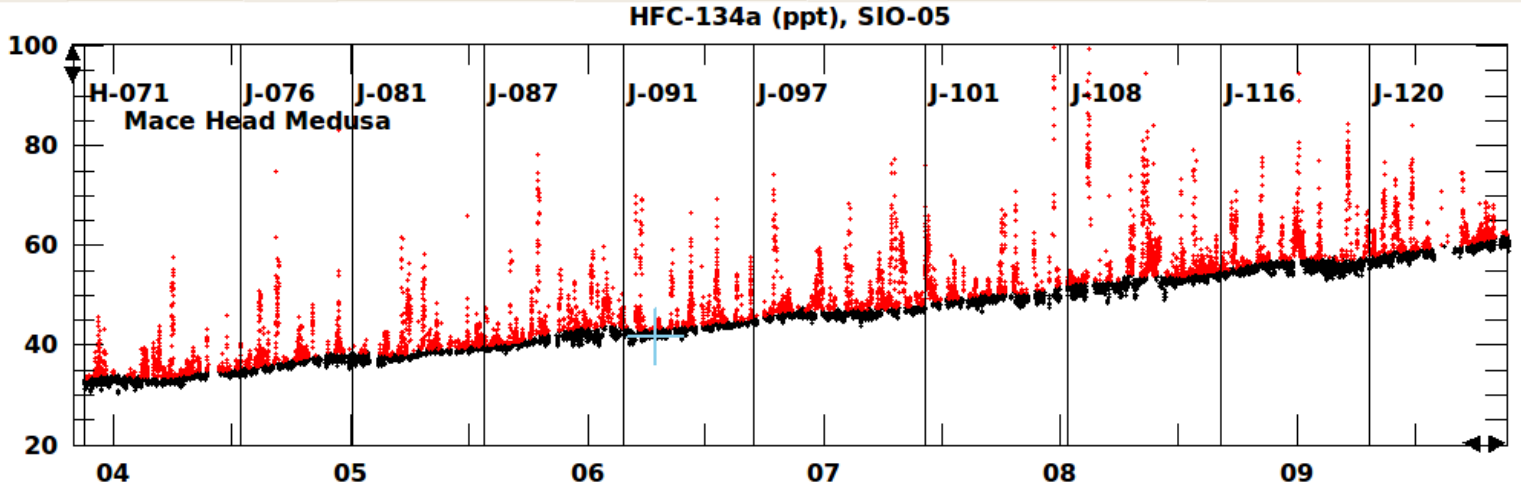
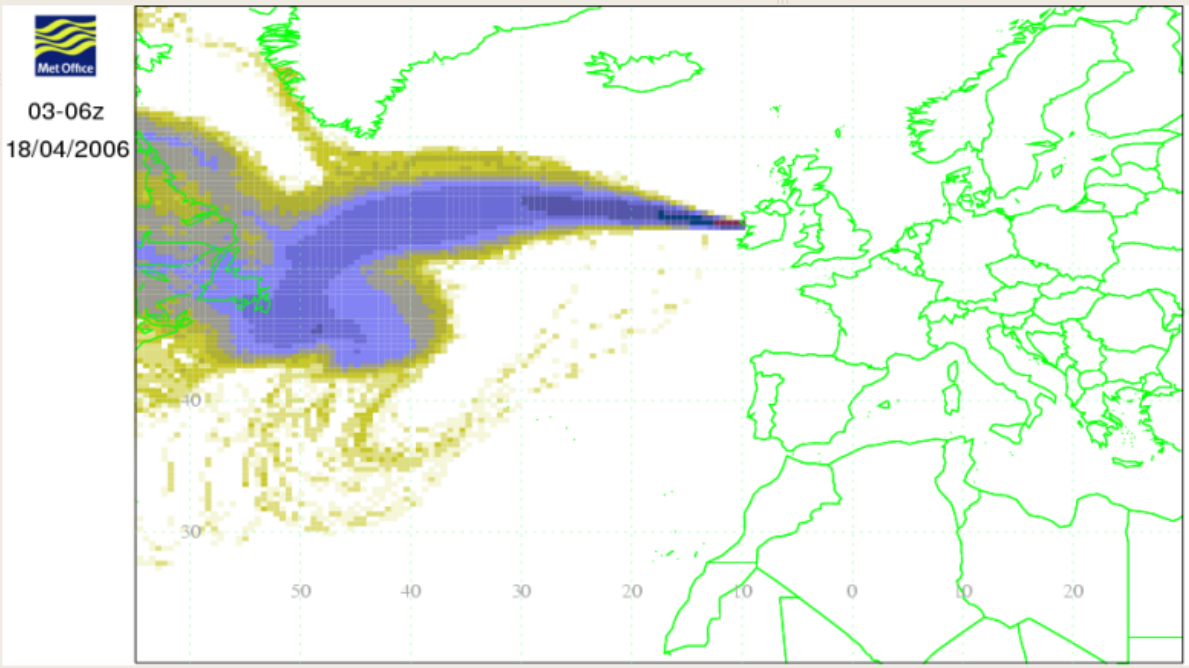
- La Jolla Medusa7
- Aspendale Medusa
- Gosan Medusa
- Jungfraujoch Medusa
- Shangdianzi Medusa
- Zeppelin Medusa
- Zeppelin ADS
- Mte Cimone ADS
- Aspendale ADS
- Carnsore ADS
- Bristol ADS
- Jungfraujoch ADS
- Cape Grim ADS
- Mace Head ADS
- Cape Grim SF6 ECD

- show multiple sites
- show single site
- show monthly means





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GCWerks-compare (/agage/summary/agageplot-gcms) (on gaslab)

File Options View

Gas: HFC-134a Runtype: air Period: 2004 - 2010 Xaxis: time Yaxis: C (reported)

- Cape Grim Medusa
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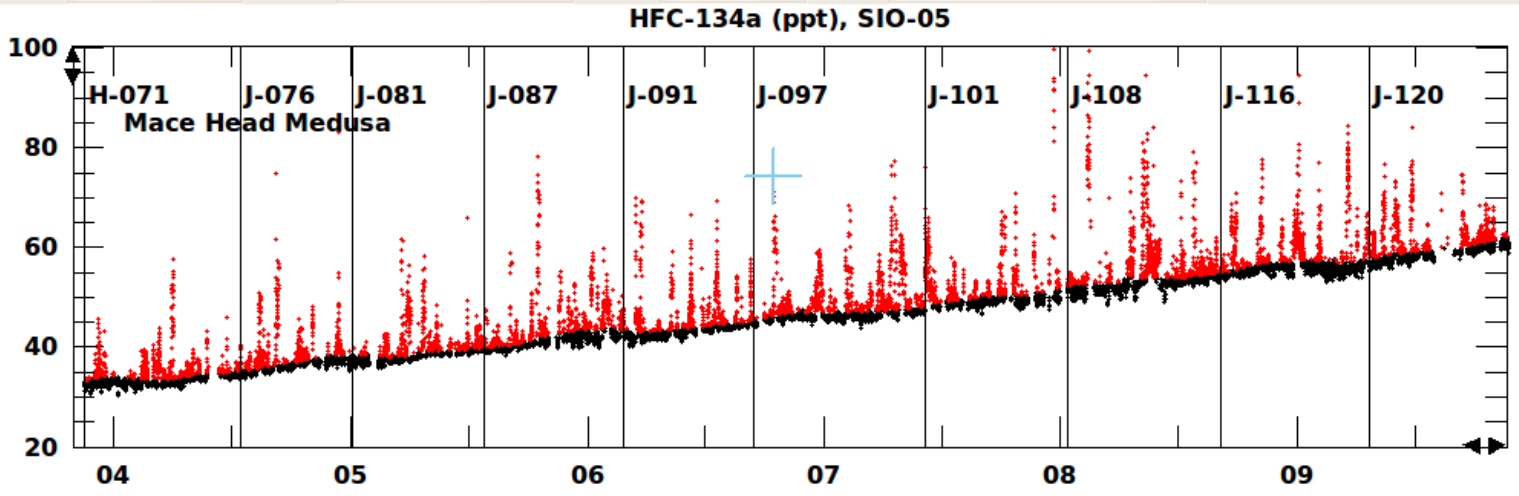

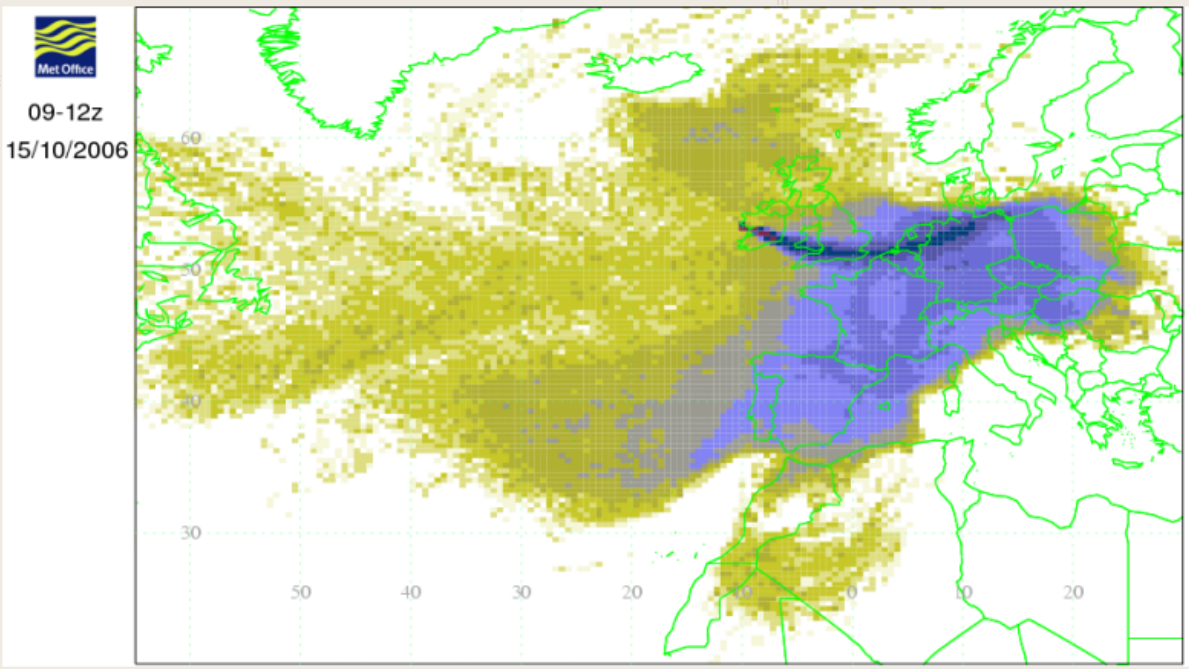

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Downscaling From Global to Regional, Emissions Verification and Policy

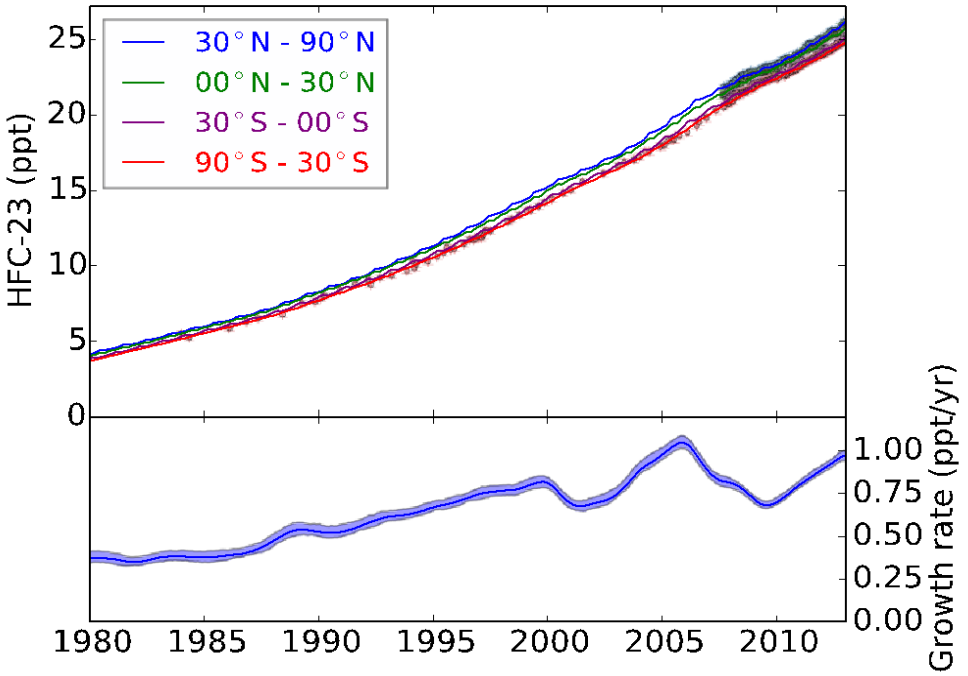
The emphasis has shifted from global to regional and national, and from ODSs to GHGs.

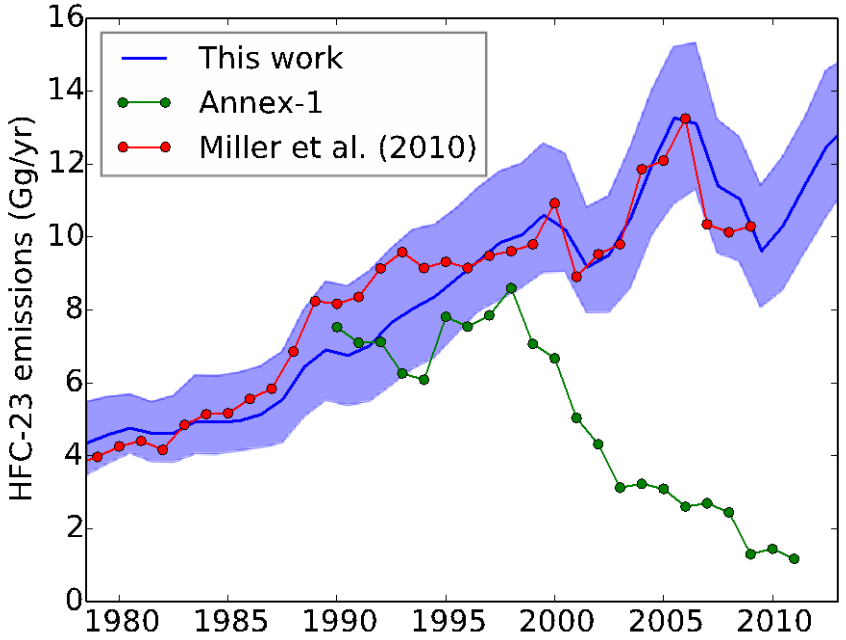
HFC-23 (CHF_3) is a powerful greenhouse gas (GWP = 12,400) produced as a by-product of HCFC-22 production.

AGAGE *in situ* & archive tank measurements show historic rise, recent slowdown & more recent increase.

Global HFC-23 emissions show temporary drop in emissions consistent with incineration of this gas under the Kyoto Protocol CDM program. Most recent increase is possibly related to increased HCFC-22 production without CDM.

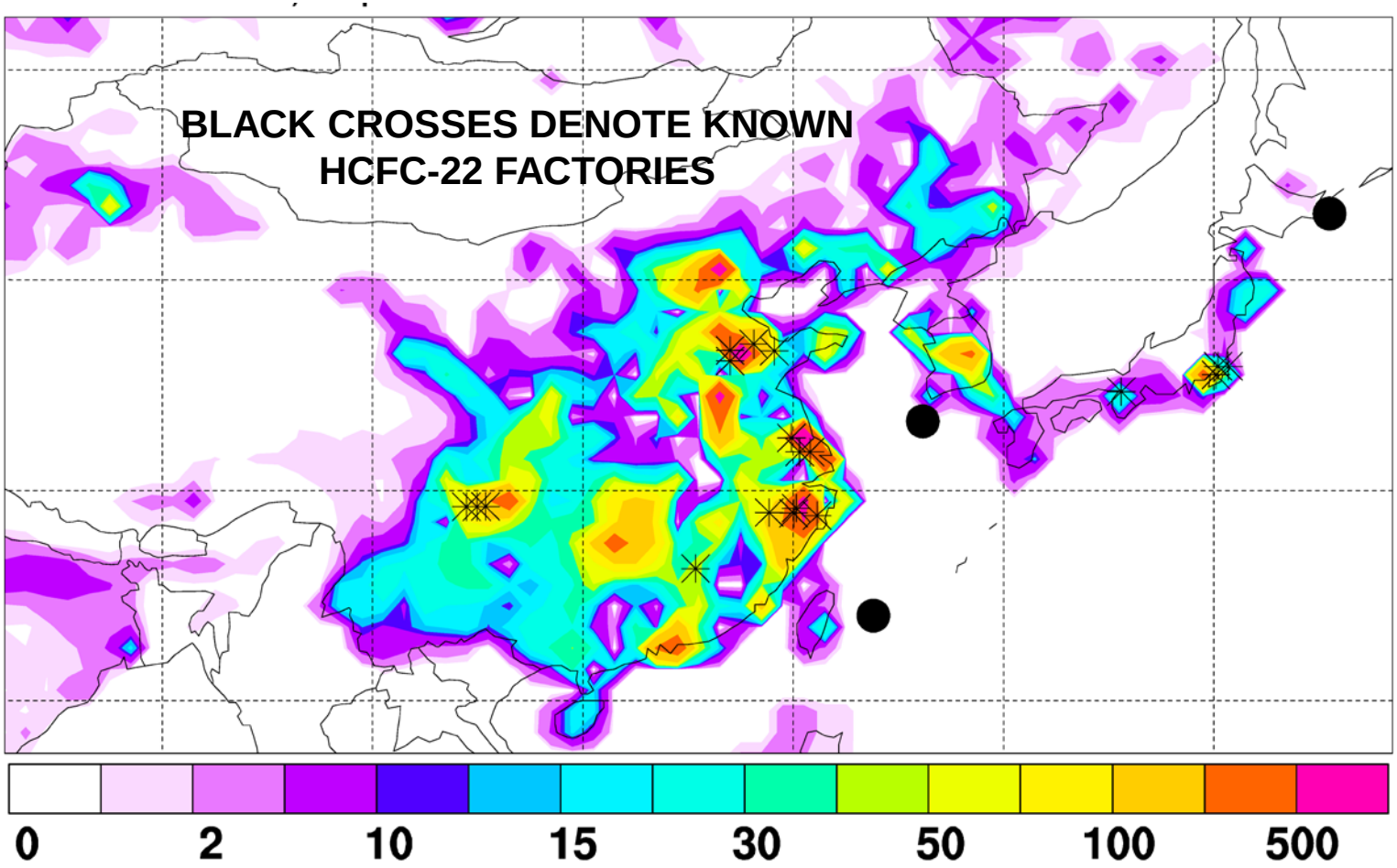
Miller *et al.*, *Atmos. Chem. Phys.*, 2010:
Rigby et al. unpublished update



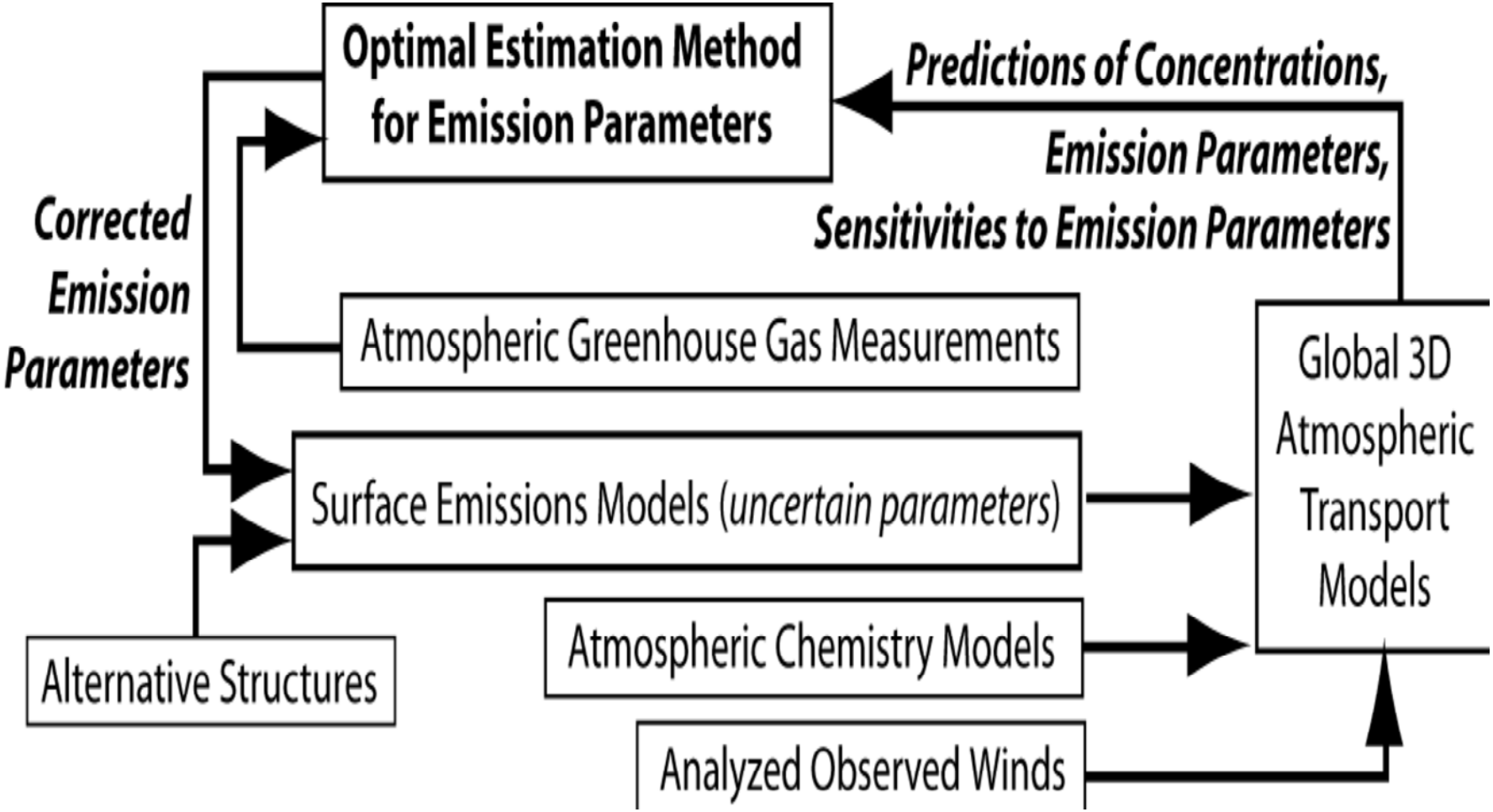


HFC-23 (CHF_3) East Asian Emissions Estimation

AGAGE and NIES Atmospheric Measurements at 3 Stations for 2008 (pg/m^2/sec, Stohl et al., *Atmos. Chem. Phys.*, 2010)



The Way Forward -- The Estimation Challenge



Future Observational Network Needs

- There are large discrepancies for some GHGs between global "bottom-up" emissions inventories and "top-down" global emissions as determined from atmospheric measurements.
- Inverse models are able to assimilate measurements from many atmospheric measurement stations, thus reducing uncertainties in regional emissions estimates.
- Establishment of new stations whose locations are chosen for inverse "top down" modeling of regional, national and sub-national GHG emissions.
- A shift toward high-frequency or continuous measurements as the temporal and spatial resolutions needed for policy-relevant emissions modeling increase.
- Adoption of new measurement technologies such as laser-based techniques for the more abundant GHGs (CO_2, CH_4, CO, N_2O) and their isotopes, time-of-flight mass spectrometry (TOFMS), and new pre-concentration techniques (e.g. Stirling Engine, Perseus). Each will have to be adapted for robust automated field applications.

“Trust but verify” -- Ronald Reagan

Following COP-21 and Paris Agreement’s “pledge and review” approach to emissions reduction, there is a greatly increased need for independent verification.

Ultimately, the success of an atmospheric monitoring network depends on the skills and dedication of extraordinary individuals.

Here are a few of the many experimentalists who have made AGAGE what it is today: Jens Mühle, Peter Salameh, Chris Harth, Ben Miller, Tim Arnold, Martin Vollmer, Peter Simmonds, Laurie Porter, Paul Krummel, Paul Steele, Dickon Young, Simon O’Doherty, Gerry Spain, Mark Cunningham, Randy Dickau…

And collaborators who have helped to make the AGAGE and NOAA programs together stronger than the sum of their parts: Jim Elkins, Steve Montzka, Brad Hall, Ben Miller, Ed Dlugokencky...

Thank You