Appendix

1 Instrumental

The map in Figure 1 shows the location of the three new sites, Angus, Ridge Hill and Tacolneston along with the original site at Mace Head, which has been operational since 1987. All new sites are operational. The site at Ridge Hill was set-up in February 2012 and Tacolneston began operating at the end of July 2012. Deployment at Tacolneston was delayed as planning permission was required to position the University of Bristol mobile lab (a custom built shipping container) at the site. Angus data has been collected since late 2005 and the University of Edinburgh have provided data from the beginning of March 2011. Problems with the GC-ECD at Angus from the beginning of the project contract have meant N_2O data for the whole of 2011 is unusable in calculating emission estimates using the inversion methodology InTEM (discussed in detail in the main report). Table 1 gives an overview of the gases, which are measured at each of the sites and specifies which instrument each gas is measured on. Full details on all instrumentation can be found at the project website (www.metoffice.gov.uk/atmospheric-trends).

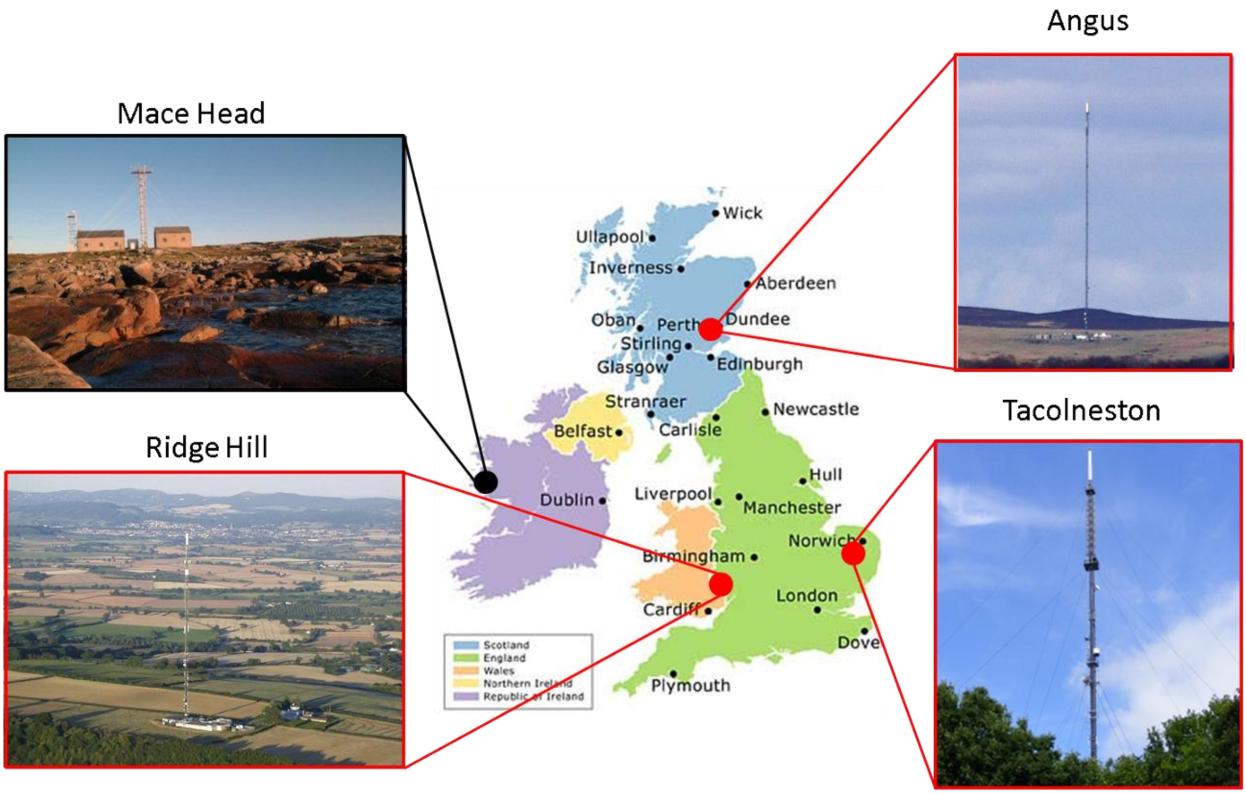


Figure 1 The location of Mace Head and the three new sites in the UK Deriving Emissions linked to Climate Change network (UK DECC Network).

Sites -> Species	Mace Head MHD	Tacolneston TAC	Ridge Hill RGL	Angus* TTA
CO_2	Picarro 2301*(1)*	Picarro 2301*(1)*	Picarro 2301*(1)*	Picarro 2301*(1)* LiCor 7000*(1)* *
CH_4	Picarro 2301(1), GC-FID*(40)*	Picarro 2301*(1)*	Picarro 2301*(1)*	Picarro 2301*(1)* GC-FID*(40)* *
N_2O	GC-ECD*(40)*	GC-ECD*(20)*	GC-ECD*(20)*	GC-ECD*(40)*
SF_6	Medusa*(120)*	GC-ECD*(20)*, Medusa*(120)*	GC-ECD*(20)*	GC-ECD*(40)*
H_2	GC-RGA*(40)*	GC-RGA*(20)*	-	-
CO	GC-RGA*(40)*	GC-RGA*(20)*	-	-
CF_4	Medusa*(120)*	Medusa*(120)*	-	-
C_2F_6	Medusa*(120)*	Medusa*(120)*	-	-
C_3F_8	Medusa*(120)*	Medusa*(120)*	-	-
$c\text{-}C_4F_8$	Medusa*(120)*	-	-	-
HFC-23	Medusa*(120)*	Medusa*(120)*	-	-
HFC-32	Medusa*(120)*	Medusa*(120)*	-	-
HFC-134a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-152a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-125	Medusa*(120)*	Medusa*(120)*	-	-
HFC-143a	Medusa*(120)*	Medusa*(120)*	-	-
HFC-227ea	Medusa*(120)*	Medusa*(120)*	-	-
HFC-236fa	Medusa*(120)*	Medusa*(120)*	-	-
HFC-43-10mee	Medusa*(120)*	-	-	-
HFC-365mfc	Medusa*(120)*	Medusa*(120)*	-	-
HFC-245fa	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-22	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-141b	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-142b	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-124	Medusa*(120)*	Medusa*(120)*	-	-
HCFC-123	-	Medusa*(120)*	-	-
CFC-11	Medusa*(120)*	Medusa*(120)*	-	-
CFC-12	Medusa*(120)*	Medusa*(120)*	-	-
CFC-13	Medusa*(120)*	Medusa*(120)*	-	-
CFC-113	Medusa*(120)*	Medusa*(120)*	-	-
CFC-114	Medusa*(120*	Medusa*(120)*	-	-
CFC-115	Medusa*(120)*	Medusa*(120)*	-	-
H-1211	Medusa*(120)*	Medusa*(120)*	-	-
H-1301	Medusa*(120)*	Medusa*(120)*	-	-
H-2402	Medusa*(120)*	Medusa*(120)*	-	-
CH_3Cl	Medusa*(120)*	Medusa*(120)*	-	-
CH_3Br	Medusa*(120)*	Medusa*(120)*	-	-
CH_3I	Medusa*(120)*	Medusa*(120)*	-	-
CH_2Cl_2	Medusa*(120)*	Medusa*(120)*	-	-
CH_2Br_2	Medusa*(120)*	Medusa*(120)*	-	-
$CHCl_3$	Medusa*(120)*	Medusa*(120)*	-	-
$CHBr_3$	Medusa*(120)*	Medusa*(120)*	-	-
CCl_4	Medusa*(120)*	Medusa*(120)*	-	-
CH_3CCl_3	Medusa*(120)*	Medusa*(120)*	-	-
$CHCl{=}CCl_2$	Medusa*(120)*	Medusa*(120)*	-	-
$CCl_2{=}CCl_2$	Medusa*(120)*	Medusa*(120)*	-	-

Table 1 Operational sites, instrumentation and observed species. Number in brackets indicates frequency of calibrated air measurement in minutes. (* denotes instruments that were used prior to the University of Bristol's operation of the station).

2 Sites

2.1 Mace Head

2.1.1 Medusa-GCMS

Overall, the Medusa performance during the reporting period was marred by Omega and trap failure issues resulting in a loss of 6 weeks of data. The highlight of the period was the inception of NF_3 measurements.

A number of issues occurred with the backup generator (burnt out heater unit, blowing fuses), all of which were dealt with by the service company on the day following. Valve 4 (V4) was identified as the cause of EPC4 problems. The actuator and controller were replaced on 130816, since then no EPC4 issues were noted. The MS source was changed twice in quick succession (130715 and 130717) as the cleaned source initially installed was clearly contaminated. The Cryotiger was shut down to clear blocked head on 130730.

On 131209, an oscillation on the Trap 2 (T2) temperature trace was noted when it was heated to -126ºC, though not at higher temperatures (Figure 2). In light of recent trap heating issues, it was deemed prudent to suspend sampling until further investigation could be carried out.

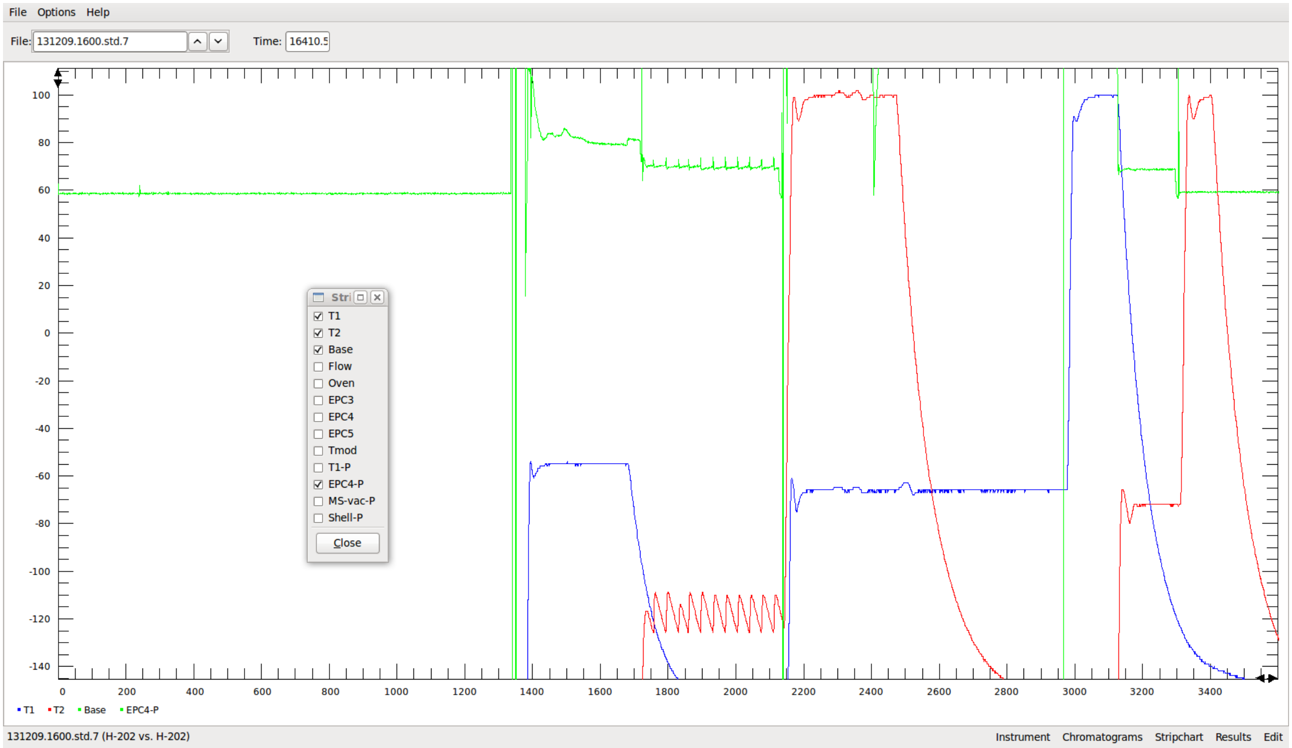


Figure 2 Oscillations in T2

Close examination of stripcharts showed the oscillation started about 131125, appearing intermittently with increasing frequency and increased magnitude (Figure 3).

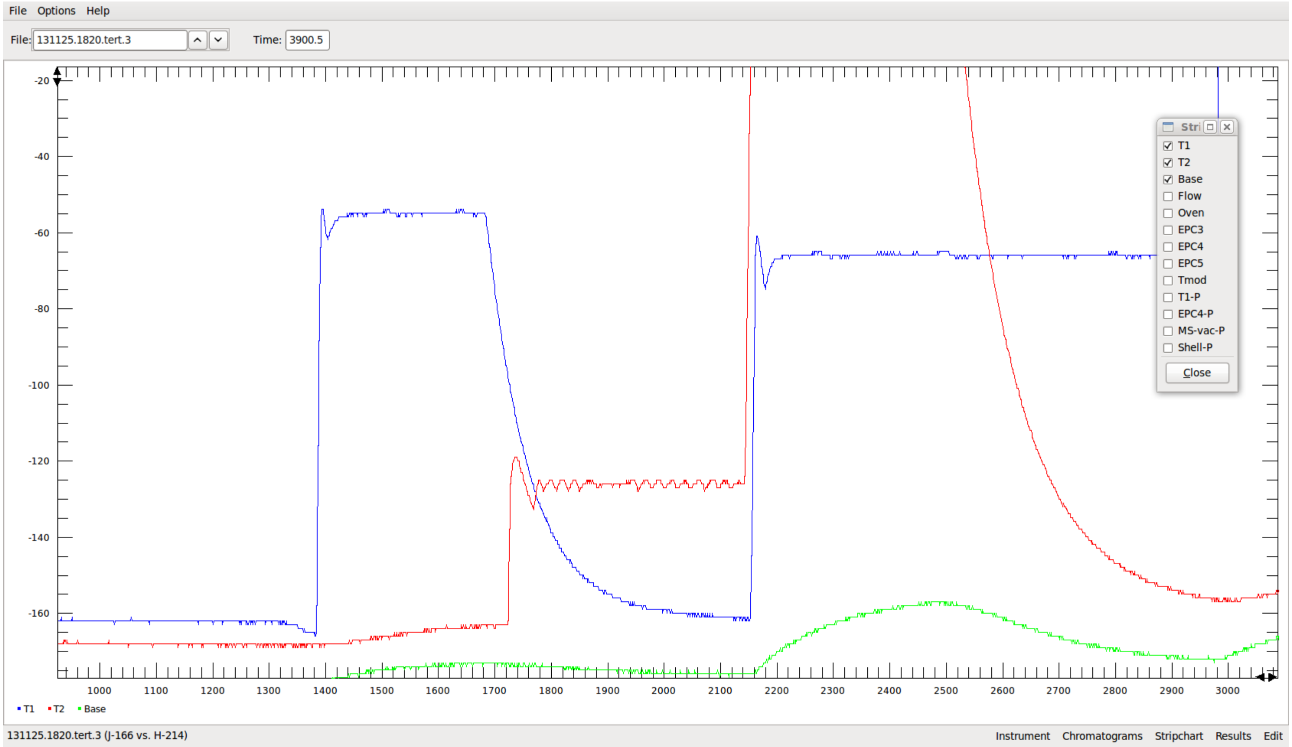


Figure 3 Oscillations in T2

The nature of the oscillation was that the temperature would overshoot, cool down to the setpoint and heat again. (During later testing, the control voltage output from the Omega was observed; it would switch from maximum (6VDC) to zero, applying max voltage when the temperature cooled to the setpoint and switching off when the temperature had overshot by ~16º C) (Figure 4).

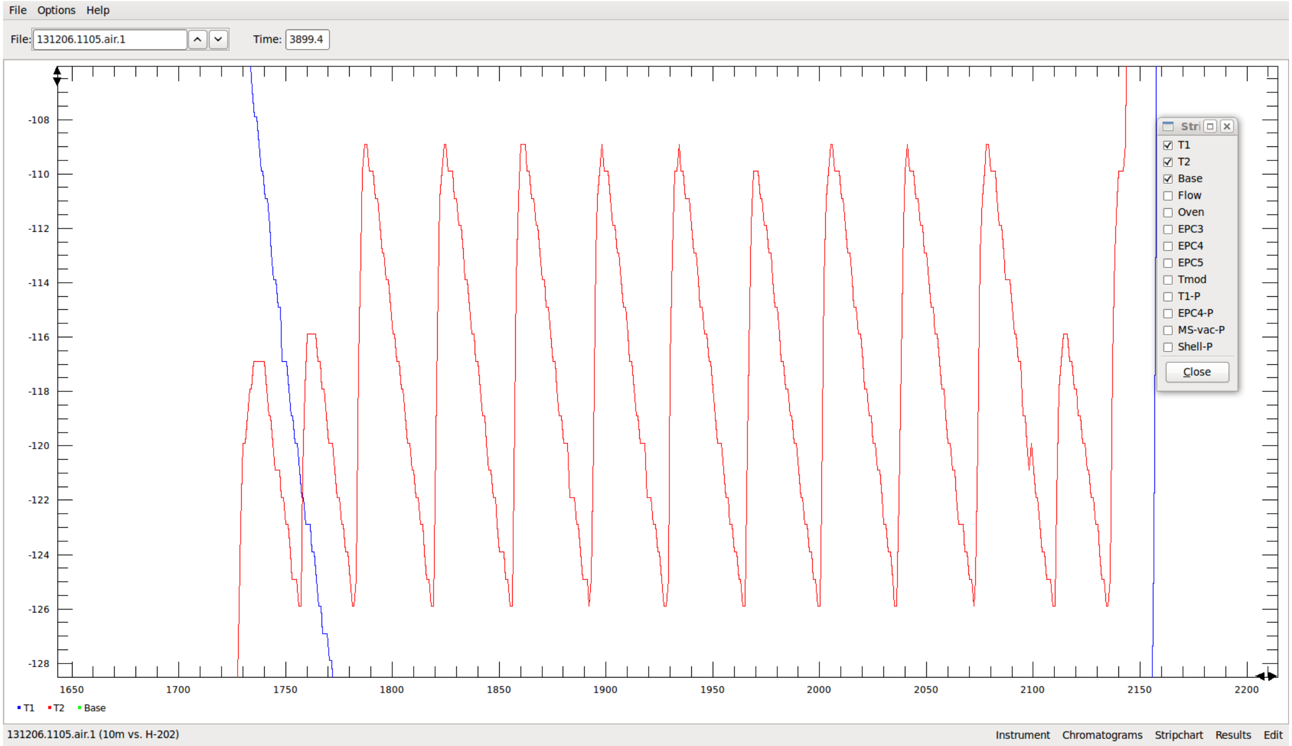


Figure 4 Oscillations in T2

The first possibility considered was that the trap was being partly blocked due to the sample being insufficiently dried – i.e. that the TOC was not producing dry air. The TOC was checked and found to be cycling normally, the MD system was not showing any signs of wet samples and the indicating drier on the Medusa nafion supply did not show any sign of exhaustion therefore the TOC was OK.

Given that the last trap problem was related to an Omega failure, that was the first Medusa component tested. The fact that there were no oscillations at higher temperatures suggested the Omega was OK and this was a relatively quick and easy test to confirm that. The baseplate and T2 Omegas were swapped and reprogrammed. The oscillation remained at -126ºC therefore the Omega was likely OK.

Such oscillations typically occur when a thermocouple detaches or is in the processes of detaching from a trap standoff. The Medusa shell was opened to examine T2. The thermocouple appeared to be securely bonded to the standoff however it could not be assumed that the thermocouple still had consistently good thermal contact with the standoff and it remained the prime suspect as the source of the problem.

The only other relevant part of the system to test was the trap power supply. Since the previous trap issue, T2 has been supplied from the 'spare' supply in the trap heating box. Although it was unlikely to have failed, this was to have been the next physical change after running some heating tests.

The aim of the heating tests was to determine the nature of the apparent temperature dependence and see if there was a critical point, above which the oscillation did not occur.
Using the trap conditioning runfile as a template, T2 was heated to different temperatures for 100s with some cooldown time between heating phases. This showed the critical point was at ~-120ºC. At or above this, the heating profile looked reasonably normal.

As a comparison, T1 was also heated to the same range of temperatures as T2. Normally, the lowest temperature T1 is set to is -66ºC however we wanted (and expected) to confirm this issue was only related to T2 (Figure 5).

Surprisingly, the oscillations also occurred on the T1 heating profiles indicating 2 things -

1) T2 thermocouple was probably OK
2) The cause of the oscillations had to be something common to both traps

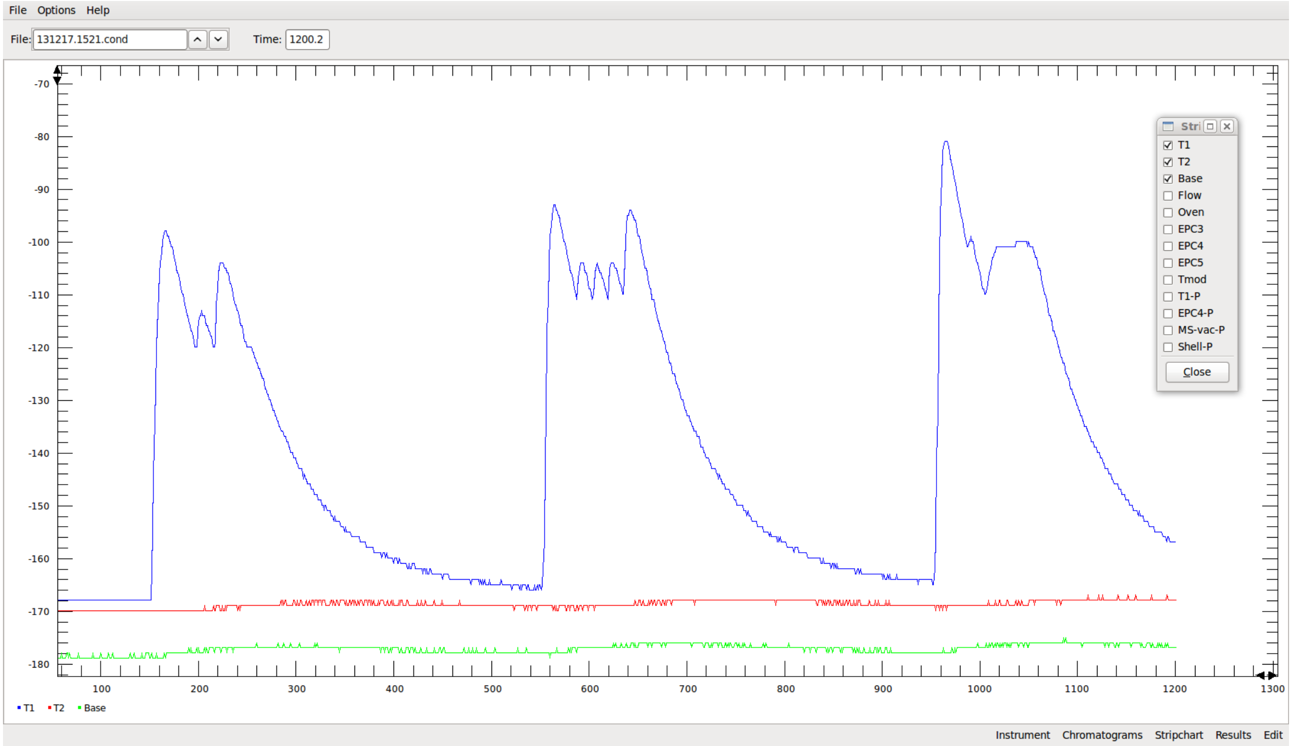


Figure 5 Testing of the trap-heating issues in T2 with T1, revealing similar problems.

In effect, the only thing the traps have in common is the baseplate and it has been getting colder in the recent past (since 131103), dropping to -179/-180ºC whereas in the past it would normally hover around -177ºC. If we assume the slightly colder temperature is the root cause of the effect, raising the baseplate temperature slightly should eliminate it. As a quick test, the Varian solenoid was turned off which has the effect of increasing the baseplate temperature as the shell loses vacuum. Repeating the trap heating tests at -126ºC shows no oscillation in T2 with the baseplate at -177ºC.

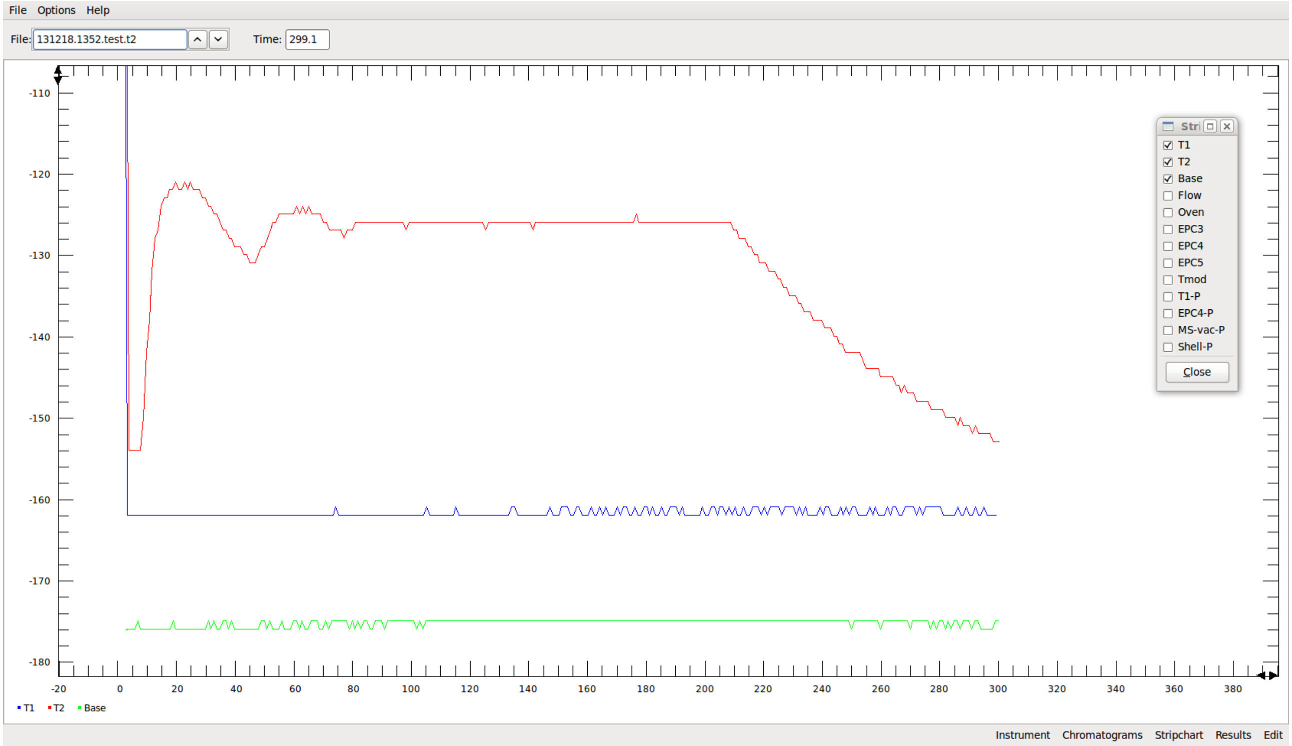


Figure 6

Repeating test on T1 showed no oscillations at -60ºC and above

Conclusions:
It seems the PID parameters need to be tuned. This effect has presumably always been there, we simply have not been controlling traps at low enough temperatures to see it. Since starting NF3 measurements, T2 has been heated to -126ºC which is 6ºC lower than previously. It should also be noted that T2 is an EMPA trap, which uses heavier gauge steel than the original Miller traps, so one might expect to have to retune the PID settings.

Since a higher baseplate temperature eliminates the effect, one quick and dirty solution would be to switch off the diffusion oil pump, which will result on a 1-2ºC rise in baseplate temperature. This would allow us to resume sampling and wait until after the holiday period to retune the PID parameters or indulge in further investigations.

An initial test to examine the effect of changing one PID parameter (the proportioning band)

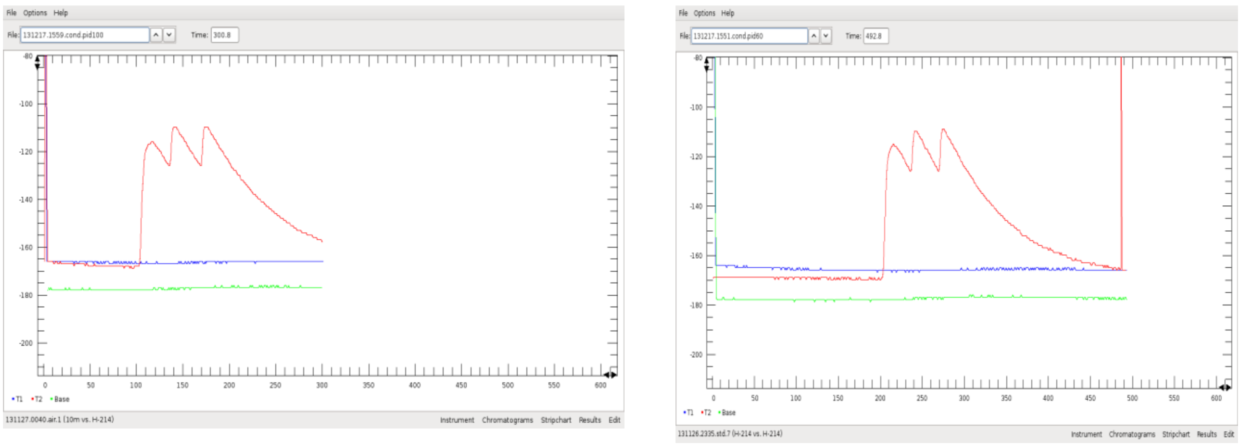


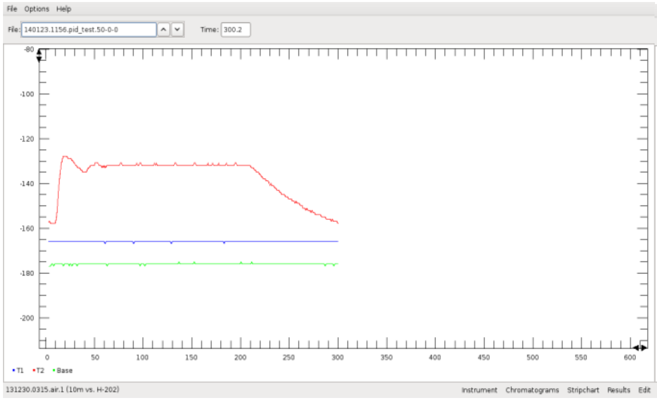
Figure 7 Testing effect of PID parameters at (a) P=50 and (b)P=100 respectively

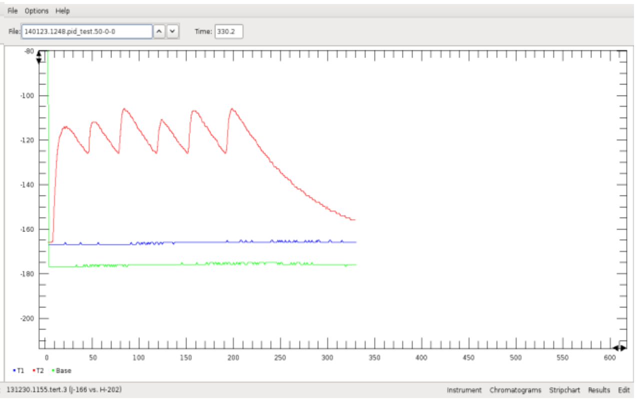
was carried out on 131217. Increasing P should reduce cycling but this was not found to be the case (Figure 7).

The diff pump was taken out of line on 131219 so that the baseplate temperature would increase slightly. Temperature oscillations still occurred on trap 2 but seemed to be less frequent than before.

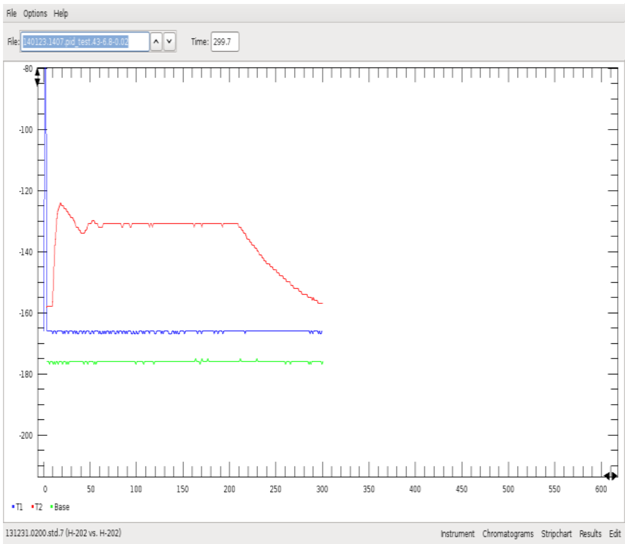
Systematic tests to examine the effects of changing PID parameters were carried out on 140123. At this stage, problems with the Falcon UPS and the vacuum shell roughing pump had been resolved so the system was in a stable condition for testing. Results were inconsistent, getting different outcomes while utilising the same parameters, pointing us back towards a hardware issue (

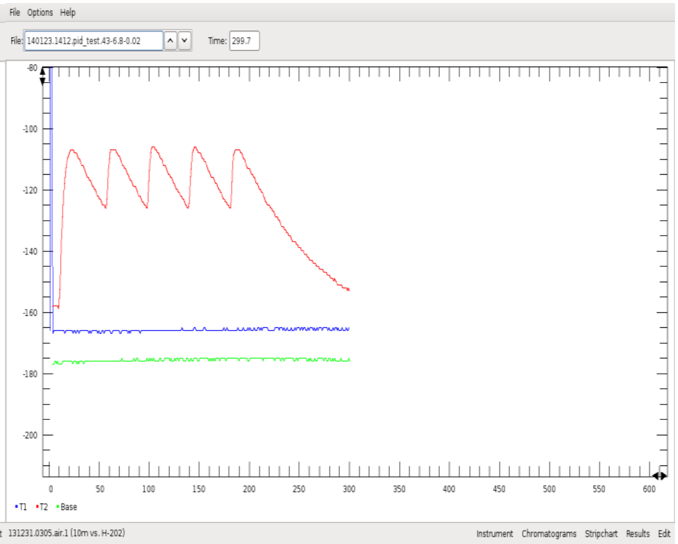
Figure 8)





(a) (b)





(c) (d)

Figure 8 (a) P=50 I=0 D=0 (b) P=50 I=0 D=0 (c) P=43 I=6.8 D=0.02 (d) P=43 I=6.8 D=0.02

The Omega was changed on 140124 however trap 2 temperature still oscillated. The power supply for trap 2 was the 'spare' torriodal in the heating supply box – as a test, the trap was reconnected to its' original torroidal supply. Much to our surprise, the oscillations disappeared (Figure 9).

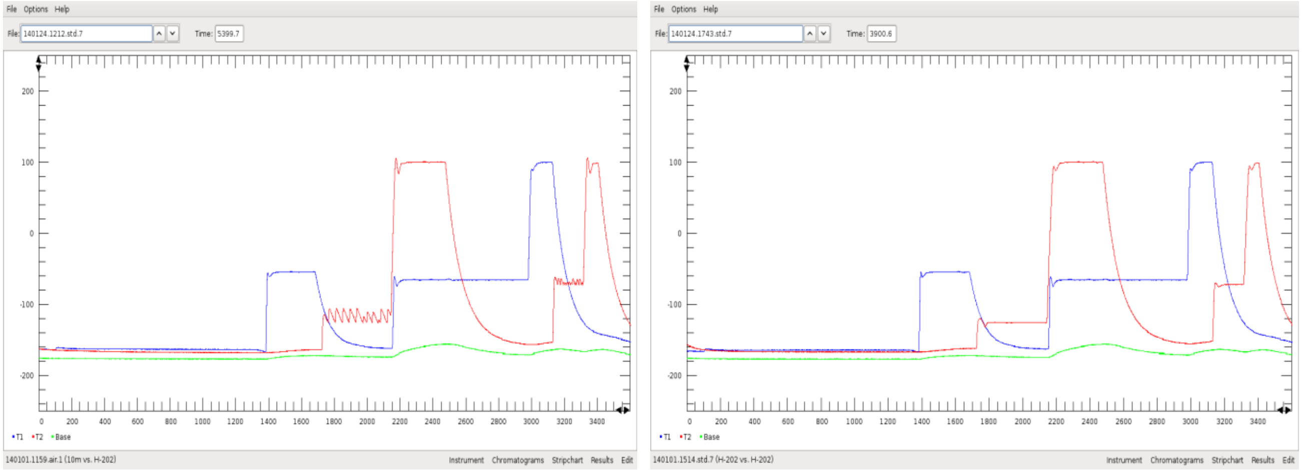


Figure 9 (a) T2 running off 'spare' torroidal (b) running of original torroidal

After a period of normal sampling, NF3 optimisation tests were run. During these tests, the oscillations re-appeared and got worse with time. (Figure 10)

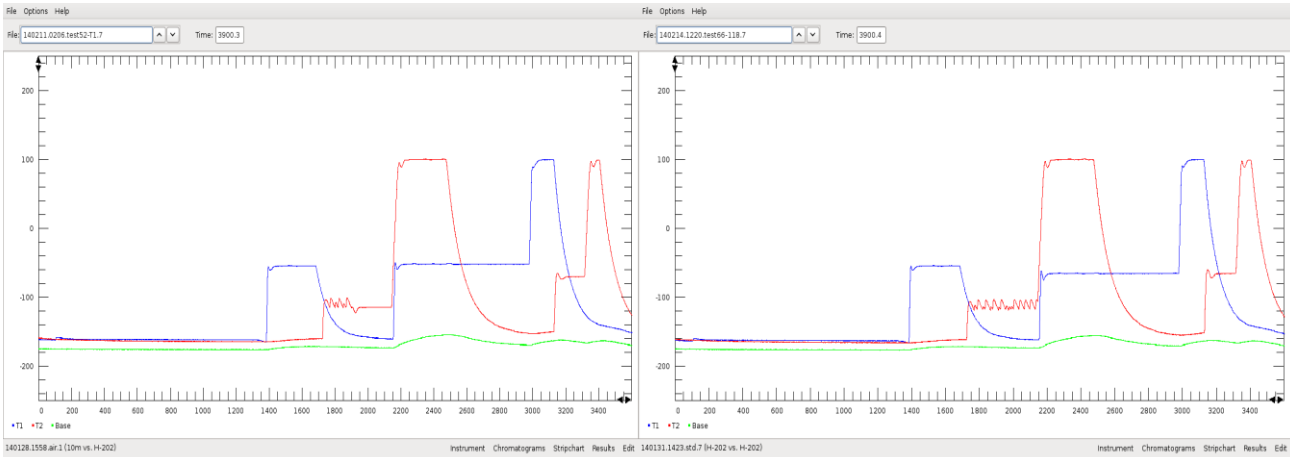


Figure 10 (a) Return of the T2 oscillation (b) Oscillation getting worse with time

The NF3 tests were completed after repeating a number invalid runs caused by T2 temperature cycling.

On 140218, in the course of playing around with the trap 2 temperature settings, a cure of sorts for the heating problem (AKA the bodge) was accidentally discovered. By heating the trap to a temperature a little lower than the setpoint and then commanding it to the final setpoint, the oscillations were eliminated – more on this later

In order to rule out the possibility of a faulty power supply, the next step was to install a completely new trap heating supply, which was sent from Bristol. This was done on 140219 but unfortunately it had no effect and we reverted to the original trap heating supply box.

At this stage, the 'bodge' was implemented which gave good initial results (Figure 11b) and after some trial and error, a near perfect T2 temperature profile was achieved (Figure 11c).

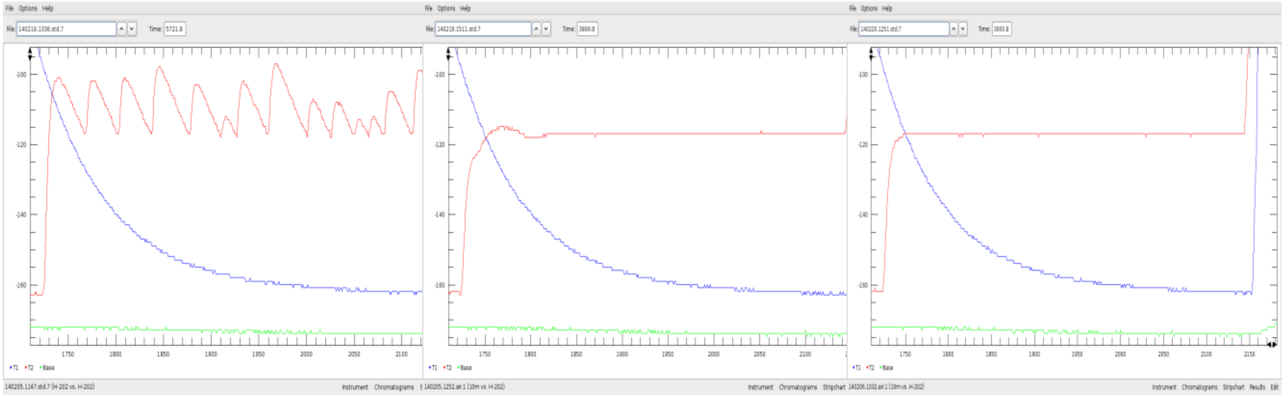


Figure 11 (a) No bodge (b) Slight bodge (c) Well tuned bodge

It's important to note and this is obvious from the plots, that the nature of the trap heating profile is unchanged as a result of this 'bodge'. The trap is heated to a 'pre-heat' temperature for a short period, typically about 10 C less than the setpoint for about 20 to 30 seconds. The trap is then heated to the setpoint and switched off at the point it would normally be switched off in the runfile. The tuning is achieved by making adjustments to the 'pre-heat' setpoint and the timing

This was never intended as a long-term solution, rather it allowed acquisition of data while we considered alternative approaches to the issue. Over time, T2 temperature began to overshoot slightly and the 'bodge' parameters were adjusted to compensate however by 140313, the oscillation was definitely on the way back (Figure 12).

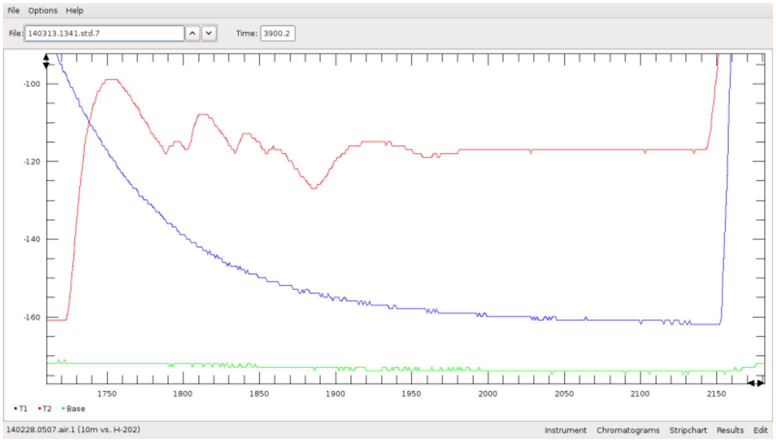


Figure 12 Return of the T2 oscillation

Knowing that adjusting the PID parameters was unlikely to produce meaningful results, the only other adjustment on the Omega likely to have an impact was the %Hi parameter which was changed on 140313. This parameter controls the maximum voltage, which can be applied to the trap and essentially varies the heating rate. Other Medusa systems in which traps had been changed required this parameter to be adjusted so we had some hope that it might help; unfortunately it didn't really. Lowering the value did have some impact on the oscillation but at a cost of slowing down the heating rate and eventually, the oscillations returned. The nominal setting for trap 2 on all Medusas is 60%. We lowered the setting to 50% - any lower was definitely too low (Figure 13).

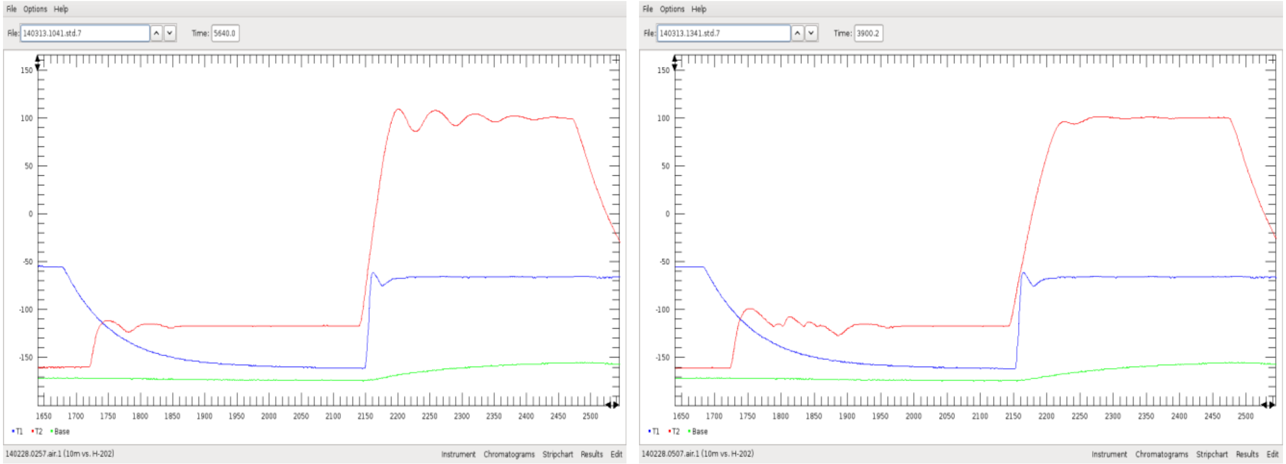


Figure 13 Adjustment of the Omega (a) %Hi=60% (b) %Hi = 50%

Currently this is a summary of where we are at;

Trap 2 is being run at %Hi=50% using a pre-heating bodge to try to minimise trap temperature oscillations. We have tried changing the Omega controller and the power supply, we have adjusted the PID parameters and the maximum power output on the Omega, we have checked and re-checked wiring connections and we have examined the trap and thermocouple for any obvious faults. At this point, we believe the issue may be the bonding of the thermocouple to the standoff and we await delivery of replacement standoffs from EMPA for testing.

2.1.2 GC-MD

The MD proved yet again to be a most reliable system and performed well for the reporting period. Most of the data loss resulted from ancillary equipment failure or late gas delivery.

2.2 Ridge Hill

The site at Ridge Hill in Herefordshire has been operational since the 23rd of February 2012. Sampling lines at 45 and 90 meters were installed in the first week of February and civil works were completed on the 12th of February.

2.2.1 CRDS

The Picarro 2301 Cavity Ring Down Spectrometer (CRDS) has been running well at Ridge Hill over the last 12 months. The CRDS samples air from the two tower heights of 45 m and 90 m, alternating every 30 minutes. The CRDS operates by measuring CO_2 and CH_4 in an evacuated cavity at very low pressure. The GCWerks software now downloads CRDS data daily for easy viewing in a similar manner to other GC based instruments.

2.2.2 GC-ECD

The gas chromatograph with electron capture detector (ECD), which measures N_2O, and SF_6 at Ridge Hill, ran well during the past 12 months. Fortnightly site visits are being made to ensure all instrumentation is running well and there are sufficient calibration and carrier gases.

2.3 Tacolneston

The site at Tacolneston in Norfolk has been operational since the 25th of July 2012. Sampling lines at 54, 100 and 185 meters were installed in November 2011.

Work was done starting in October 2013 to remove the old tower at Tacolneston, partially impeding access to the site during that time. Work has been completed and site access has been restored. Figure 14 shows the new site.

Figure 14 The "new look" of Tacolneston after work was completed to remove the old tower.

2.3.1 Medusa-GCMS

In May 2013, there was another rapid failure causing loss of data. On the 20th, one of the filaments on the MS source burned out. The alternate filament was used only for that to burn out on the 23rd. There was no need to delay the visit to sort this out as we now get monthly, rather than daily, permits. Both filaments were replaced and the instrument restarted only for the MS to loose communication with the computer on the 24th. This time a soft reboot was successful and the instrument restarted again. Data was lost from 2pm on 20th until 5pm on the 24th.

A number of compounds (PFC-318, C4F10, C6F14, n-C3 to C5 and i-C4 and C5 alkanes, c-propane and HFC-4310mee) have been added to the analysis list during this period. Although they are being measured, there is no calibration for the alkanes at present.

At the start of June, the normal analytical routine was interrupted in order to run a couple of standards from a round-robin experiment for NMHCs. These were run between 130603 (1122) and 130604 (1000). On 130708 the run order for sequence.blank was changed from std-blank-std-labair to std-labair-std-blank. This was in response to a suggestion made at the DECC4 meeting in Bristol to see if it had any effect on the quality of the data.

There have been a number of problems with communications to the MS during this period. On arrival, for a regular visit on 130723, the instrument was still producing stripcharts but all devices were aborted. A soft-reboot could not re-establish communications but a hard re-boot was successful. However by the next day communications were lost again and it was not possible to regain them remotely. Visiting the site on the 130725, to change the ethernet cable, it was still not possible to gain communication and cycling the power switch left the front display of the MS blank. Another attempt to cycle the power, on 130806, did re-establish communications and the instrument was tuned and restarted on 130807 after allowing it to stabilise after such a long time. However, the next day found that the instrument was still not working and needed another visit to hard-reboot it. Communications had again been lost on 130814 and it was decided to replace the ethernet hub and cable to the MS; the latter being plugged straight from the hub to the back of the MS, rather than via the wall sockets in the container. With the on-going problems, and the possibility that it was a communication board problem inside the MS itself, it was decided to replace the MS with one from University of Bristol. This was done on 130819 and after pumping down overnight, and cycling the GC program as it had been idle for some time, the instrument was re-tuned and the instrument restarted.

On 130823 it was found that the sample traps were not heating properly. The Cryotiger unit was switched off after the Bank Holiday, to allow it to warm up overnight, and then the procedure detailed in Cryotiger_revival.txt was followed to get the baseplate cooling to the correct temperature again. The routine sequence was restarted on 130828 but by the next day the MS was again not producing chromatograms. From the error code, it appeared to be due to a burnt out filament but switching the filament did not produce any response either. Both filaments were replaced on 130902 and after allowing the MS to pump down again the instrument was retuned.

At some point before 130902, the Jun-Air compressor had stopped working – shown by an increase in the water readings on the Picarro. The Medusa was not restarted so that the compressor could be sent to Bristol for repair. An OFN cylinder was connected to the nafion counter-flow line on 130912 and the instrument restarted. The repaired compressor was re-installed by Simon on 131002. No useful data had been collected from 130720 until 130912 with the exception of a few results between 130820 and 130822.

Work started in October on the dismantling of the old tower at the entrance of the site and this means that we no longer have free access to the site. On foul weather days (rain, fog or high winds), it is possible to apply for a permit on the day although this is sometimes slow in being processed. Every other week the site is vacated by mid-day on the Friday and so the running of sequence.tert was moved to Fridays from 131011 to allow the usual balancing of the standards on a regular visit day. This work was completed towards the end of April 2014, regular site-visits can now be restarted.

2.3.2 TAC-MD

This instrument has been working well. There was one instrument failure during May, on the 16th. It is not clear what caused this failure. It was possible to restart the instrument remotely, rather than needing someone to visit the site to start the PP1 module as was necessary in December. Data was lost from 8:30pm on the 16th until 8:10am on the 17th.

It has long been realised that the standard is used up at a greater rate than other sites even when using different ports for the standard. In addition the loss of the cylinder filling capability at Mace Head has meant that it was sometimes necessary to stop the instrument whilst a replacement cylinder was obtained. That was the reason for the instrument to be stopped on 130730 when data was lost from 0754 until 1704 on 130806. An attempt was made to locate any leaks on the line on 130814 with data lost between 1030 and 1547.

At some point before 130902, the Jun-Air compressor stopped working – shown by an increase in the water readings on the Picarro. The instrument was stopped so that the compressor could be sent to Bristol for repair. An OFN cylinder was connected to the nafion counter-flow line on 130912 but the counter-flow was reduced from 5 to 3.5 in order to preserve the gas. The instrument was restarted at 1240. The repaired compressor was re-installed by Simon on 131002 who also spent some time looking for a leak in the standard line. It was decided to switch the standard to port 9 and that does appear to have made an improvement although that suggests that there are problems with ports 3, 5 and 7 as the standards have needed to be changed about every 2 months, or so. Also during this visit, a replacement All-Sensor was installed as the present one was not giving readings on the stripchart.

During a remote log in (by Simon) on 130920 it was noticed that there was a problem with poor precision for the standards. It appeared that some of the standards were giving “ambient air” values suggesting that there was a problem with the inlet valve. The sequence was altered to increase the number of standard runs to see if this affected the data. The valve’s movement was checked several times during the next site visit (130923) and found to be working properly.

2.3.3 CRDS

Overall the CRDS instrument at Tacolneston ran well during the measurement period. There were a number of valve co-ordinator problems (shutdowns) when using remote desktop login. This function was disabled and logmein set up for remote access (4th July 2013).

The site compressor failed in September, this resulted in no nafion counter-purge flow and hence sample drying. The Picarro ran in this mode until the repaired compressor was re-installed on 2nd Oct 2013.

2.4 Angus

A visit to the Tall Tower at Angus, 10 km north of Dundee, was made on Monday the 9th of May 2011 to see how the tower lines and instrumentation were set-up. The site was acquired by the University of Bristol in January 2012. The Picarro G2301 was installed 29 May 2012. One sampling line at 222 meters exists at this site.

2.4.1 CRDS

The CRDS has generally been operating well during the measurement period. The main problems at this site have been due to the lack of inlet cup and shield to prevent liquid water from entering the sampling line. Owing to very wet conditions over winter 2013-2014 there were several water contamination episodes, where H2O and cavity pressure were strongly correlated with the CO_2 data (Figure 15). The installation of a sample cup/shield is being planned to mitigate future data loss owing to water contamination.

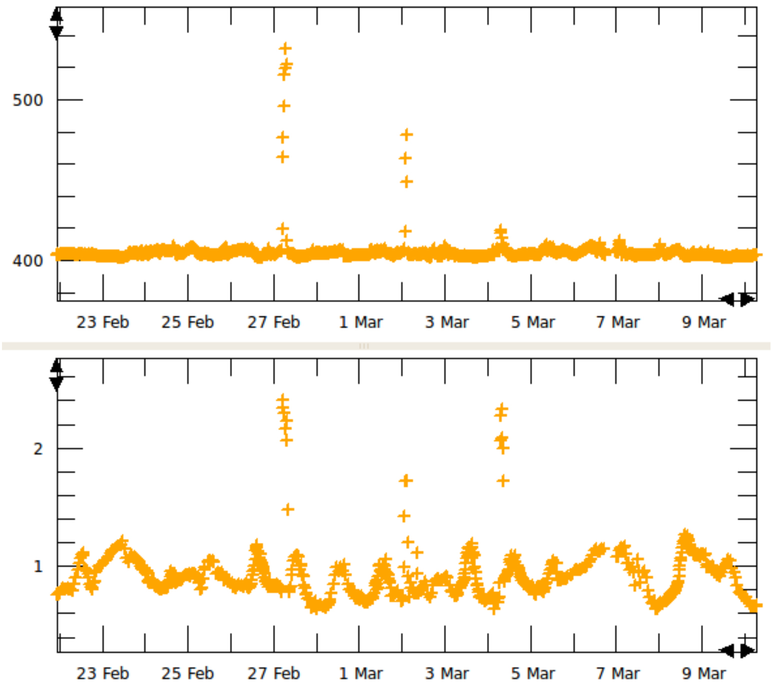


Figure 15 Correlated signals between CO2 data (upper panel) and water (lower panel) during suspected water contamination episodes

An inter-comparison exercise with InGOS, measuring three “round-robin” cylinders, was performed In February 2013. This inter-comparison exercise is used to show data consistency and comparability with other European sites (Figure 16)

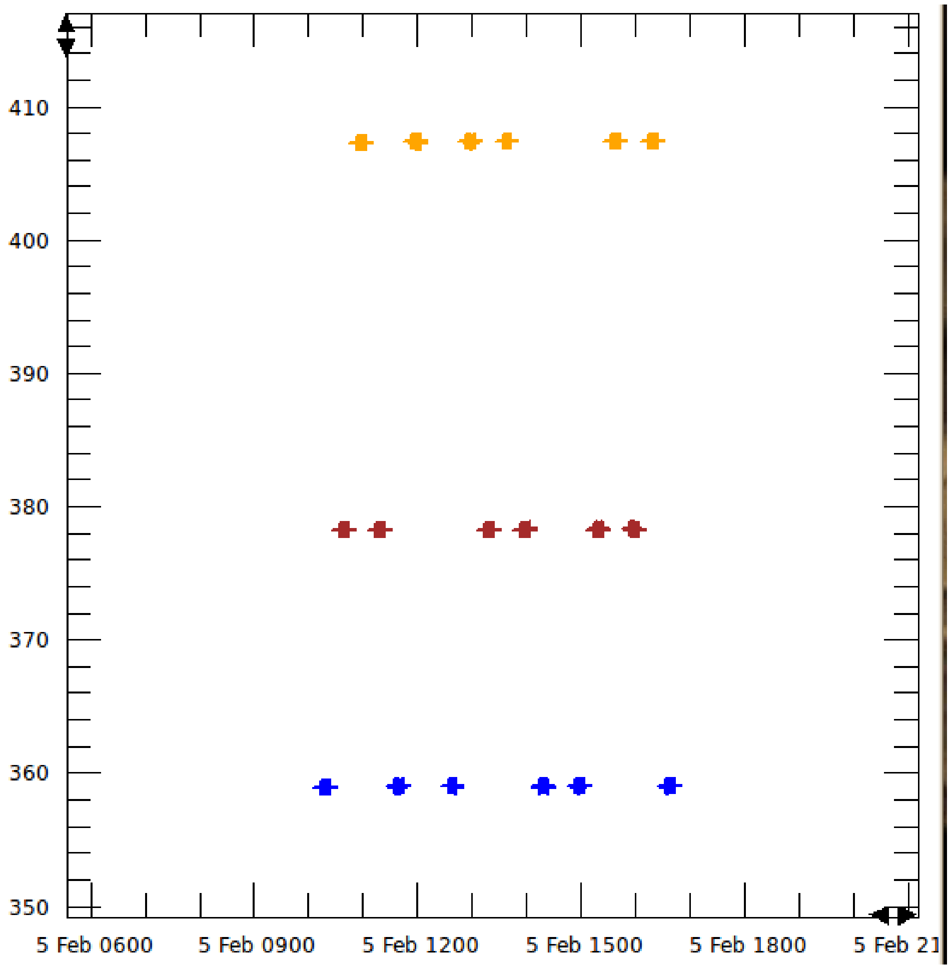


Figure 16 Inter-comparison experiment with the European InGOS project. A series of tanks were measured in replicate at Angus and compared with results from other instruments/stations.

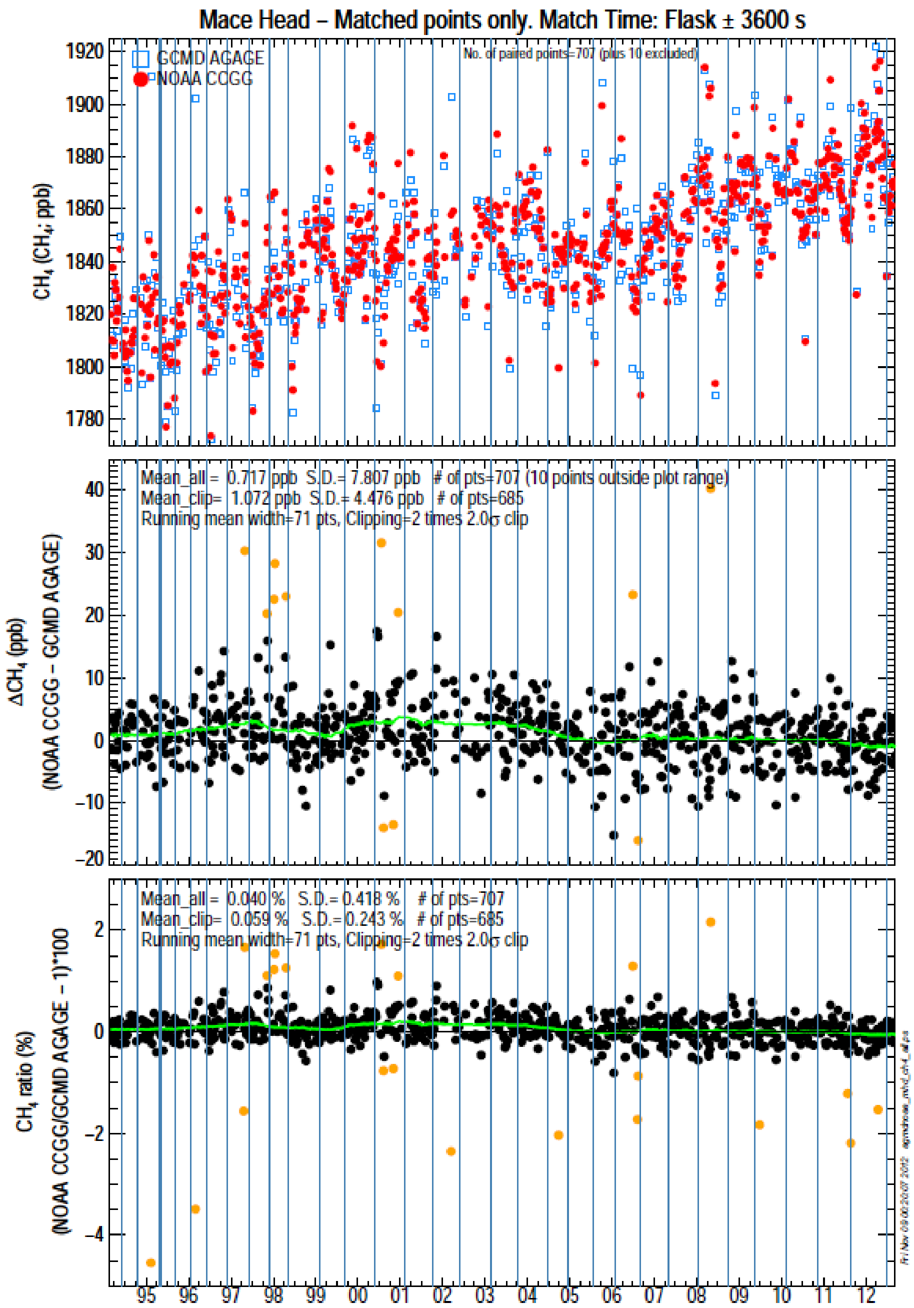
3 Calibration and Intercomparisons

The calibration scales employed by AGAGE are used for all species measured in the network with the exception of CO_2 at all sites and CH_4 at Ridge Hill and Tacolneston, which are measured on the CRDS instrument. The calibration methodology used at these sites is discussed in the Appendix (and on the website, http://www.metoffice.gov.uk/atmospheric-trends/).

3.1 AGAGE and NOAA comparisons

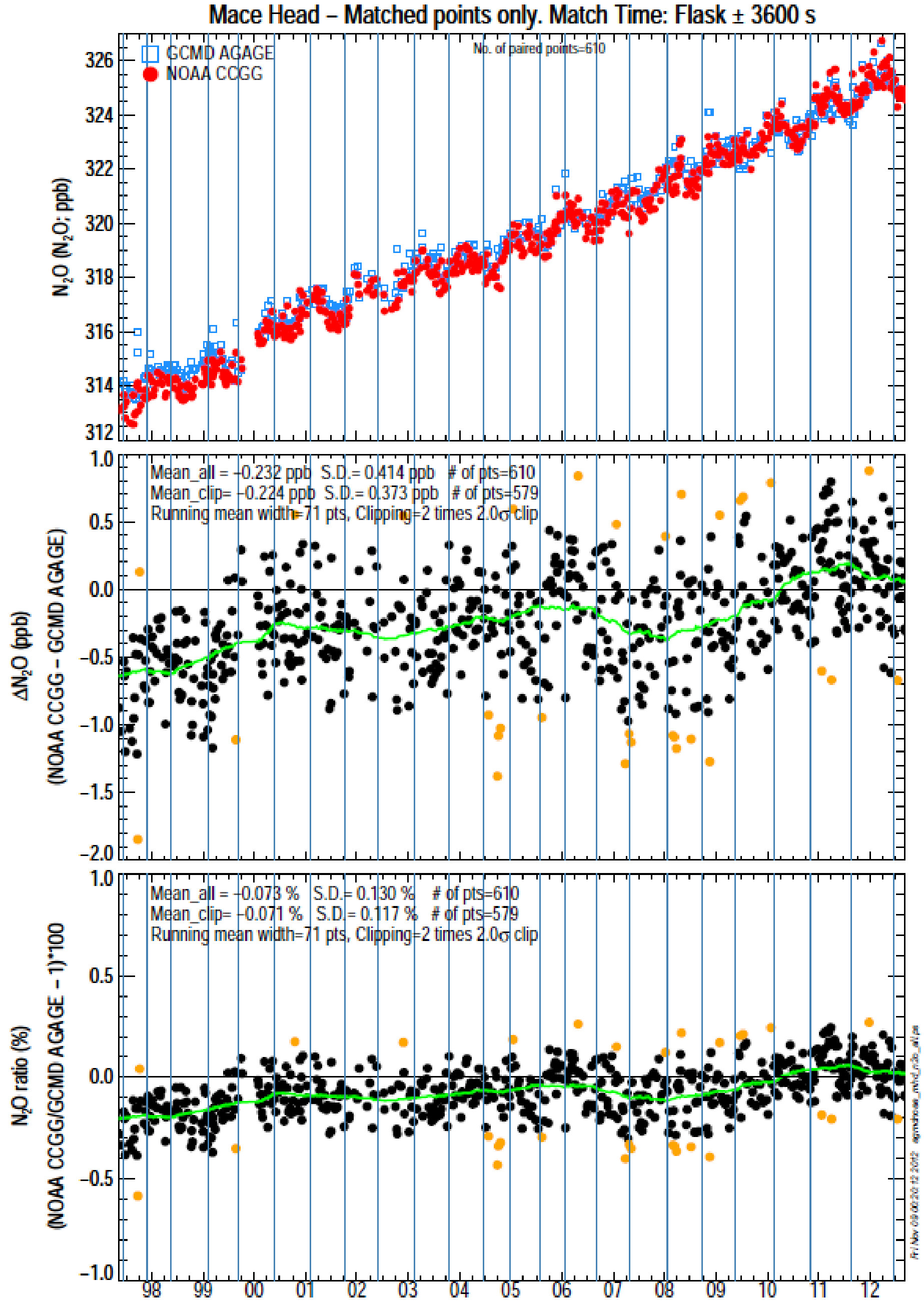
The Mace Head data is continuously compared to data from other groups within Europe and across the globe to ensure data consistency and comparability. Figure 17 (a)-(c) shows examples of a comparison of the AGAGE *in situ* data with NOAA flask samples from Mace Head for three of the key species we measure (CH_4, N_2O and SF_6). Although not shown here, comparisons of all AGAGE MD and Medusa species are conducted where both networks make concurrent measurements.

The plots illustrate the excellent agreement in measured values (and calibration). For CH_4 the difference between NOAA and AGAGE data is 1.07 ± 4.48 ppb (0.06 ± 0.24%), for N_2O it is −0.22 ± 0.37 ppb (−0.07 ± 0.12%), and for SF_6 0.04 ± 0.06 ppt (0.6 ± 0.91%).

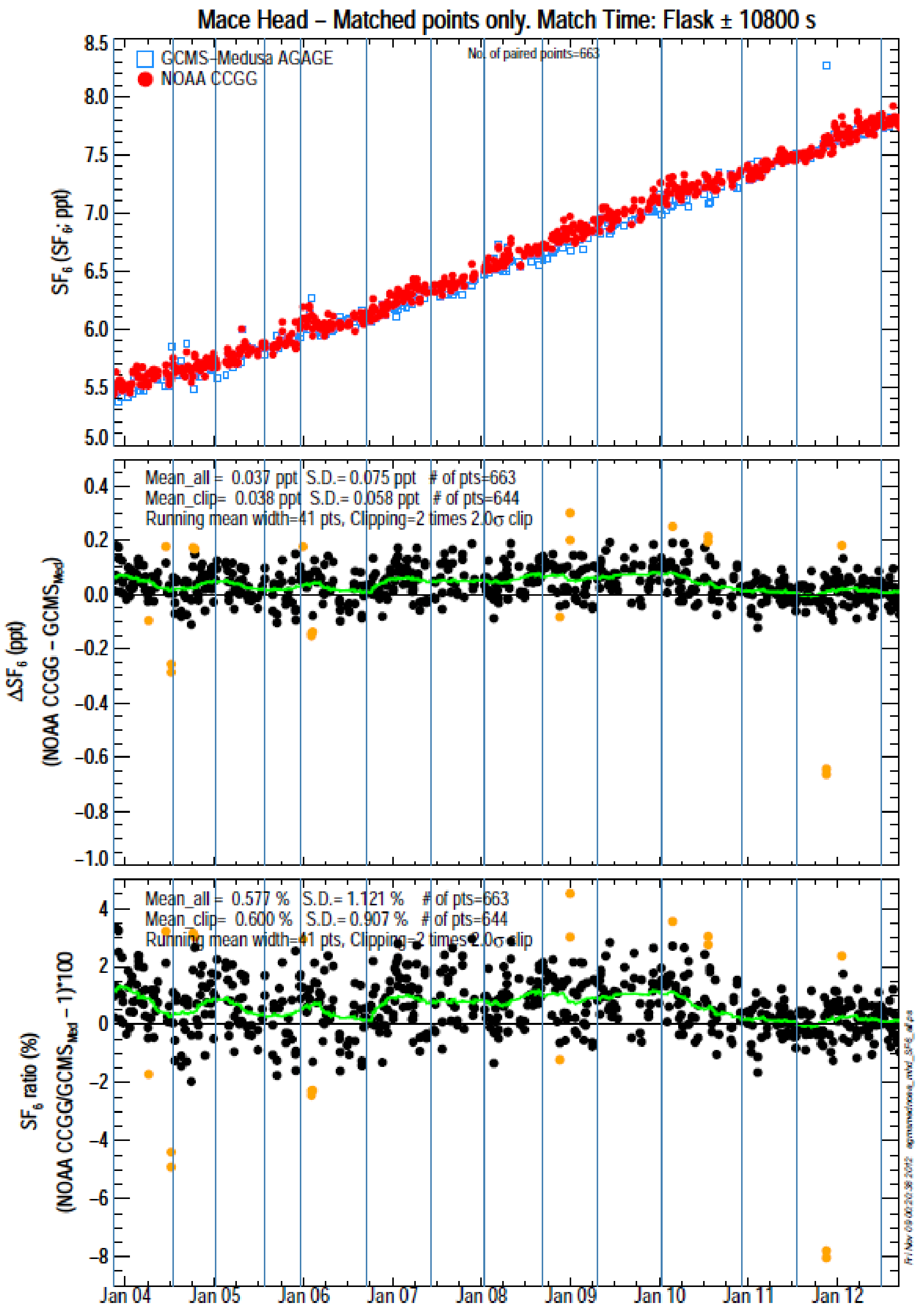


Mace Head – Matched points only. Match Time: Flask ± 3600 s
GCMD AGAGE
NOAA CCGG
No. of paired points=707 (plus 10 excluded)
CH4 (CH4; ppb)
Mean_all = 0.717 ppb S.D.= 7.807 ppb # of pts=707 (10 points outside plot range)
Mean_clip= 1.072 ppb S.D.= 4.476 ppb # of pts=685
Running mean width=71 pts, Clipping=2 times 2.0σ clip
ΔCH4 (ppb)
(NOAA CCGG – GCMD AGAGE)
Mean_all = 0.040 % S.D.= 0.418 % # of pts=707
Mean_clip= 0.059 % S.D.= 0.243 % # of pts=685
Running mean width=71 pts, Clipping=2 times 2.0σ clip
CH4 ratio (%)
(NOAA CCGG/GCMD AGAGE – 1)*100
95 96 97 98 99 00 01 02 03 04 05 06 07 08 09 10 11 12

(a)


Mace Head – Matched points only. Match Time: Flask ± 3600 s
GCMD AGAGE
NOAA CCGG
No. of paired points=610
N_2O (N_2O; ppb)
Mean_all = -0.232 ppb S.D.= 0.414 ppb # of pts=610
Mean_clip= -0.224 ppb S.D.= 0.373 ppb # of pts=579
Running mean width=71 pts, Clipping=2 times 2.0σ clip
ΔN_2O (ppb)
(NOAA CCGG – GCMD AGAGE)
Mean_all = -0.073 % S.D.= 0.130 % # of pts=610
Mean_clip= -0.071 % S.D.= 0.117 % # of pts=579
Running mean width=71 pts, Clipping=2 times 2.0σ clip
N_2O ratio (%)
(NOAA CCGG/GCMD AGAGE – 1)*100
98
99
00
01
02
03
04
05
06
07
08
09
10
11
12

(b)



(c)

Figure 17 (a-c) Comparison of AGAGE MHD in situ date with NOAA flaks data. Top plot is the matched data, middle shows a difference plot and bottom plot shows the percentage difference.

3.1.1 AGAGE and University of Heidelberg comparison

This comparison was reported in the last annual report. A more detailed account of the comparison was submitted to Atmospheric Chemistry and Physics Discussion (ACPD) and is available on-line for comment and discussion until 20th June 2014.

http://www.atmos-chem-phys-discuss.net/14/10429/2014/

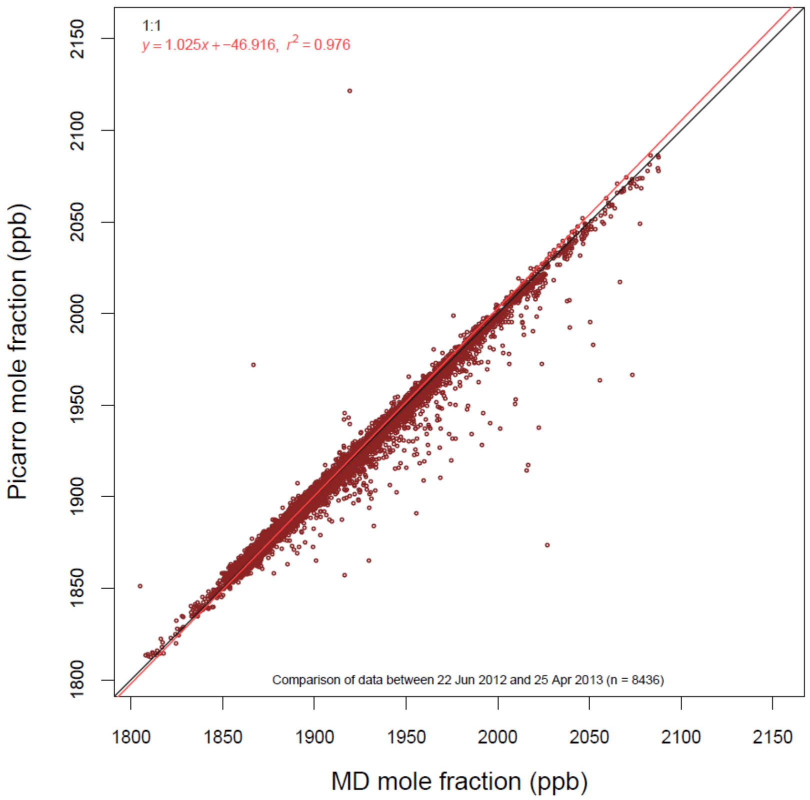


Figure 18 Correlation plot of the matched data between MD mole fraction and Picarro (CRDS) mole fraction.

The correlation coefficient (r^2) is high, indicating good correlation across the concentration range, however, the scatter of datapoints below the 1:1 line indicate that the Picarro CRDS tends to periodically report lower values than the AGAGE GC-MD instrument in the 1900-2100ppb range. These individual data points will be examined more fully to determine if this is an instrumental bias or incorrect assignment of mole fractions whilst data processing. However, it should also be noted that the Picarro CRDS only measures the ^{12}C isotope and so CH_4 events that are anomalously high in the lesser isotopes of ^{13}C and ^{14}C will not be reported by the CRDS whereas the GC-MD FID will account for all isotopes together.