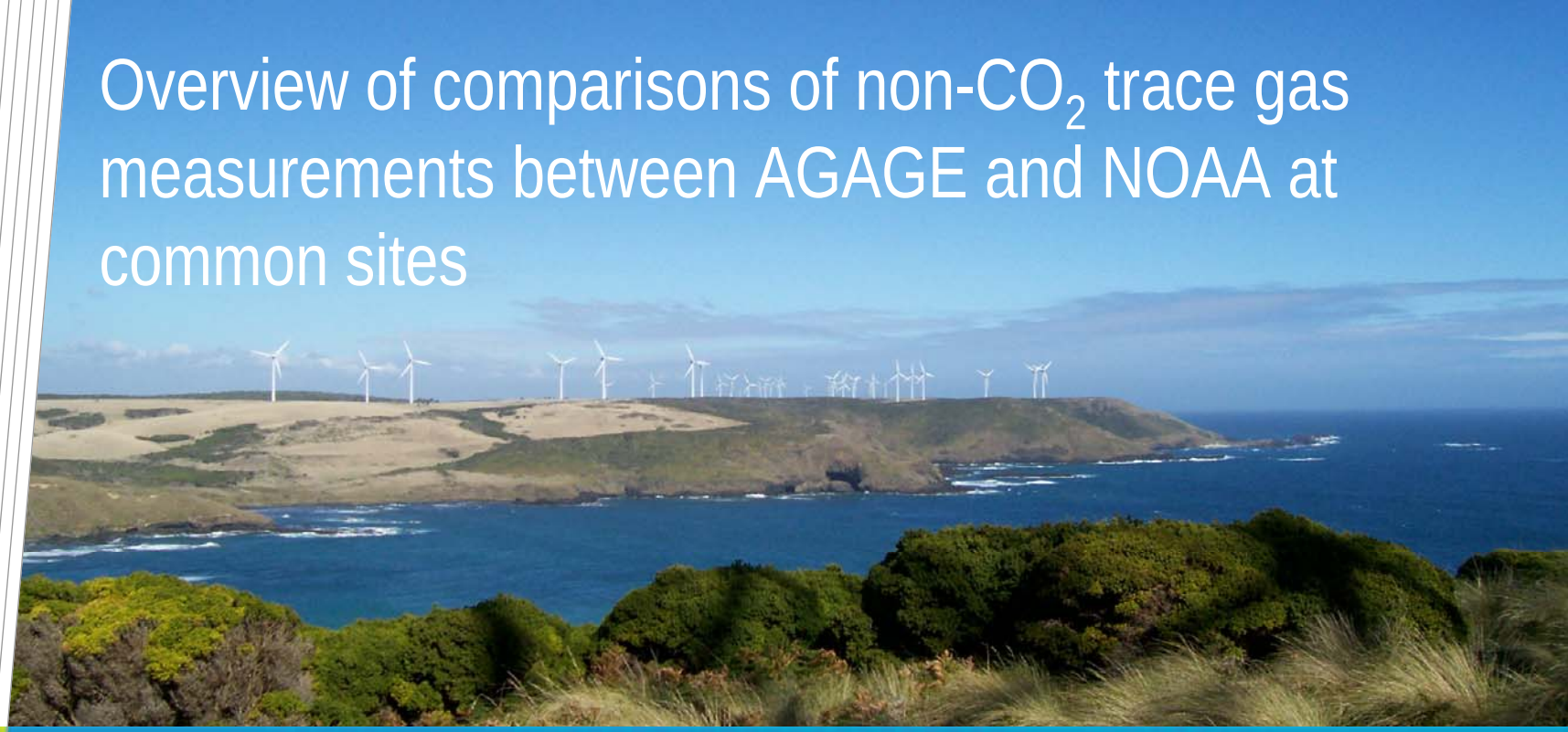
Overview of comparisons of non-CO_2 trace gas measurements between AGAGE and NOAA at common sites



P.B. Krummel[1], S.A. Montzka[2], C. Harth[3], B.R. Miller[2], J. Mühle[3], E.J. Dlugokencky[2], P.K. Salameh[3], B.D. Hall[2], S. O'Doherty[4], L.P. Steele[1], G.S. Dutton[2], D. Young[4], J.D. Nance[2], J.W. Elkins[2], L. Miller[2], P.J. Fraser[1], N. Derek[1], R.F. Weiss[3], P.G. Simmonds[4], and R.G. Prinn[5]

[1]Centre for Australian Weather & Climate Research/CSIRO Marine & Atmospheric Research, Aspendale, Victoria, Australia
[2]NOAA Earth System Research Laboratory, Boulder, Colorado, USA
[3]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California, USA
[4]School of Chemistry, University of Bristol, Bristol, UK
[5]Department of Earth, Atmospheric and Planetary Sciences, MIT, Cambridge, Massachusetts, USA

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Overview

This presentation will focus on comparisons between AGAGE *in situ* and NOAA flask or *in situ* data at five common sites

Awareness in this community of non-CO_2 comparison activities carried out as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) program in collaboration with NOAA & other laboratories

Outline:

Why do comparisons?

How these comparisons evolved

Participants/species/sites

Comparison techniques/outputs

Old summary table and example of planned new formats

Why perform comparisons?

- Gives us the ability to report relationships between different calibration scales in publications or web pages
- Knowing these relationships enables us to merge or combine data sets from different laboratories/scales for joint studies
- For a given species, enables us to compare measurements from different instruments and/or measurement techniques – within same measurement program or between two laboratories/networks etc.
- If done regularly, helps in the early identification of problems that may have gone undiagnosed for longer

How these comparisons evolved

- Started with comparisons of CSIRO GASLAB flask data versus AGAGE *in situ* at Cape Grim, specifically CH_4, then N_2O, CO & H_2
- Extended for GASLAB CO_2 flask data vs *in situ* measurements at Cape Grim
- Next NOAA CH_4 flask data vs AGAGE *in situ* at the 4 (now 5) common sites, results reported at regular AGAGE science meetings
- Soon after, started comparing about 4 halocarbon species at Cape Grim between NOAA and AGAGE … the number of species soon multiplied … and comparisons were extended to the rest of the AGAGE stations …
- As time went on, more panels were added to output, code improved …
- As more instruments were developed and deployed, more comparisons were performed
- Recently, discussing with Ken Masarie the comparison techniques and future directions

Participants in trace gas comparisons to AGAGE

AGAGE (GC-ECD/FID/MRD, GCMS) – AGAGE team, 5 sites, > 34 species

NOAA/ESRL/GMD CCGG flask (GC-FID/ECD) - Ed Dlugokencky, 5 sites, 3 species
NOAA/ESRL/GMD HATS flask (GCMS) - Steve Montzka, 4 sites, up to 27 species
NOAA/ESRL/GMD HATS flask (GC-ECD) - Jim Butler/David Nance, 4 sites, up to 8 species
NOAA/ESRL/GMD HATS CATS *in situ* (GC-ECD) - Geoff Dutton, 1 site (Samoa), 11 species

Uni. of Heidelberg flask (GC-ECD) – Ingeborg Levin , 1 site (Cape Grim), 1 species
CSIRO flask (GC-FID/ECD/MRD) – Steele/Langenfelds/Krummel, 1 site (Cape Grim), 4 species
NIES flask (GCMS) – Yoko Yokouchi, 1 site (Cape Grim), 12 species

SIO flask – Ben Miller/Martin Vollmer, 1 site (Cape Grim), 5 species
UEA flask (GCMS) – David Oram, 1 site (Cape Grim), 24 species

** A lot of data and ALL different data formats!

Comparisons performed approx every 6 months, results made available to all participants, copies archived and form part of the metadata

NOAA species compared to AGAGE *in situ records*

31 species in total:

CH_4, N_2O, SF_6

CFC-11, CFC-12, CFC-13, CFC-113, CFC-115

HCFC-22, HCFC-141b, HCFC-142b

HFC-23, HFC-125, HFC-134a, HFC-143a, HFC-152a

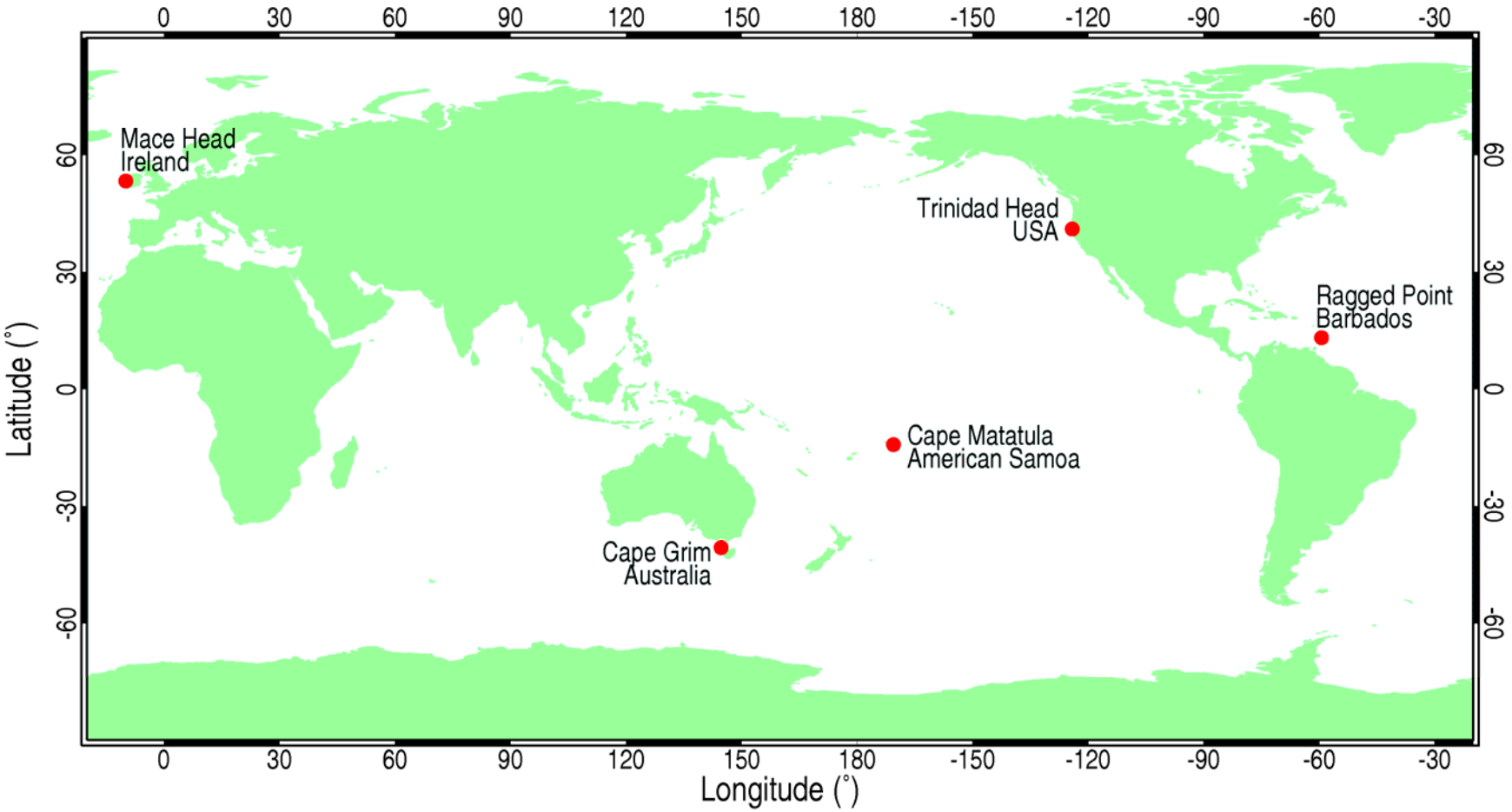
H-1211, H-1301, H-2402

CH_3CCl_3, CCl_4, CCl_2CCl_2

CH_3Cl, $CHCl_3$, CH_3Br, CH_2Cl_2, CH_3I, $CHBr_3$, CH_2Br_2

C_6H_6, OCS

AGAGE sites



Comparisons

- Controlled by input files – 24 input fields
  - Including data sources; species; smoothing/clipping parameters; begin/end times; match time window etc.
- Matching performed by taking flask sampling time and looking for nearest *in situ* data point within a specified time window
- Full output produces 10 panels:
  - Time series of all data; time series of matched data
  - 1:1 plot; time series of concentration difference
  - conc diff vs flask conc; conc diff vs *in situ* conc
  - Time series of % conc diff; % conc diff vs flask conc
  - conc diff vs matched time diff; conc diff vs abs(matched time diff)
- Also produces 3-panel 'quick-look' plots
- ASCII data files of matched data points produced
- Can plot vertical lines indicating cal/std tank changes for both NOAA & AGAGE; also other options can be customised eg smoothing/clipping
- Code written in IDL; currently working on a major overhaul of the code

Comparison table summary – old style

Old format: every species at every site listed; ~20 A4 pages showing statistics for all comparisons; tedious/time consuming to update; not so 'user friendly'

Species (units)	Site	Data Source		Comparison A-B, (A/B-1)*100, and A/B	Comparison 2σ clipped	Comparison Period (Date last updated)	Filename on CD	Notes (on concentration difference plots and/or concentration ratio plots)
		Source A type, detector, scale	Source B type, detector, scale	Conc Diff ± s.d., N Ratio ± s.d. (%), N Ratio ± s.d., N	Conc Diff ± s.d., N Ratio ± s.d. (%), N Ratio ± s.d., N	Begin month/year to End month/year		
CH_4 (ppb)	MHD	NOAA flask FID NOAA2004	AGAGE insitu FID Tohoku University	1.69±12.96, 527 0.09±0.69, 527 1.0009±0.0069, 527	1.69±5.01, 518 0.09±0.27, 518 1.0009±0.0027, 518	Mar 1994 - Jun 2008 (Oct 2008; AGAGE38)	agmdnoaa_mhd_ch4_all	Excellent agreement.
CH_4 (ppb)	THD	NOAA flask FID NOAA2004	AGAGE insitu FID Tohoku University	1.93±4.99, 269 0.10±0.27, 269 1.0010±0.0027, 269	1.68±3.85, 260 0.09±0.21, 260 1.0009±0.0021, 260	Apr 2002 - Aug 2008 (Oct 2008; AGAGE38)	agmdnoaa_thd_ch4_all	Excellent agreement.
CH_4 (ppb)	RPB	NOAA flask FID NOAA2004	AGAGE insitu FID Tohoku University	1.49±7.46, 506 0.08±0.42, 506 1.0008±0.0042, 506	1.57±5.11, 476 0.09±0.29, 476 1.0009±0.0029, 476	Jun 1996 - Aug 2008 (Oct 2008; AGAGE38)	agmdnoaa_rpb_ch4_all	Excellent agreement.
CH_4 (ppb)	SMO	NOAA flask FID NOAA2004	AGAGE insitu FID Tohoku University	0.13±3.34, 972 0.01±0.19, 972 1.0001±0.0019, 972	0.06±2.40, 940 0.00±0.14, 940 1.0000±0.0014, 940	Aug 1996 - Aug 2008 (Oct 2008; AGAGE38)	agmdnoaa_smo_ch4_all	Excellent agreement.
CH_4 (ppb)	CGO	NOAA flask FID NOAA2004	AGAGE insitu FID Tohoku University	0.22±1.98, 640 0.01±0.12, 640 1.0001±0.0012, 640	0.18±1.60, 605 0.01±0.09, 605 1.0001±0.0009, 605	Sep 1993 - Jul 2008 (Oct 2008; AGAGE38)	agmdnoaa_cgo_ch4_all	Excellent agreement.
CH_4 (ppb)	CGA	CSIRO flask FID NOAA04	AGAGE insitu FID Tohoku University	0.69±2.19, 1493 0.04±0.13, 1493 1.0004±0.0013, 1493	0.71±1.87, 1415 0.04±0.11, 1415 1.0004±0.0011, 1415	Aug 1993 - Sep 2008 (Oct 2008; AGAGE38)	agmdcsir_cga_ch4_all	Excellent agreement – small +ve offset. CSIRO data now on NOAA04 scale.
CO (ppb)	CGO	CSIRO flask MRD CSIRO94	AGAGE insitu MRD CSIRO94	1.75±4.46, 1102 3.95±9.11, 1102 1.0395±0.0911, 1102	1.94±3.61, 1028 4.12±7.33, 1028 1.0412±0.0733, 1028	Aug 1993 - Aug 2008 (Oct 2008; AGAGE38)	agmdcsir_cga_co_all	Comparison looking better: AGAGE data for 2003 onwards have had initial correction for non-linearities. Large step change with recent AGAGE tert tank!
H_2 (ppb)	CGO	CSIRO flask MRD CSIRO94	AGAGE insitu MRD CSIRO94	0.38±7.07, 1386 0.09±1.37, 1386 1.0009±0.0137, 1386	0.24±4.80, 1322 0.05±0.91, 1322 1.0005±0.0091, 1322	Aug 1993 - Aug 2008 (Oct 2008; AGAGE38)	agmdcsir_cga_h2_all	Overall good agreement! AGAGE data have not been corrected for non-linearity and new detector response has not been characterised. Large step change with recent AGAGE tert tank!
N_2O (ppb)	MHD	NOAA flask ECD NOAA2000	AGAGE insitu ECD SIO-98	-0.31±0.37, 416 -0.10±0.12, 416 0.9990±0.0012, 416	-0.31±0.32, 394 -0.10±0.10, 394 0.9990±0.0010, 394	May 1997 - Jun 2008 (Oct 2008; AGAGE38)	agmdnoaa_mhd_n2o_all	Good agreement – small trend up until beginning of 2006, then trend down.
N_2O (ppb)	THD	NOAA flask ECD NOAA2000	AGAGE insitu ECD SIO-98	-0.12±0.47, 268 -0.04±0.15, 268 0.9996±0.0015, 268	-0.12±0.41, 255 -0.04±0.13, 255 0.9996±0.0013, 255	Apr 2002 - Aug 2008 (Oct 2008; AGAGE38)	agmdnoaa_thd_n2o_all	Good agreement – small -ve constant offset until ~Apr 2005, trend up until Sep 2006, constant offset since.
N_2O (ppb)	RPB	NOAA flask	AGAGE insitu	-0.15±0.35, 444	-0.15±0.31, 424	Jul 1997 - Aug 2008	agmdnoaa_rpb_n2o_all	Good agreement – small -ve

Want to simplify presentation of results

Summary table

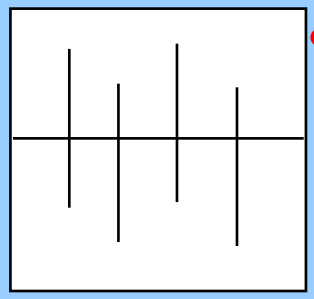
CFC-12 . . . . . .

CH4 . . . . . .

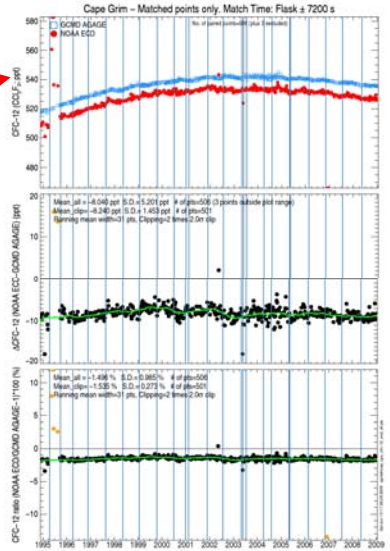
HFC-134a . . . . . .

CH3Cl . . . . . .

CFC-12 plot & statistics



cga: 1.023±0.015
smo: 0.987±0.022
thd: 1.017±0.018
mhd: 0.999±0.014



Most likely in html, all figures and statistics produced in IDL

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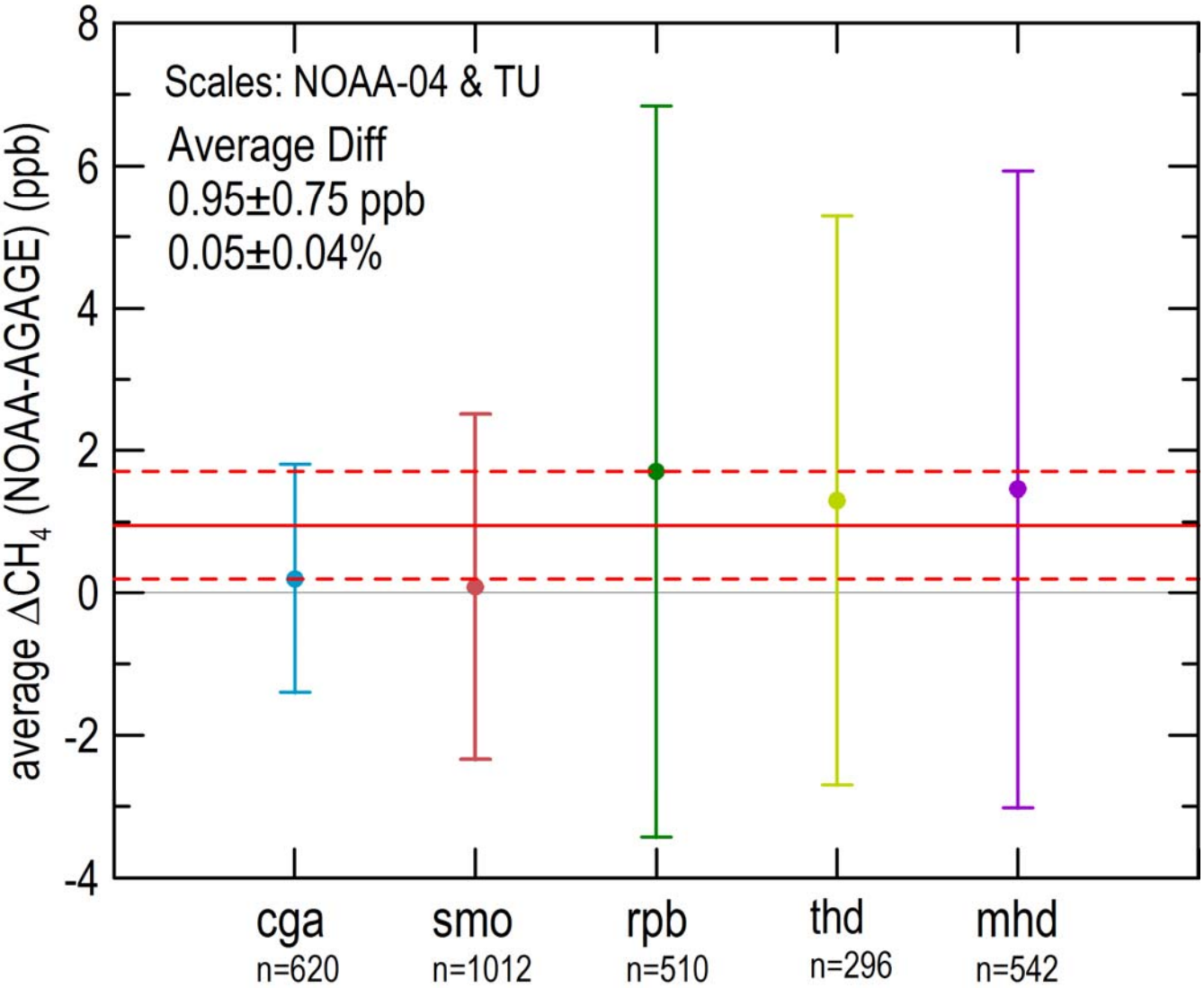
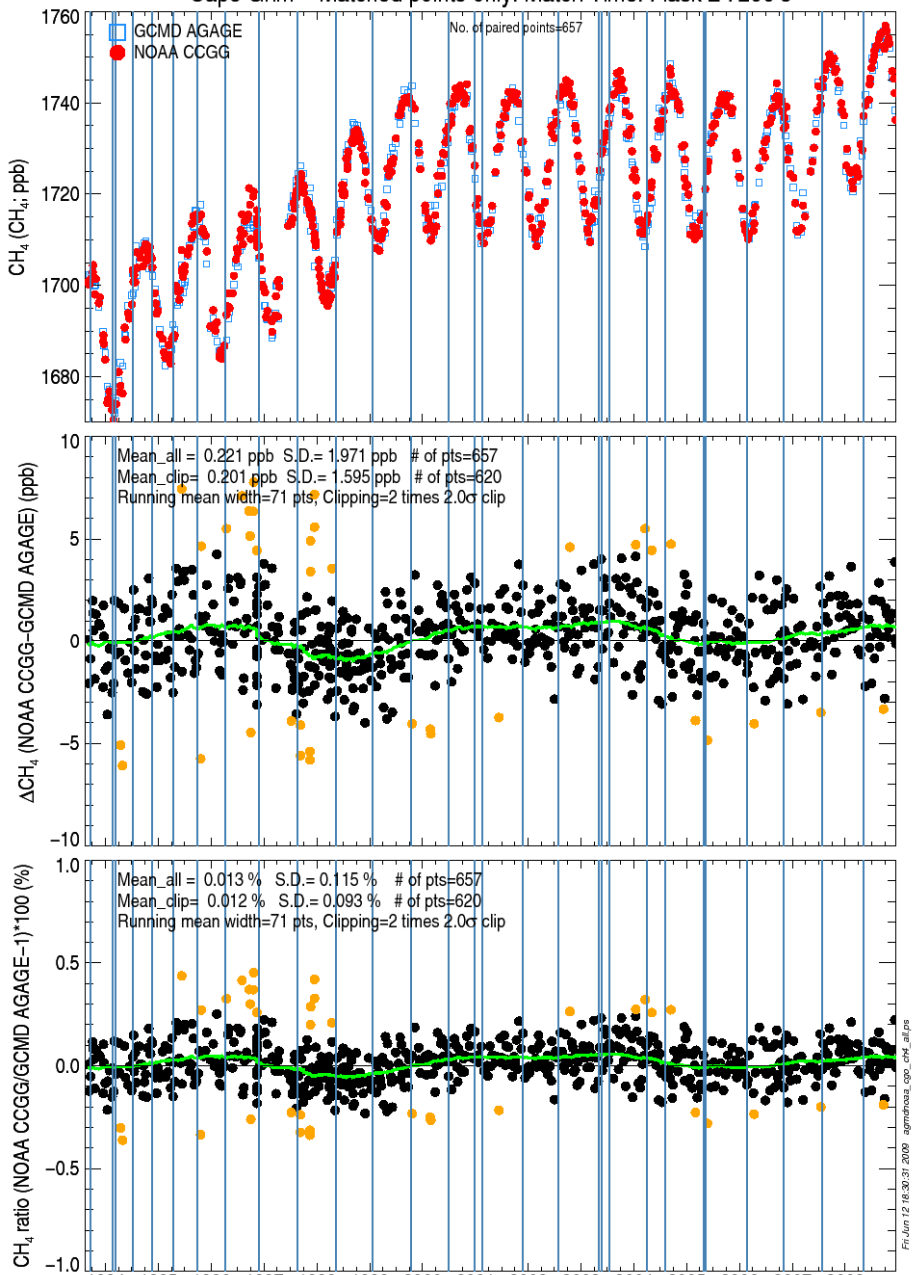
Average differences table work in progress

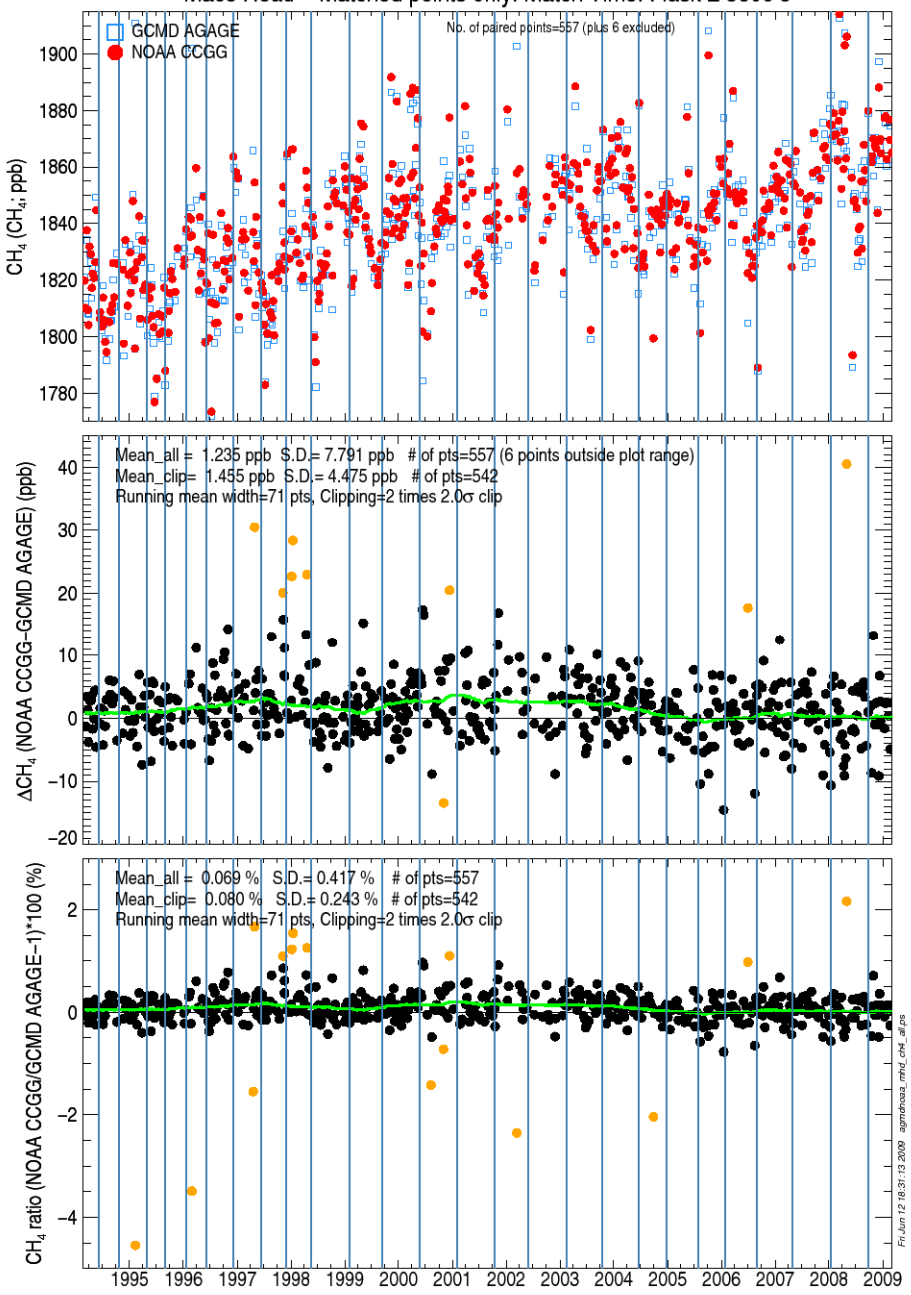
Now want to produce summary table of average differences (similar to below) for all species in NOAA/AGAGE comparisons

Species	Scales NOAA AGAGE	Av conc diff (NOAA-AGAGE)	Av % diff (NOAA/AGAGE)	Comparison period	Comments
CH_4	NOAA-2004 Tohoku Uni	0.95±0.75 ppb	0.05±0.04 %	Aug 1993 to May 2009	Excellent agreement
SF_6	NOAA-2006 SIO-05	0.03±0.02 ppt	0.52±0.30%	May 2001 to May 2009	Good agreement
CFC-12	NOAA-2001 SIO-05	-8.37±0.32 ppt	-1.55±0.06%	Nov 1994 to Jan 2009	Overall offset, no trends.
HFC-134a	NOAA-1995 SIO-05	-0.19±0.02 ppt	-0.43±0.07%	Nov 2003 to May 2009	Overall good agreement
CH_3Cl	NOAA-2003 SIO-05	3.30±8.71 ppt	0.69±1.69%	Nov 2003 to May 2009	Differences between sites; problem at Cape Grim

CH_4 summary figure & statistics




Cape Grim – Matched points only. Match Time: Flask ± 7200 s
GCMD AGAGE
NOAA CCGG
No. of paired points=657
CH4 (CH4; ppb)
Mean_all = 0.221 ppb S.D.= 1.971 ppb # of pts=657
Mean_clip= 0.201 ppb S.D.= 1.595 ppb # of pts=620
Running mean width=71 pts, Clipping=2 times 2.0σ clip
ΔCH4 (NOAA CCGG–GCMD AGAGE) (ppb)
Mean_all = 0.013 % S.D.= 0.115 % # of pts=657
Mean_clip= 0.012 % S.D.= 0.093 % # of pts=620
Running mean width=71 pts, Clipping=2 times 2.0σ clip
CH4 ratio (NOAA CCGG/GCMD AGAGE−1)*100 (%)
1994 1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008


Mace Head – Matched points only. Match Time: Flask ± 3600 s
GCMD AGAGE
NOAA CCGG
No. of paired points=557 (plus 6 excluded)
CH4 (CH4; ppb)
Mean_all = 1.235 ppb S.D.= 7.791 ppb # of pts=557 (6 points outside plot range)
Mean_clip= 1.455 ppb S.D.= 4.475 ppb # of pts=542
Running mean width=71 pts, Clipping=2 times 2.0σ clip
ΔCH4 (NOAA CCGG–GCMD AGAGE) (ppb)
Mean_all = 0.069 % S.D.= 0.417 % # of pts=557
Mean_clip= 0.080 % S.D.= 0.243 % # of pts=542
Running mean width=71 pts, Clipping=2 times 2.0σ clip
CH4 ratio (NOAA CCGG/GCMD AGAGE−1)*100 (%)
1995 1996 1997 1998 1999 2000 2001 2002 2003 2004 2005 2006 2007 2008 2009

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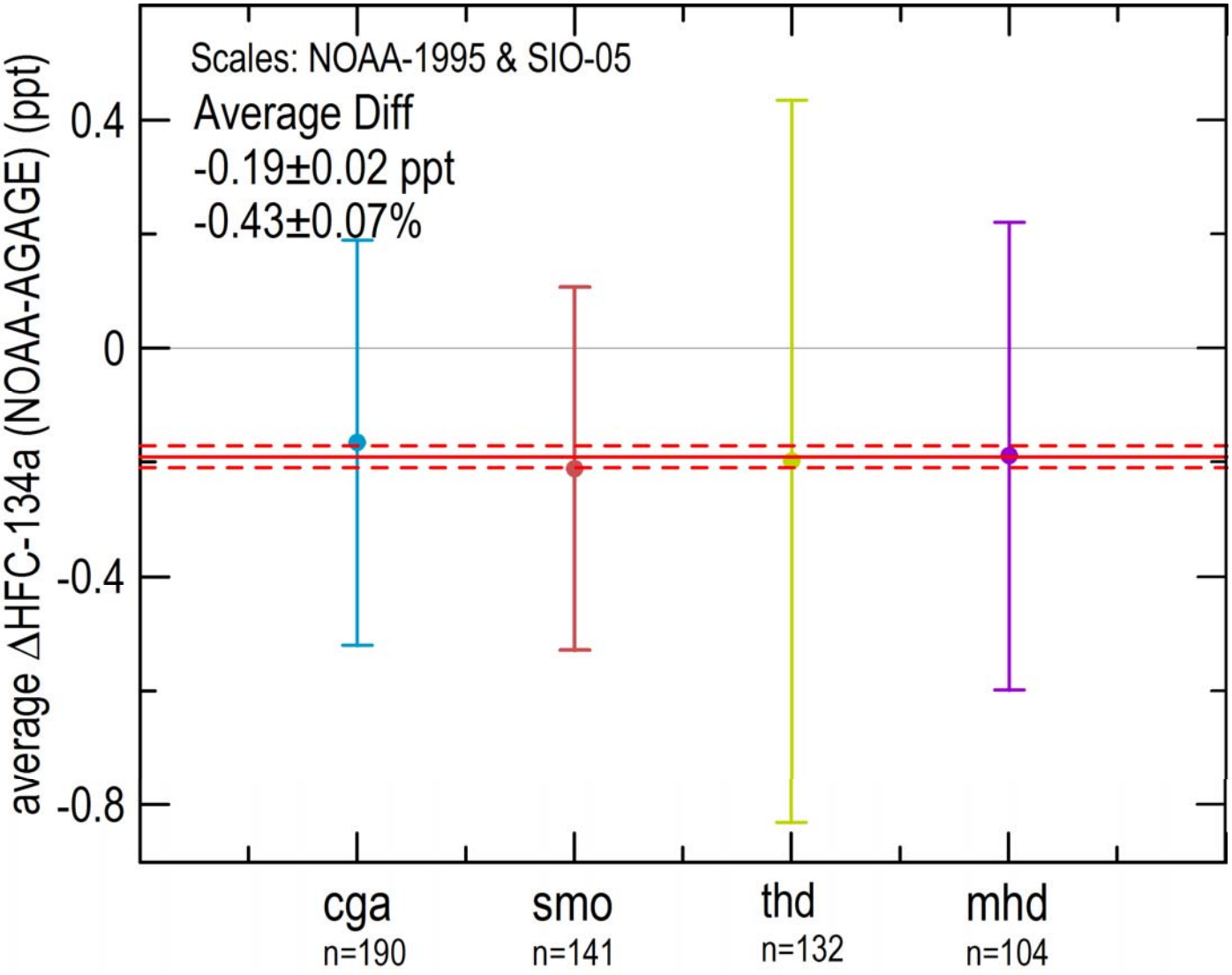
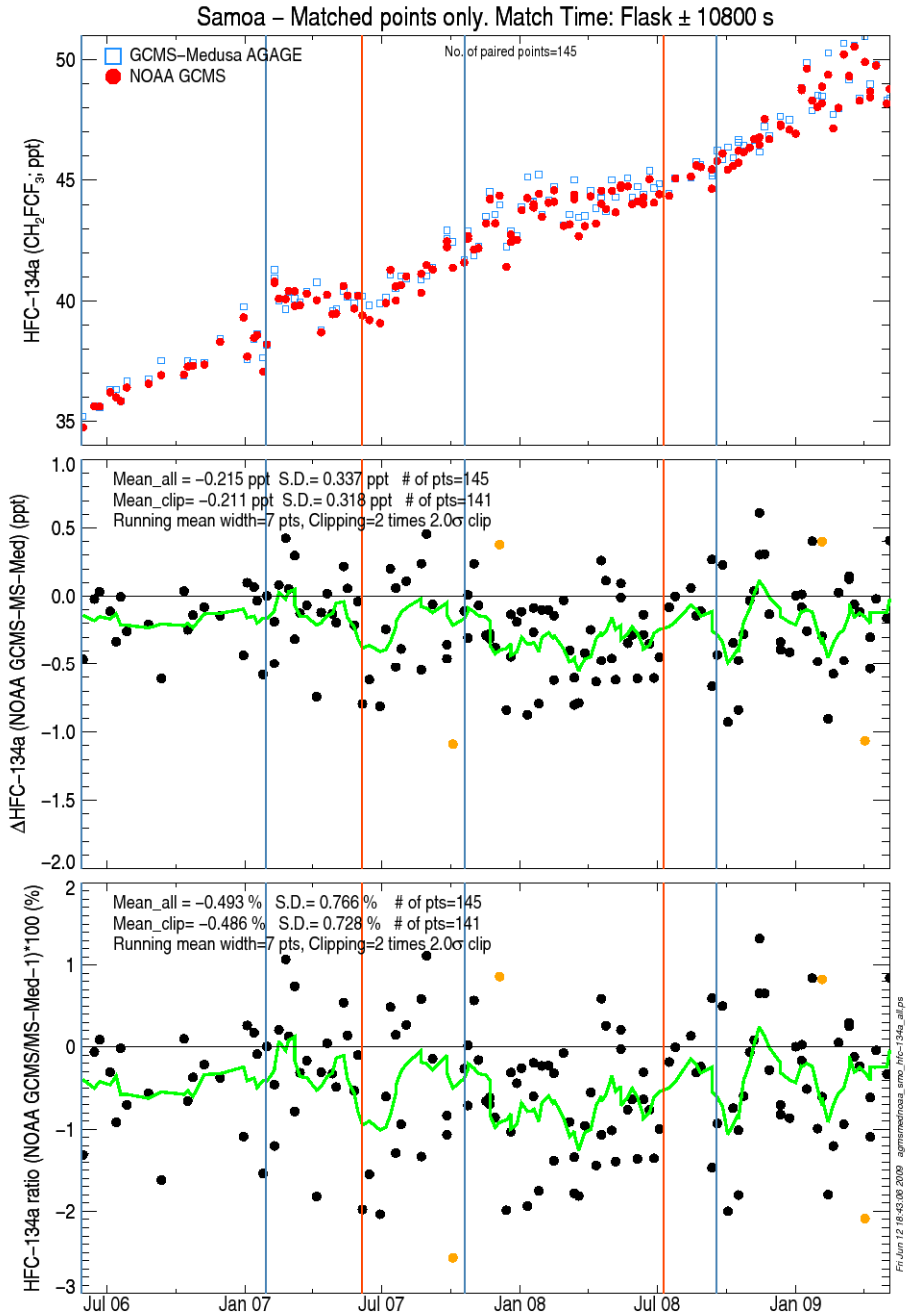
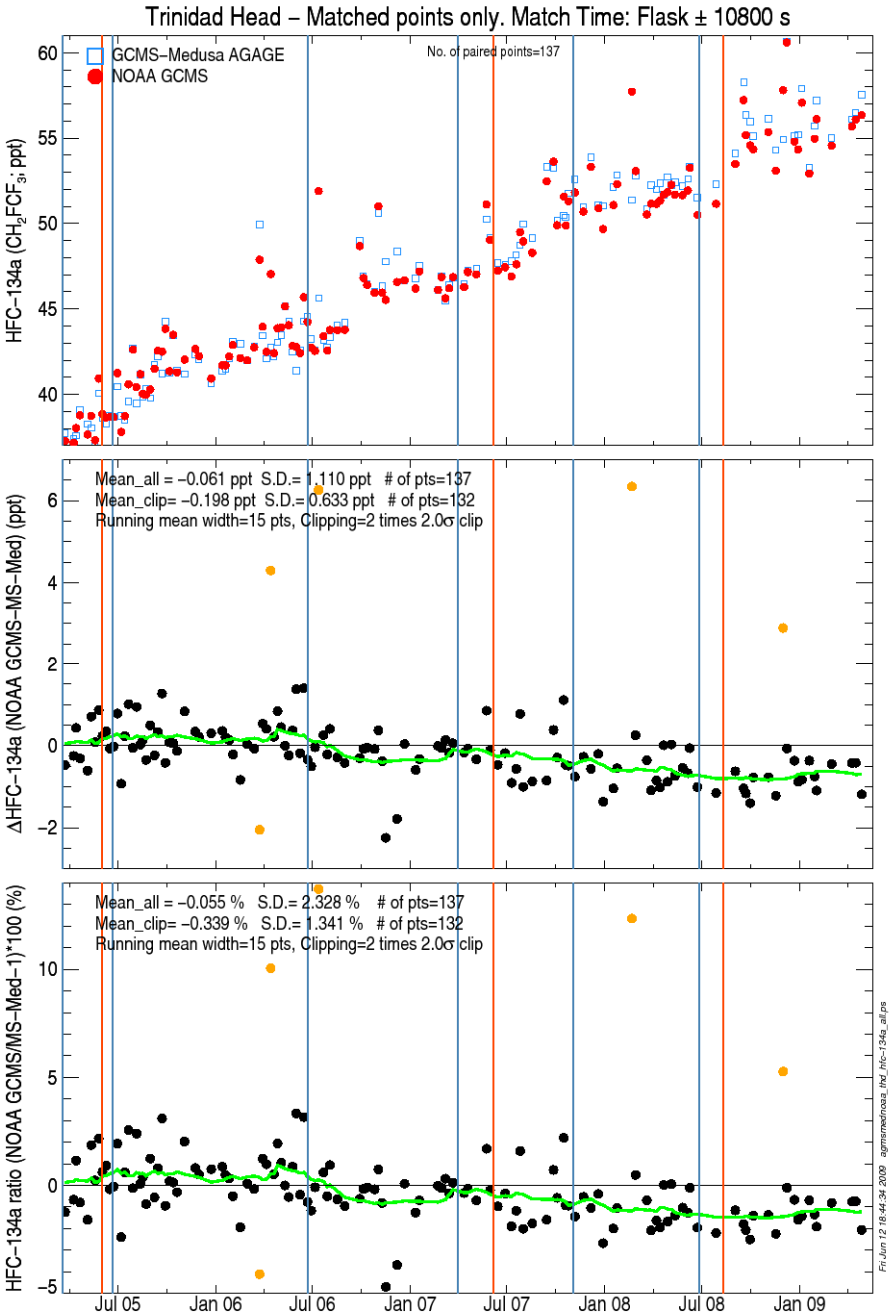
HFC-134a summary figure & statistics




Samoa – Matched points only. Match Time: Flask ± 10800 s
GCMS–Medusa AGAGE
NOAA GCMS
No. of paired points=145
HFC–134a (CH_2FCF_3; ppt)
ΔHFC–134a (NOAA GCMS–MS–Med) (ppt)
Mean_all = –0.215 ppt S.D.= 0.337 ppt # of pts=145
Mean_clip= –0.211 ppt S.D.= 0.318 ppt # of pts=141
Running mean width=7 pts, Clipping=2 times 2.0σ clip
HFC–134a ratio (NOAA GCMS/MS–Med–1)*100 (%)
Mean_all = –0.493 % S.D.= 0.766 % # of pts=145
Mean_clip= –0.486 % S.D.= 0.728 % # of pts=141
Running mean width=7 pts, Clipping=2 times 2.0σ clip
Jul 06
Jan 07
Jul 07
Jan 08
Jul 08
Jan 09


Trinidad Head – Matched points only. Match Time: Flask ± 10800 s
GCMS–Medusa AGAGE
NOAA GCMS
No. of paired points=137
HFC–134a (CH_2FCF_3; ppt)
ΔHFC–134a (NOAA GCMS–MS–Med) (ppt)
Mean_all = –0.061 ppt S.D.= 1.110 ppt # of pts=137
Mean_clip= –0.198 ppt S.D.= 0.633 ppt # of pts=132
Running mean width=15 pts, Clipping=2 times 2.0σ clip
HFC–134a ratio (NOAA GCMS/MS–Med–1)*100 (%)
Mean_all = –0.055 % S.D.= 2.328 % # of pts=137
Mean_clip= –0.339 % S.D.= 1.341 % # of pts=132
Running mean width=15 pts, Clipping=2 times 2.0σ clip
Jul 05
Jan 06
Jul 06
Jan 07
Jul 07
Jan 08
Jul 08
Jan 09

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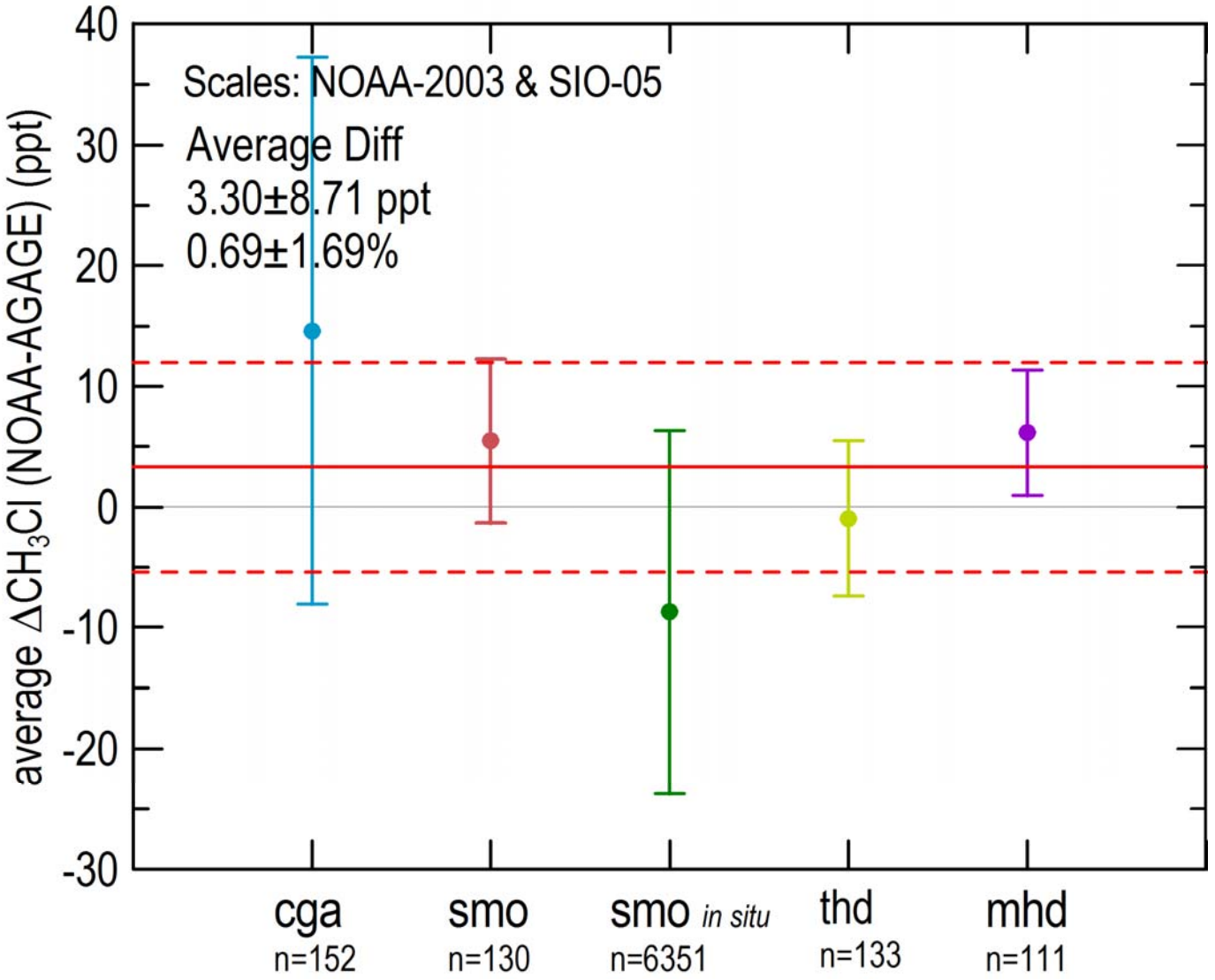
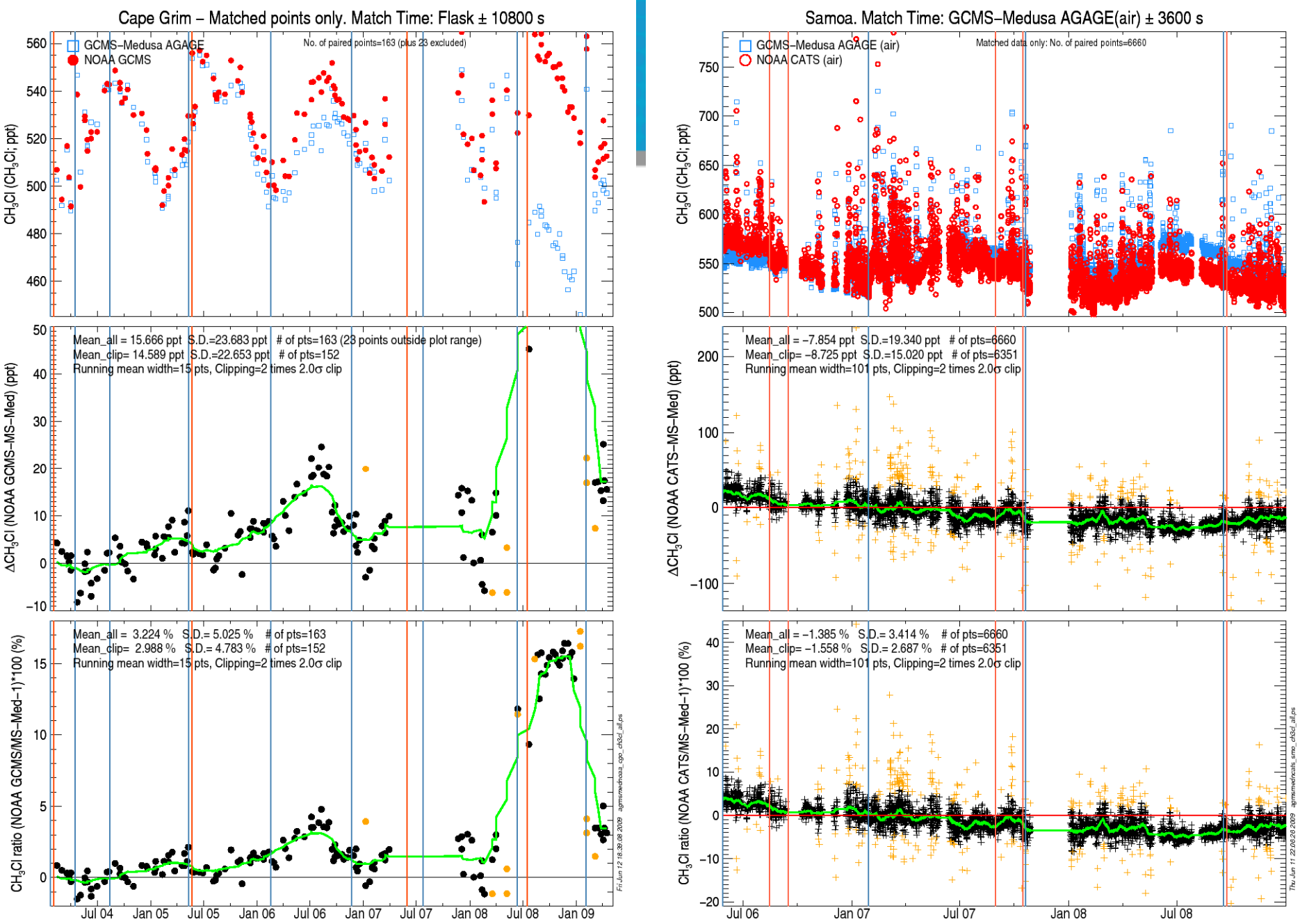
CH_3Cl summary figure & statistics




Cape Grim – Matched points only. Match Time: Flask ± 10800 s
GCMS–Medusa AGAGE
NOAA GCMS
No. of paired points=163 (plus 23 excluded)
CH3Cl (CH3Cl; ppt)
Mean_all = 15.666 ppt S.D.=23.683 ppt # of pts=163 (23 points outside plot range)
Mean_clip= 14.589 ppt S.D.=22.653 ppt # of pts=152
Running mean width=15 pts, Clipping=2 times 2.0σ clip
ΔCH3Cl (NOAA GCMS–MS–Med) (ppt)
Mean_all = 3.224 % S.D.= 5.025 % # of pts=163
Mean_clip= 2.988 % S.D.= 4.783 % # of pts=152
Running mean width=15 pts, Clipping=2 times 2.0σ clip
CH3Cl ratio (NOAA GCMS/MS–Med–1)*100 (%)
Jul 04
Jan 05
Jul 05
Jan 06
Jul 06
Jan 07
Jul 07
Jan 08
Jul 08
Jan 09
Samoa. Match Time: GCMS–Medusa AGAGE(air) ± 3600 s
GCMS–Medusa AGAGE (air)
NOAA CATS (air)
Matched data only: No. of paired points=6660
CH3Cl (CH3Cl; ppt)
Mean_all = –7.854 ppt S.D.=19.340 ppt # of pts=6660
Mean_clip= –8.725 ppt S.D.=15.020 ppt # of pts=6351
Running mean width=101 pts, Clipping=2 times 2.0σ clip
ΔCH3Cl (NOAA CATS–MS–Med) (ppt)
Mean_all = –1.385 % S.D.= 3.414 % # of pts=6660
Mean_clip= –1.558 % S.D.= 2.687 % # of pts=6351
Running mean width=101 pts, Clipping=2 times 2.0σ clip
CH3Cl ratio (NOAA CATS/MS–Med–1)*100 (%)
Jul 06
Jan 07
Jul 07
Jan 08
Jul 08

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Things to do/future …

- Rewrite code to make more modular and ‘clean-up’
- Automate further to produce site summary plots & proper uncertainty estimates
- Produce HTML summary table and ‘drill-down’ links, using output from above

- Ongoing activity and development
- Continue to work with Ken Masarie

Thank You

Acknowledgements

All station personnel involved with the collection/filling of flasks and maintenance of *in situ* programs

Participants in the comparison exercise, especially the NOAA colleagues who contribute the bulk of the flask data

The AGAGE team