

## CAPE VERDE ATMOSPHERIC OBSERVATORY (CVAO)

### Ozone calibration log

#### Instrument detail

See document of instrument coverage, 3 instruments (TEI49C (Instrument 1 S/N: 0536414593 and Instrument 4 S/N: 0730525419) and a TEI49I (Instrument 2 S/N: 0708621224)) have been the main instruments at the site although 5 (2 x TEI49C, 2 x TEI49I and a 2B technologies 202) have also been run at various times. Except for periods between September 2008 and February 2009, March-May 2009, June-August 2009 and March-June 2010 the measurement has been at least duplicated.

#### Sampling Inlet

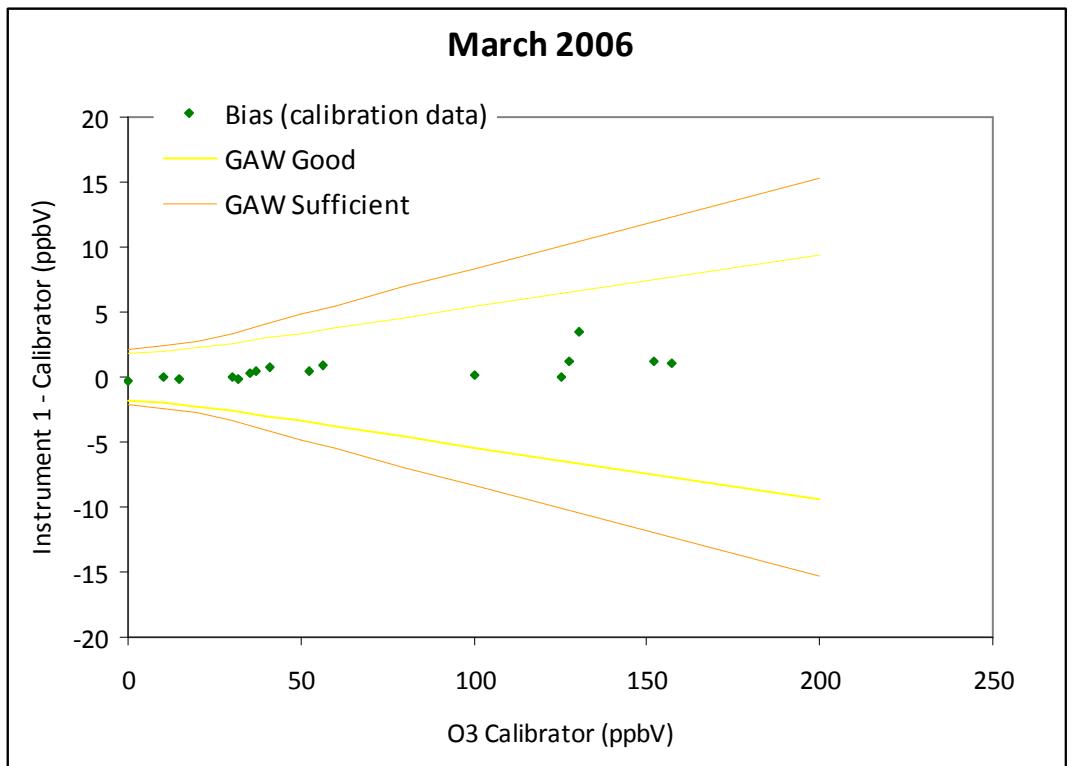
Initially sampling was done from a height of 4m through 5m of Teflon. From July 2010 the main manifold was changed to 1" glass from a height of 10m and ozone is sampled from the middle of this laminar flow through 3m of  $\frac{1}{4}$ " Teflon tubing. The sample always passes through a  $1.2\mu\text{m}$  PTFE particulate filter before reaching the instrument.

#### Calibration history summary

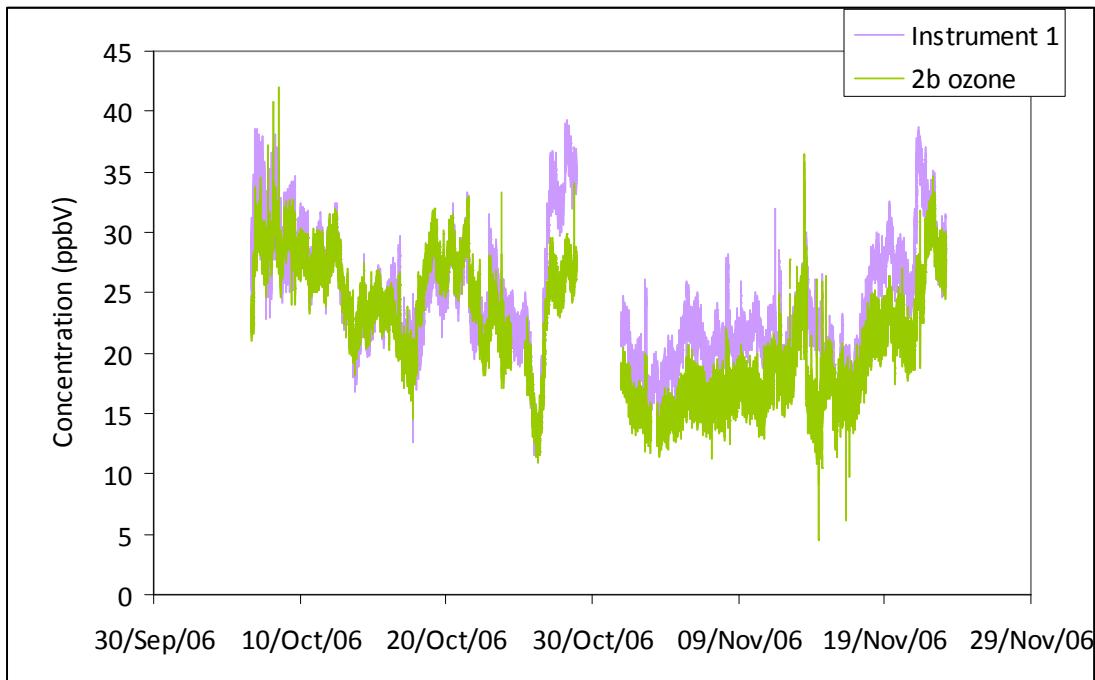
A primary standard (S/N: ) was available at the site between May and December 2007 and again between February and October 2009. At other times calibrated instruments have been sent out to Cape Verde e.g. in July 2010 and March 2011. The main instrument was initially calibrated in February 2006, and then there were calibrations only every 15 months however since February 2009 they have been every 3-6 months.

Since June 2011 a transfer standard (CVTS) has been used to calibrate the instruments and this is done every 3-4 months. The CVTS is checked against the NIST calibrated standard (TS) ideally before and after each Cape Verde trip.

The first plot shows the instrument 1 (TE49C) calibration in York before it was set up in Cape Verde. GAW criteria lines are from Klausen et al., 2003.

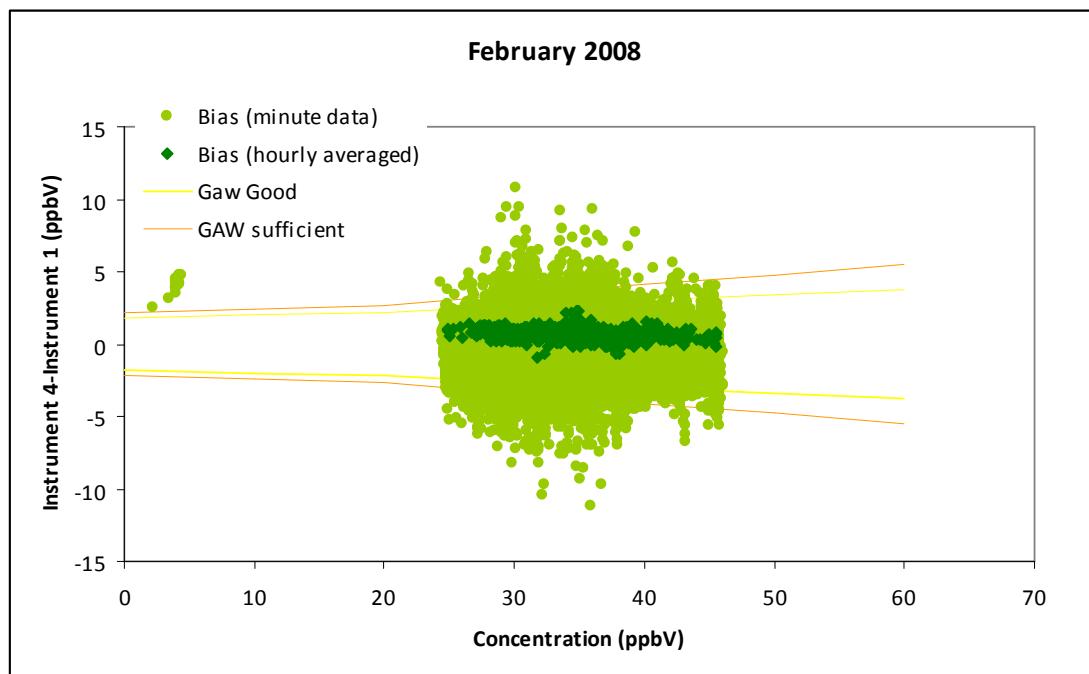


Instrument 1 was the main instrument until February 2009.  
 Initially an independently calibrated 2B ozone instrument was run alongside  
 Instrument 1 but this showed poor agreement (and stability) to the more reliable  
 NIST calibrated Instrument 1 so was replaced.

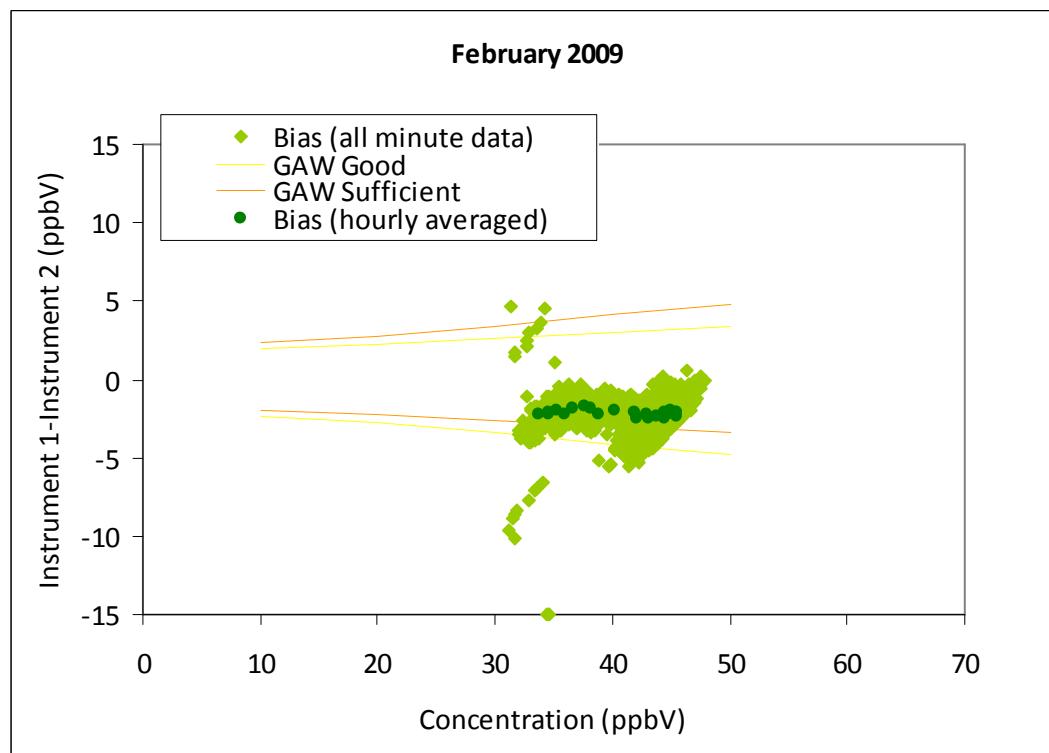


Instrument 1 was run in parallel with newly calibrated Instrument 4 from November 2007 until September 2008. The data below is from February 2008 showing that the

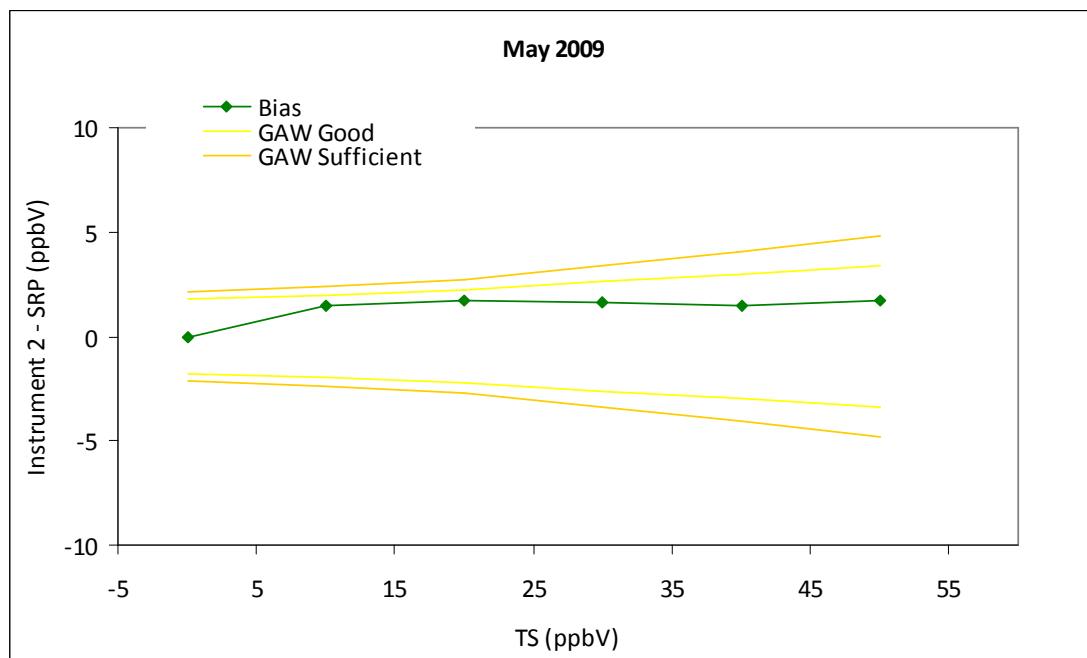
two independent instruments (although share an inlet) respond well (see minute data) and compare favourably over a range of concentrations (25-45 ppbV).



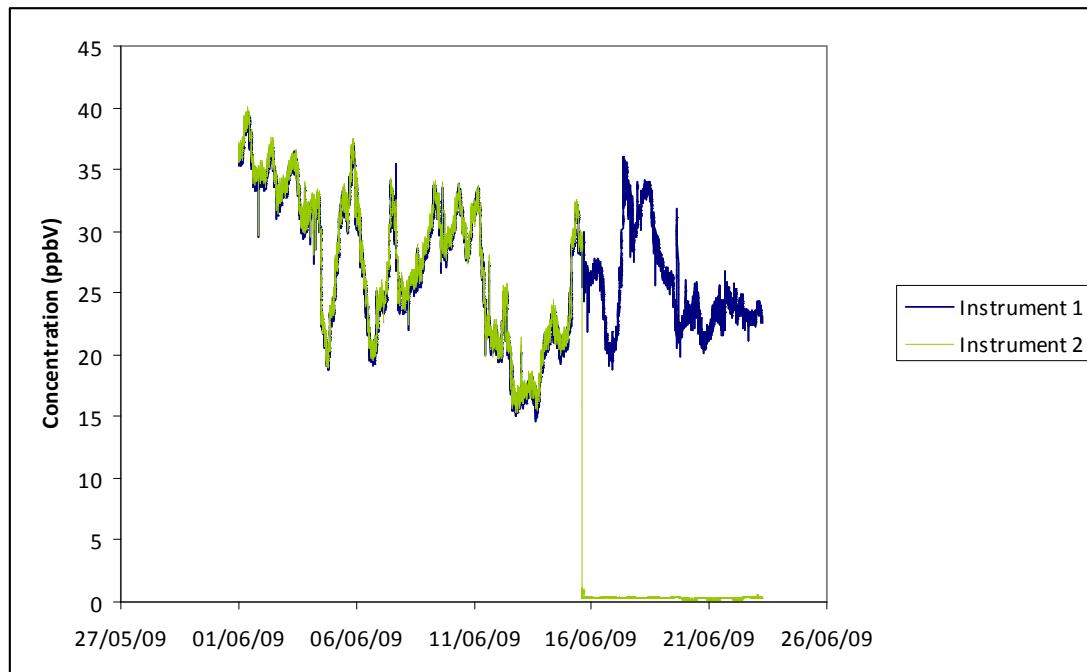
In February 2009 Instrument 2 arrived in Cape Verde. This instrument had been calibrated July 2008 using the primary standard (NPL SRP #2 traceable to NIST). Instrument 1 compared favourably to Instrument 2 although soon after Instrument 1 developed a fault with its pump.



Instrument 2 was calibrated against the Transfer Standard (TS) in May 2009.  
Instrument 2 was run as the main instrument from February 2009 until May 2009.

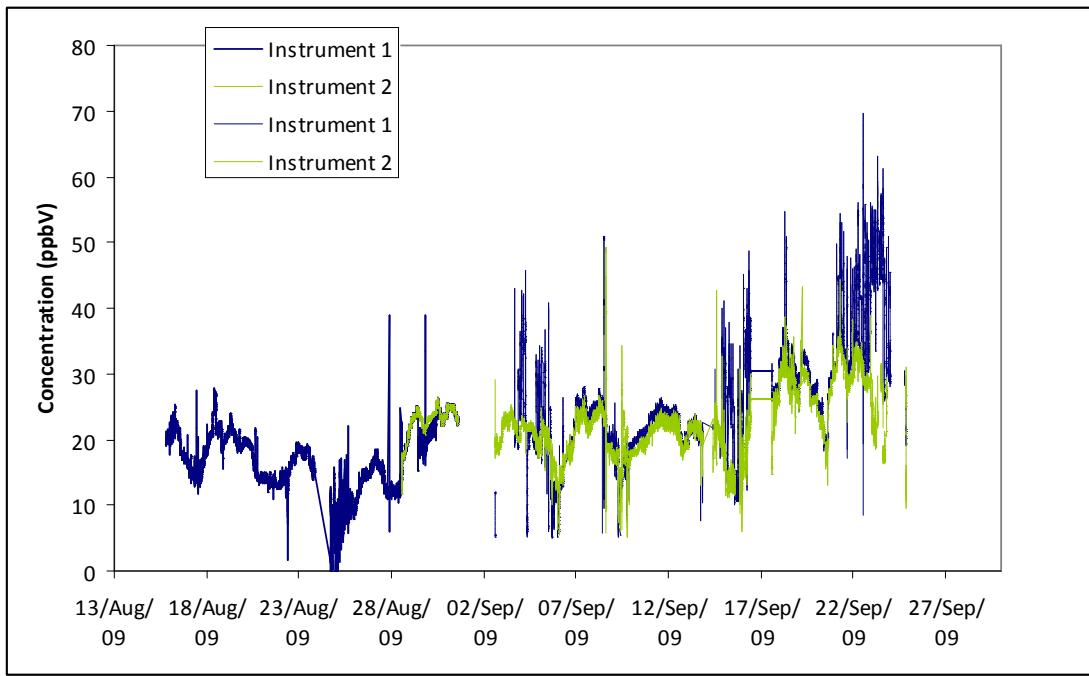


Instrument 1 and 2 were run together end of May and June.



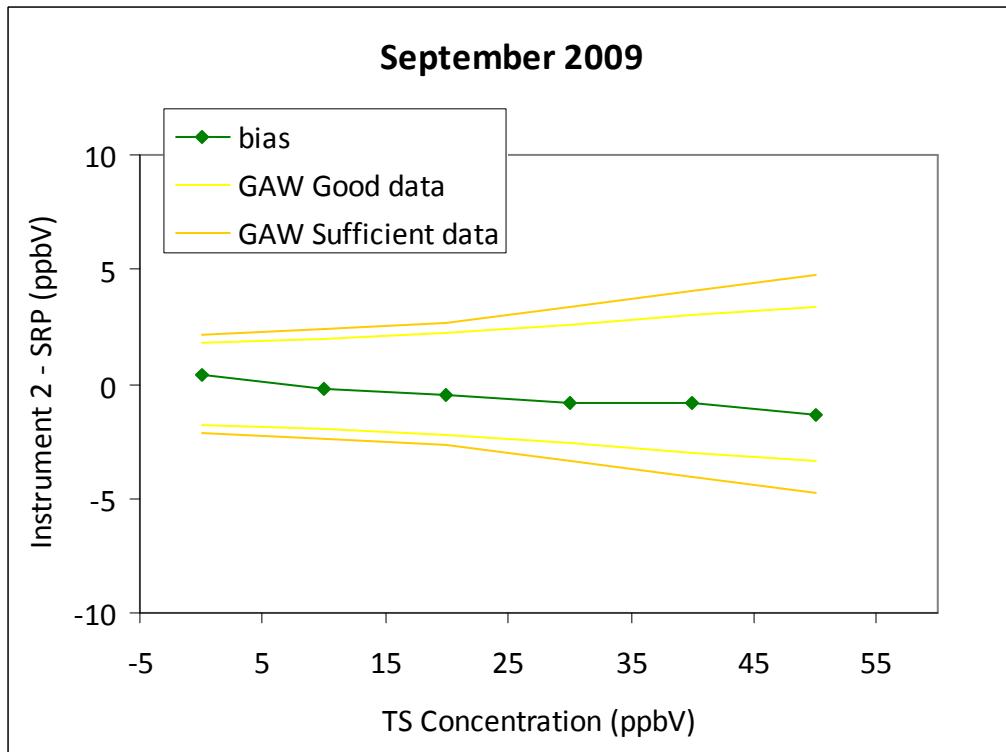
Instrument 1 was run as the main instrument during June through to August 2009.

Instruments 1 and 2 were run together end August to September 2009 until the valves broke on Instrument 1. They were fixed in October 2009.

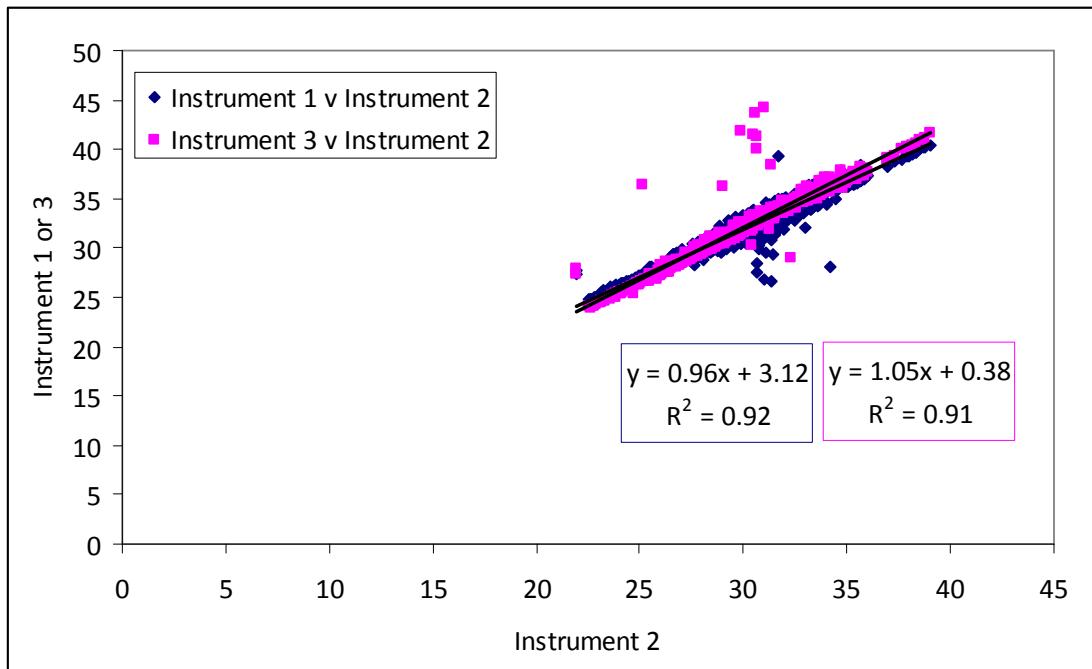


Instrument 2 was the main Instrument until November 2009.

Instrument 2 was calibrated against the Transfer Standard (TS) in September 2009.

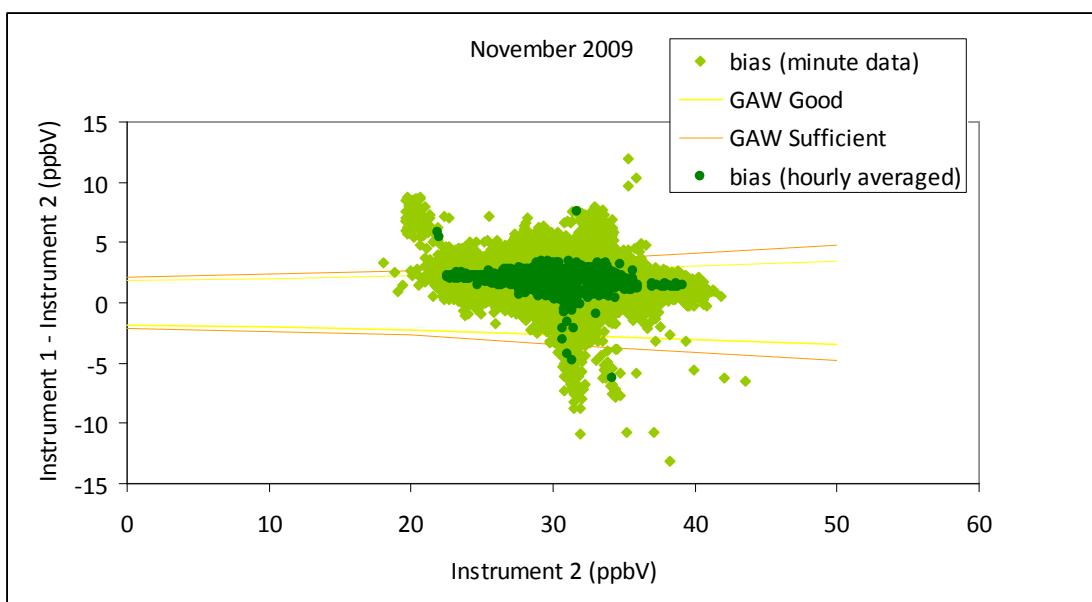


In November 2009 Instruments 1, 2 and 10 were all run together.

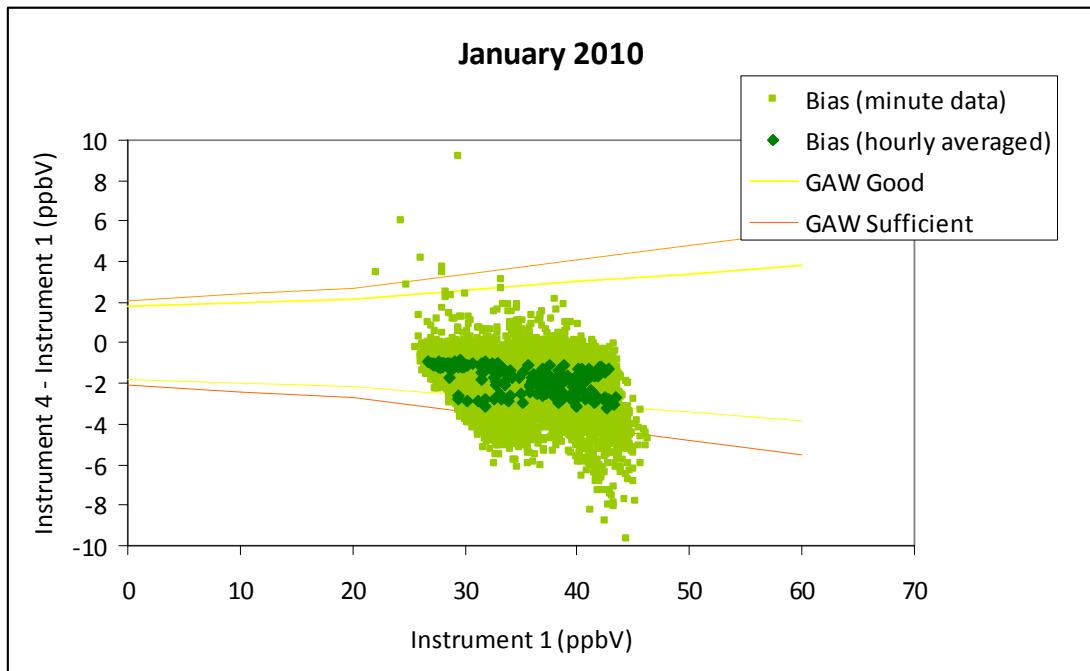


Instrument 1 compared well with Instrument 2 but Instrument 2 developed a fault (?) and was returned to UK at the end of 2009.

Rezeroed Instrument 1.

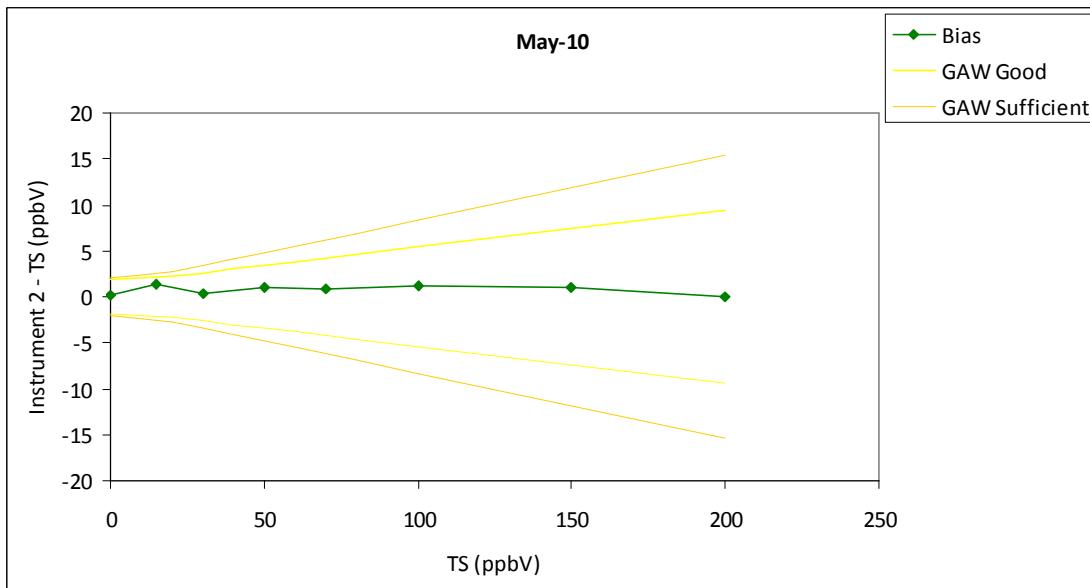


Instrument 1 was the main instrument from November 2009 until January 2010. In January 2010, Instrument 4 was sent out to Cape Verde, it had recently been calibrated against the TS. The agreement with Instrument 1 is shown below.



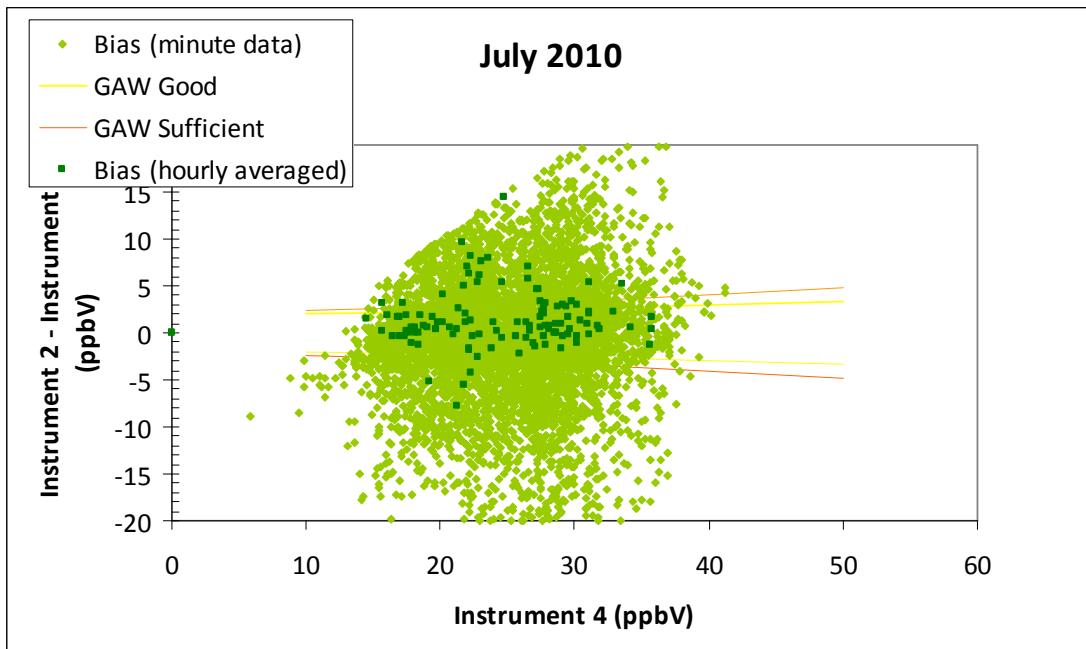
Instrument 4 was the main instrument from January 2010.

Instrument 2 was sent back for repair, calibrated in York in May 2010 using the ozone calibrator (TS) then sent back to Cape Verde in July 2010. Below is the calibration data.

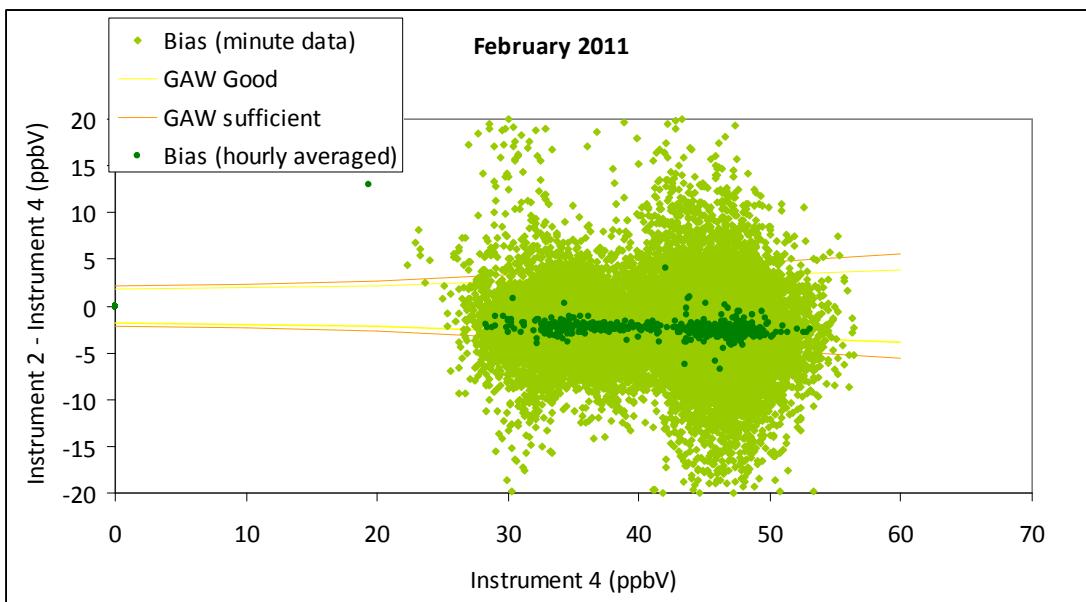


Instrument 1 was returned to the UK in July 2010 for a service.

On its return to CV Instrument 2 was run with Instrument 4 to produce the data below. Since returning to CV Instrument 2 has produced very noisy data which appears to be largely influenced by lab temperature (see different correlations below).



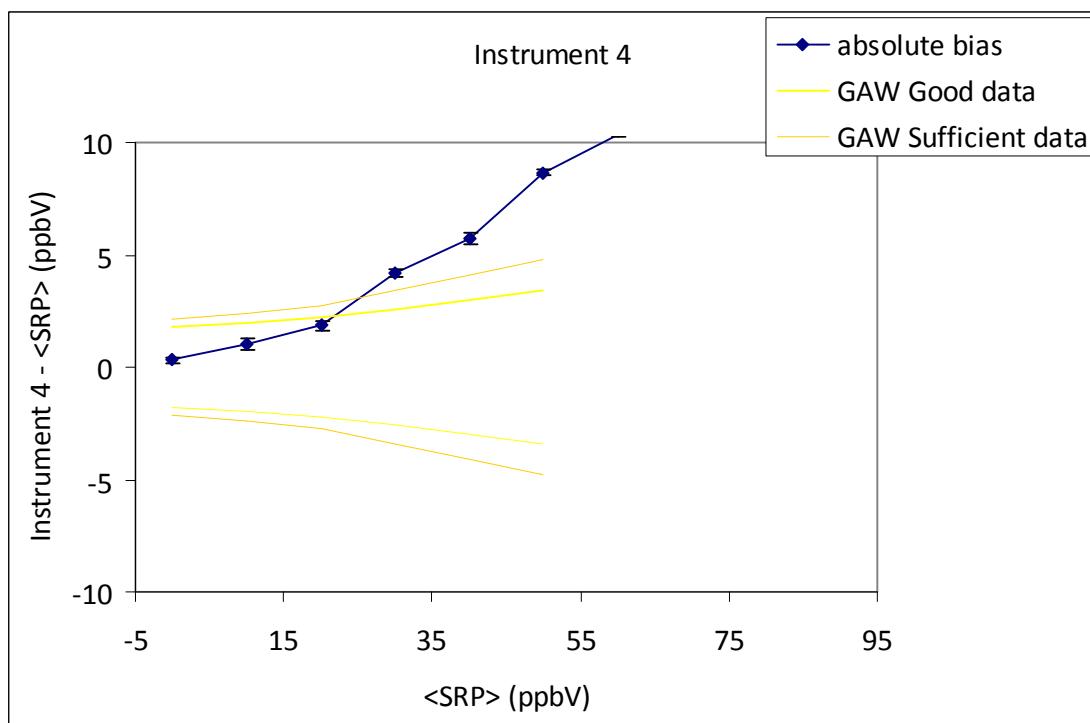
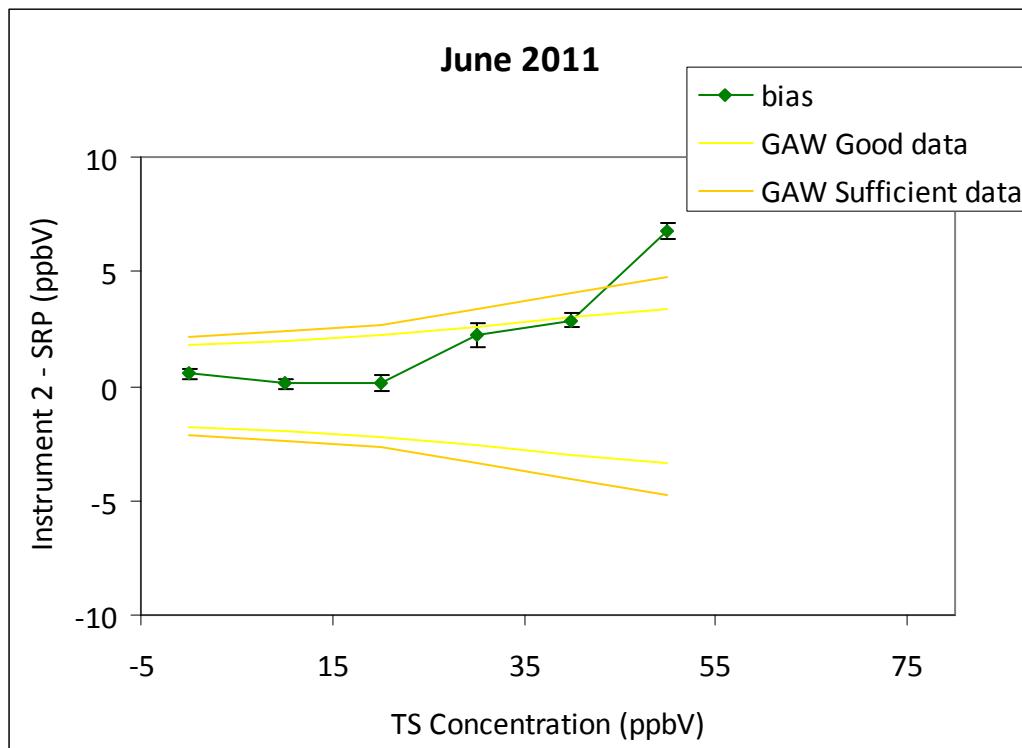
Below is data from the two instruments in February 2011. The air conditioning behind the instrument was switched off and the bias improves (although the ozone levels are generally higher).



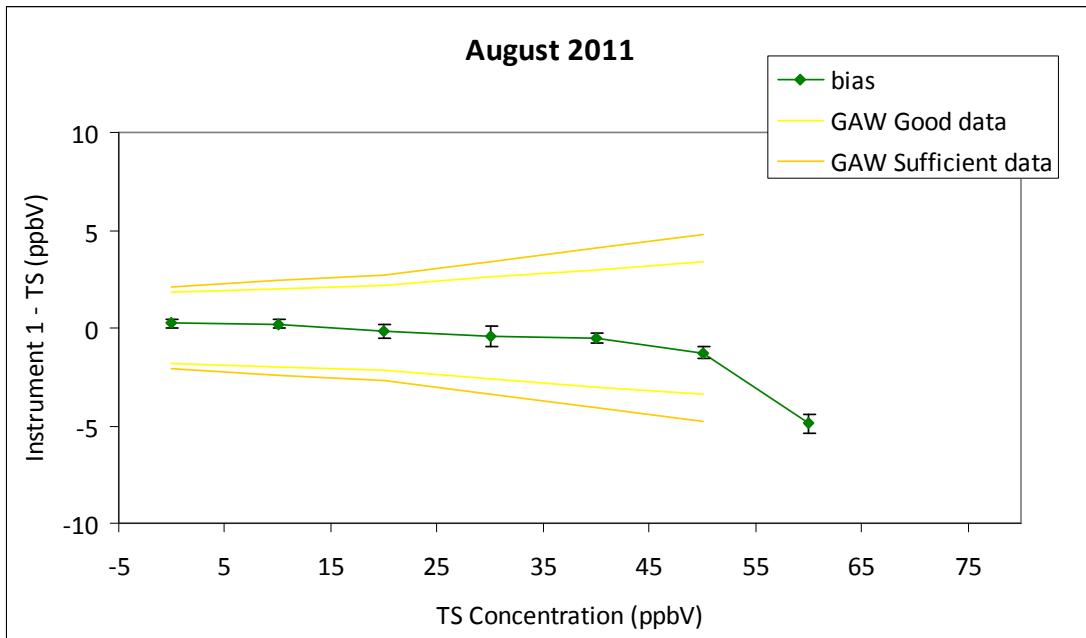
Instrument 1 was fixed, calibrated at the factory and returned to Cape Verde in March 2011, however never worked properly so was returned again in June 2011.

N.B. The TS was last calibrated using the NPL SRP#2 in May 2010.

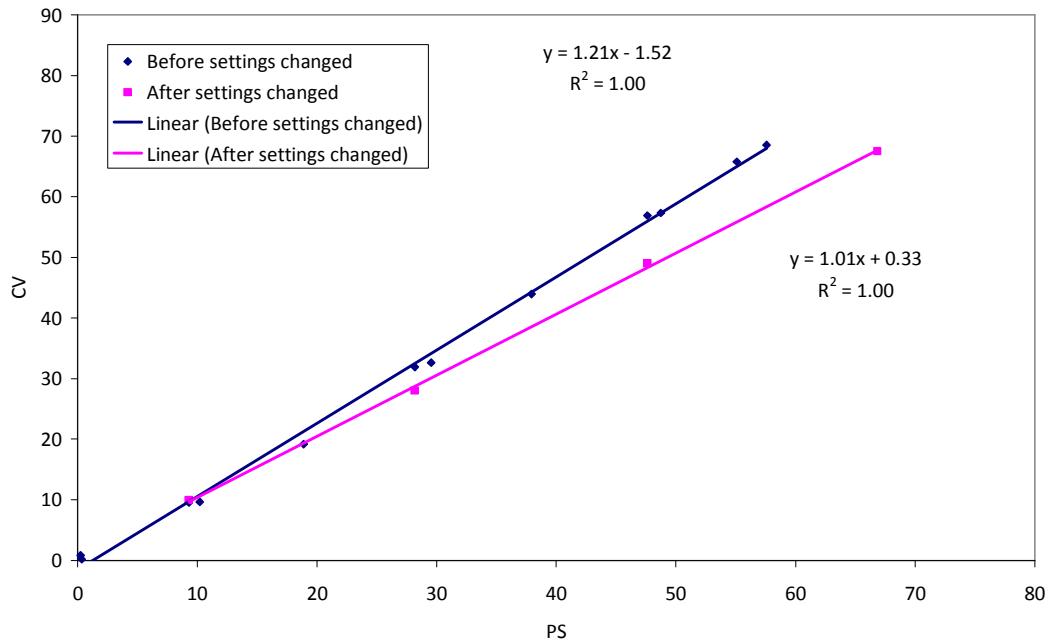
Instrument 2 and 4 agree well and both were calibrated against the new 2B calibrator. The results are below. There appeared to be some disagreement with the new calibrator particularly above 35 ppbV. It may need some adjustment to the NIST scale.



The TS itself was calibrated against the NIST scale in July 2011 (see separate documentation for certification). The 2B calibrator was then checked with the TS using instrument 1 recently calibrated and returned from the factory. Instrument 1 calibrated ok with the TS but needed some adjustment to its factors (calibration at factory not necessarily believed).

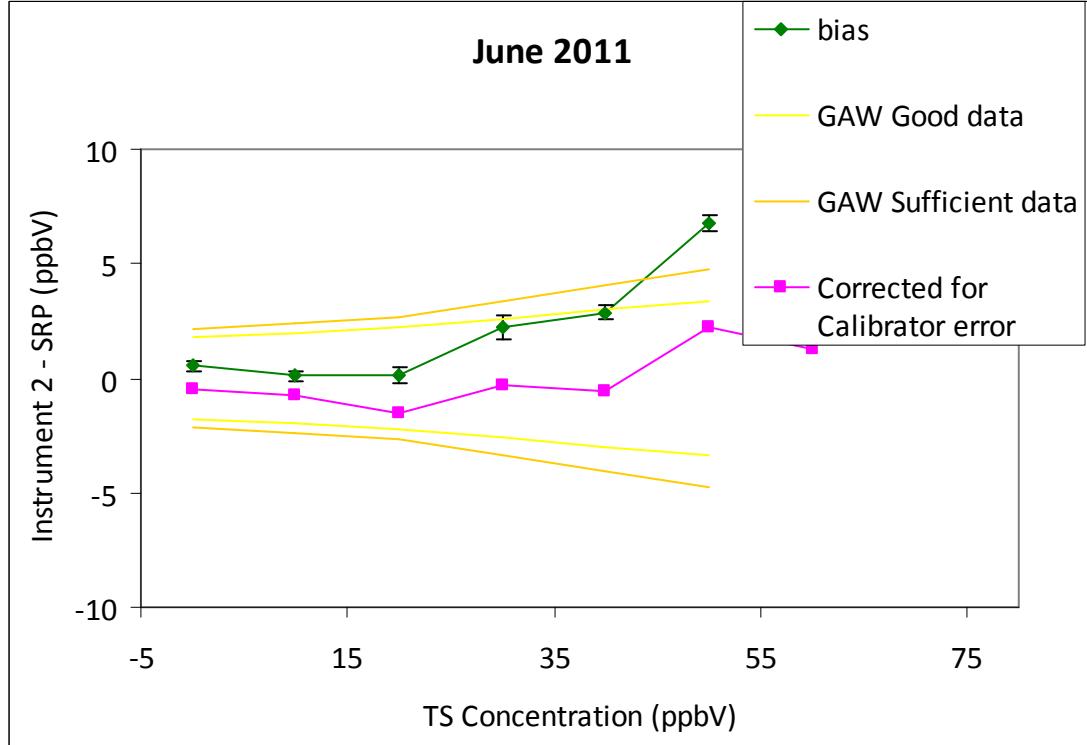
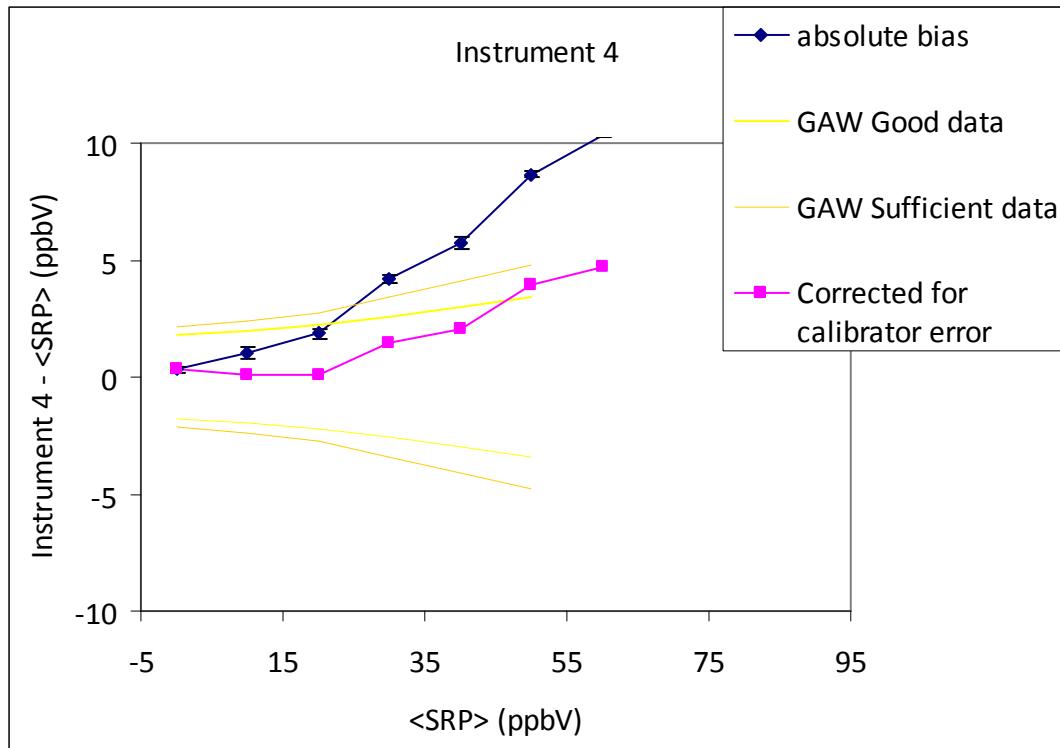


Comparison of the two calibrators showed some disagreement. The results are below.

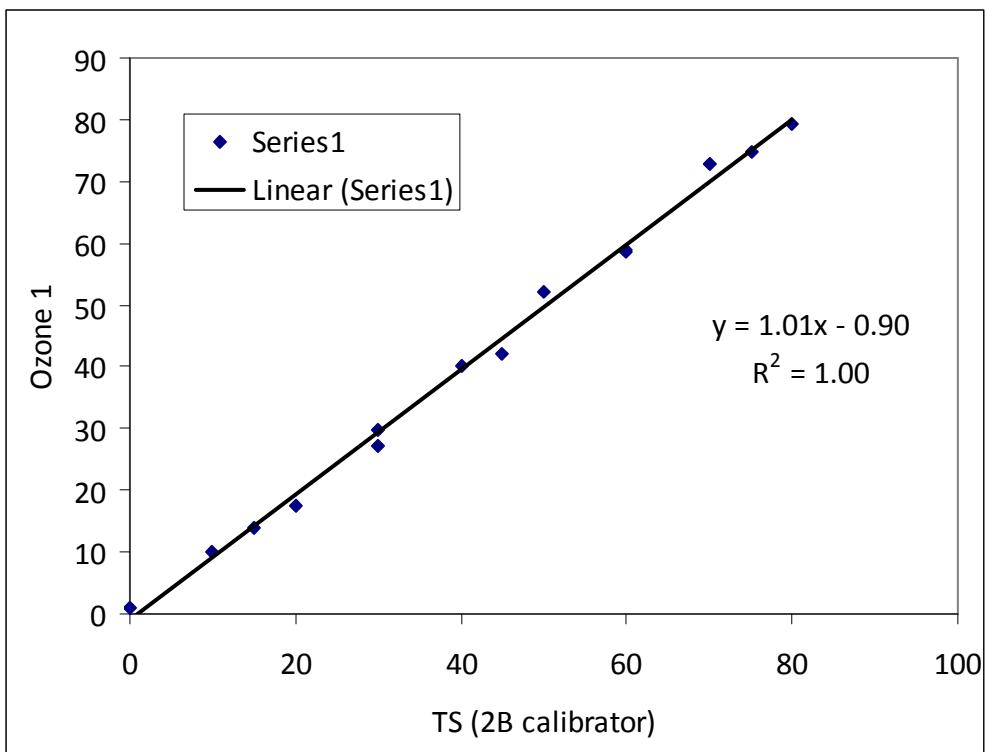


According to the TS the CTVS was calibrating ~21% too high (see plot) and had an offset. The TS had recently been calibrated against the primary standard and so we have adjusted our new CV transfer standard accordingly (calibration factor changed from 1.7 to 1.48 and offset from 2 to 3).

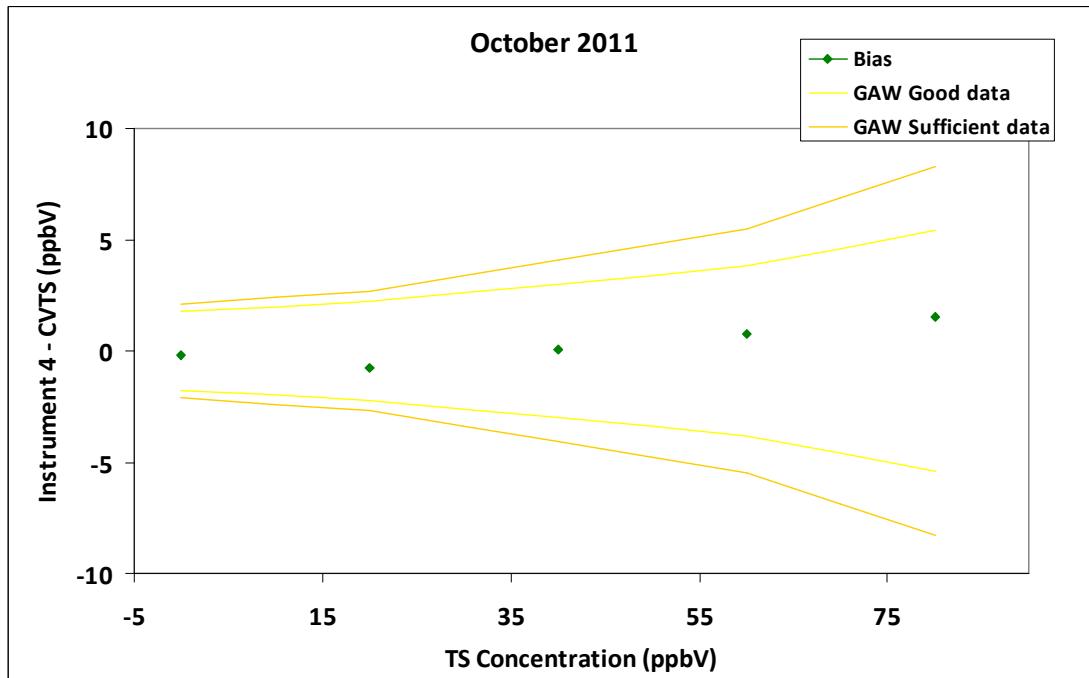
Assuming a linear degradation in the calibration settings then adjusted June calibrations look like those below:-

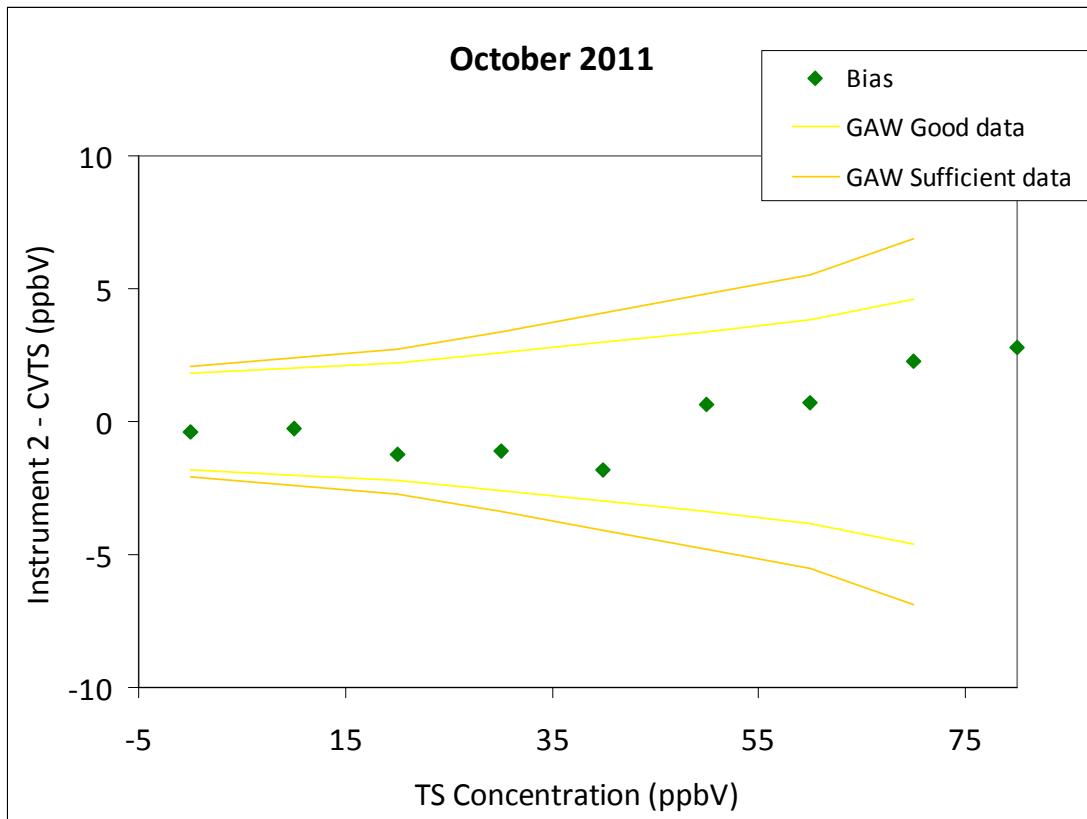


The Calibrator was checked using a recently calibrated Ozone 1 instrument before maintenance trip to CV.



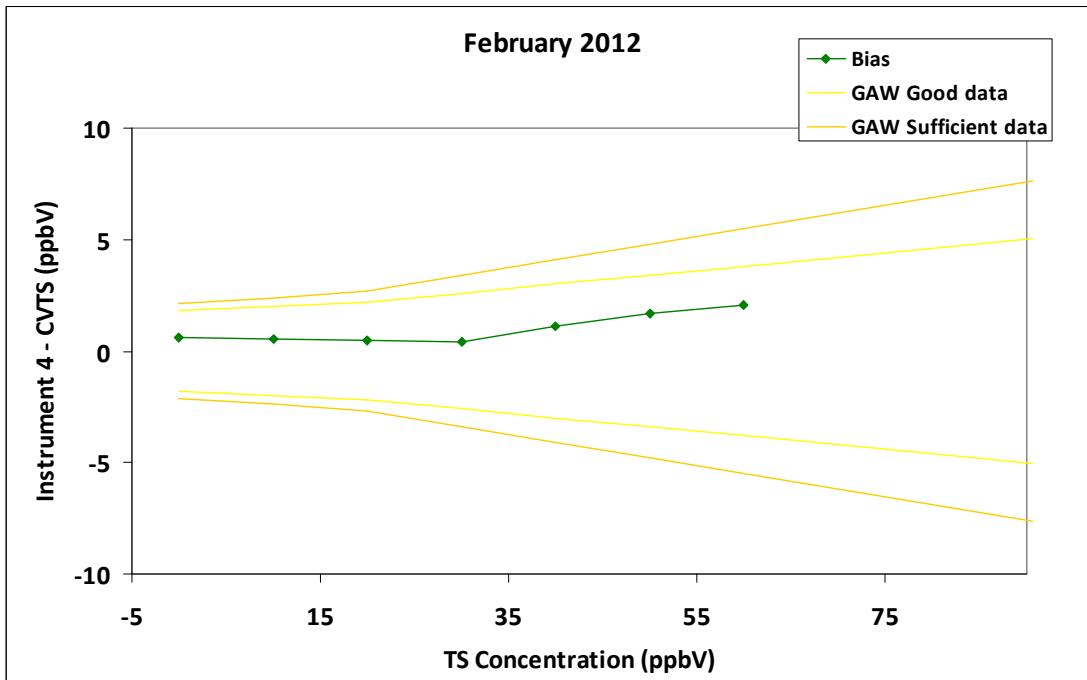
Instruments 2 and 4 were calibrated in October 2011 using the 2B transfer standard.  
Instrument 4 is still the main instrument.

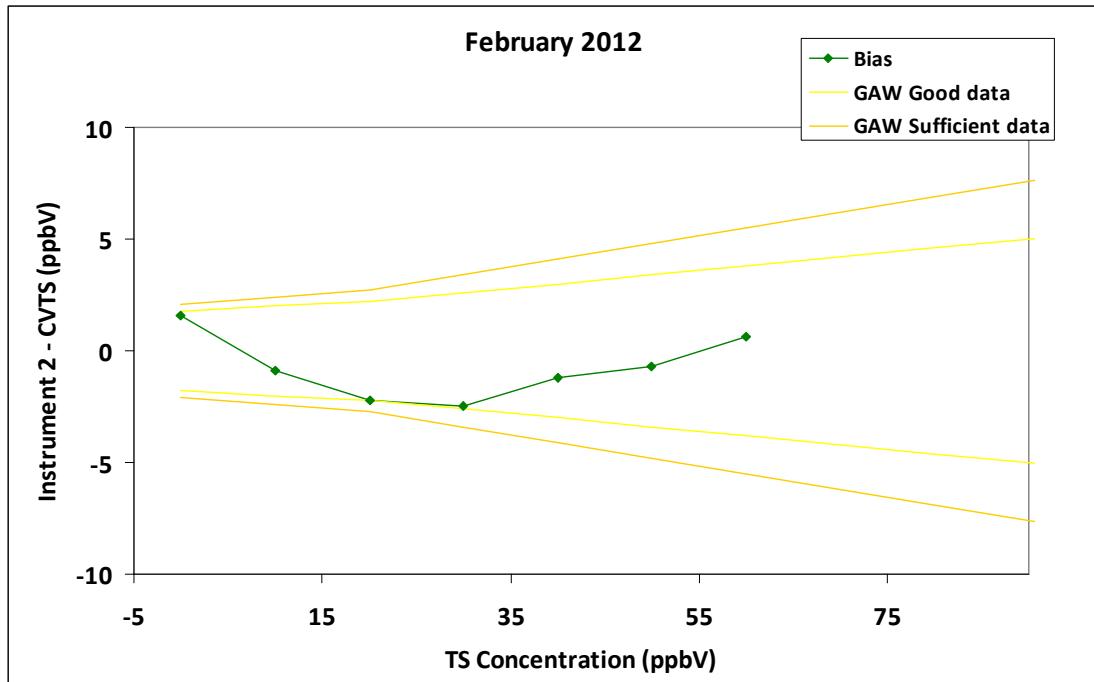




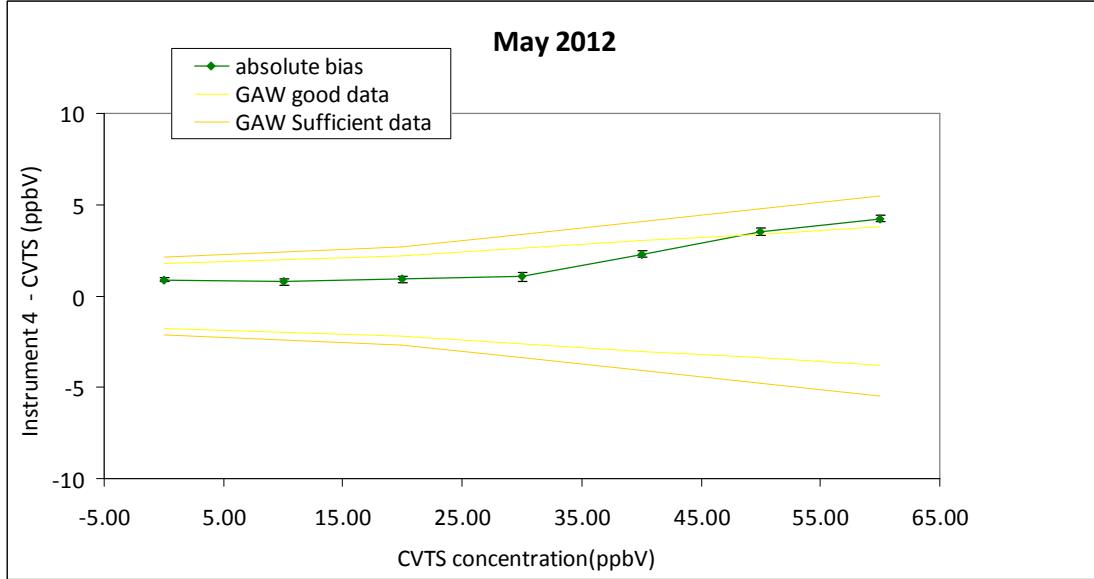
Instruments 2 and 4 were calibrated in February 2012 using the 2B transfer standard. Instrument 4 is still the main instrument.

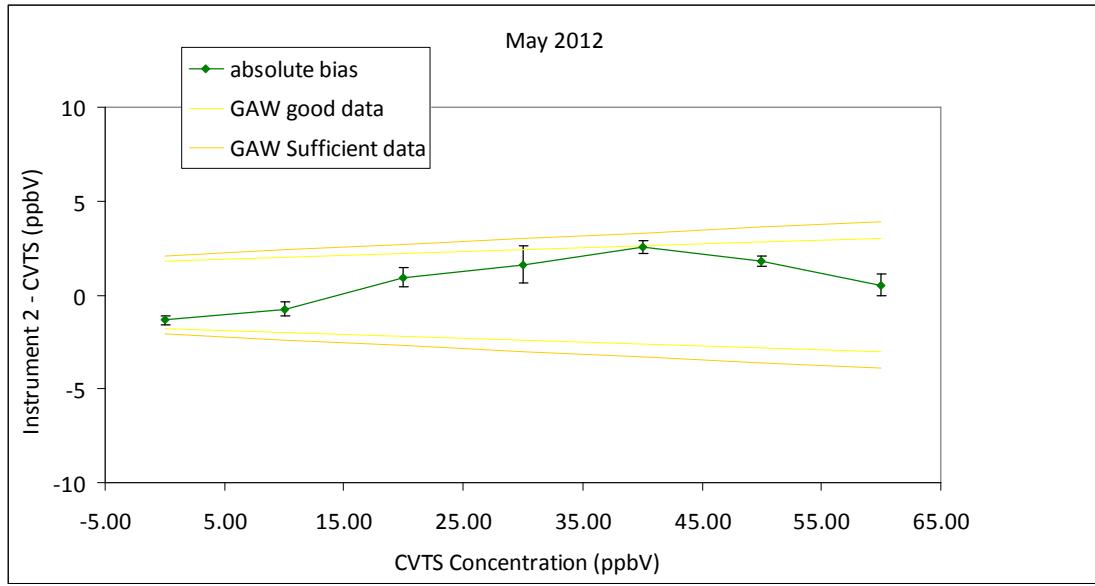
Why is there no check with FGAM Calibrator between these trips? Ozone instrument at Clearflo?





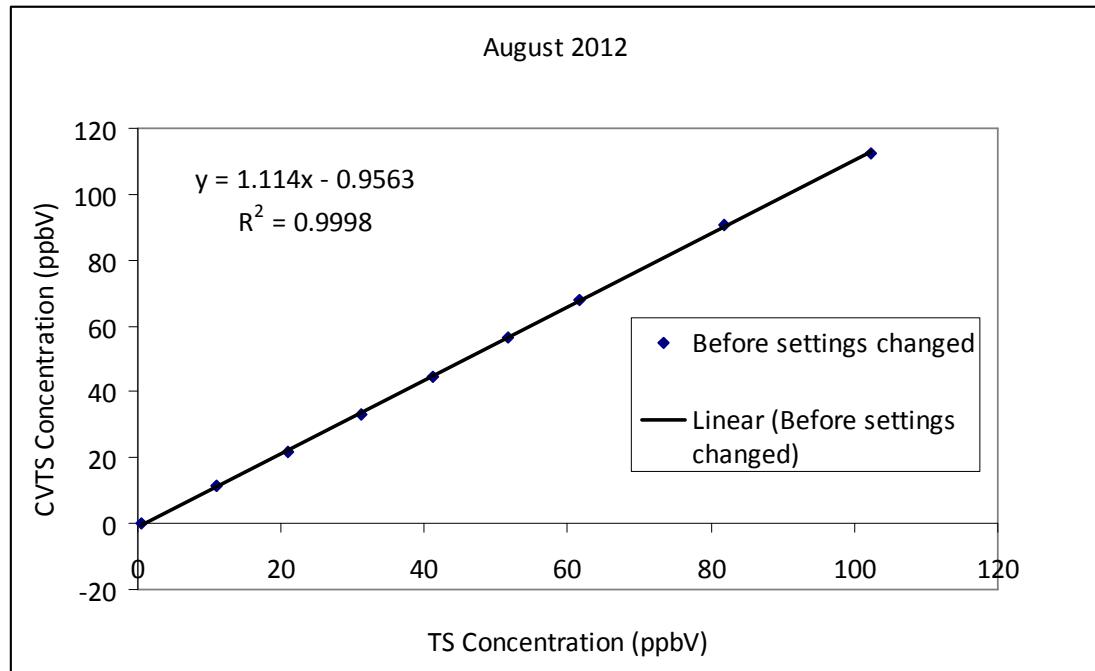
In May 2012 ozone instruments 2 and 4 were calibrated using the CVTS. The results are below.





The CVTS suggested that the ozone instruments were reading around 5% too high but settings weren't changed on the ozone instruments as the CVTS was suspected to be the problem.

The CVTS was checked against the TS in August 2012 and according to the TS was calibrating 11% too high.

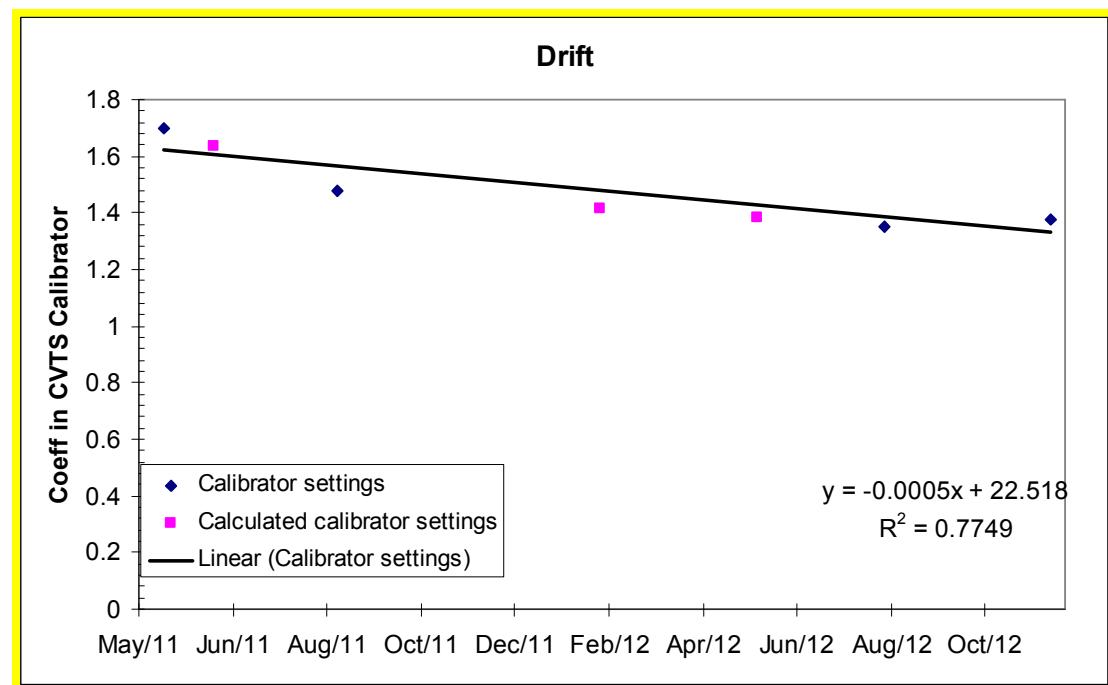


The CVTS was checked again in the lab in September.

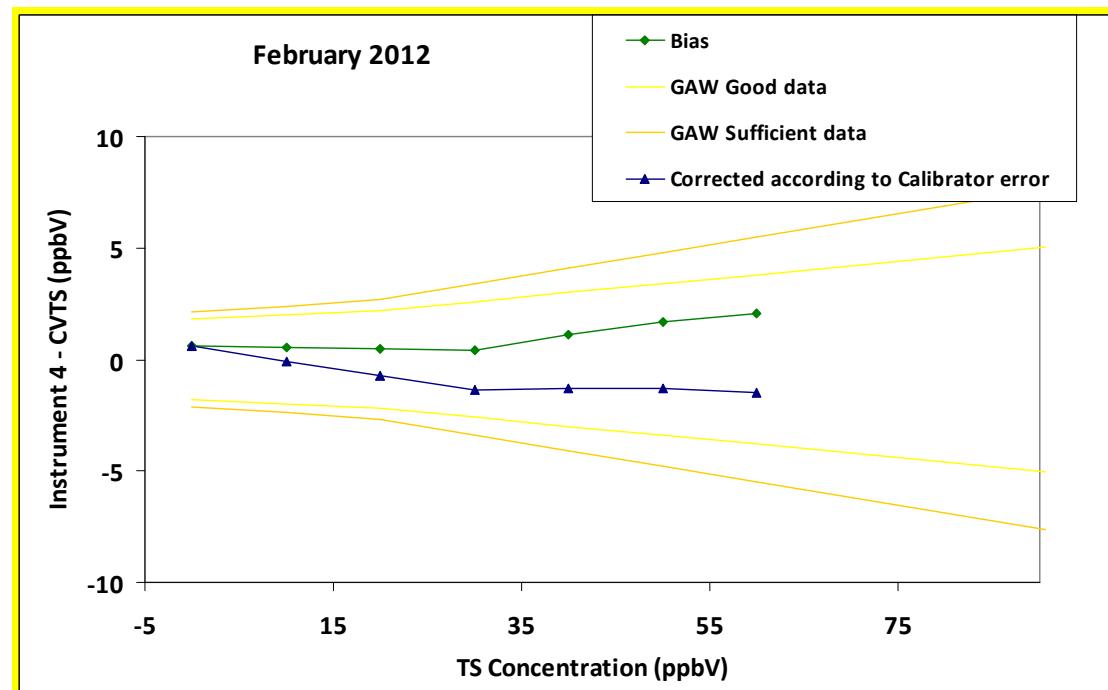
*Plot of TS against CVTS using Ozone Instrument 3 (data not available presently-instrument 3 on ship). Plot of before and after settings*

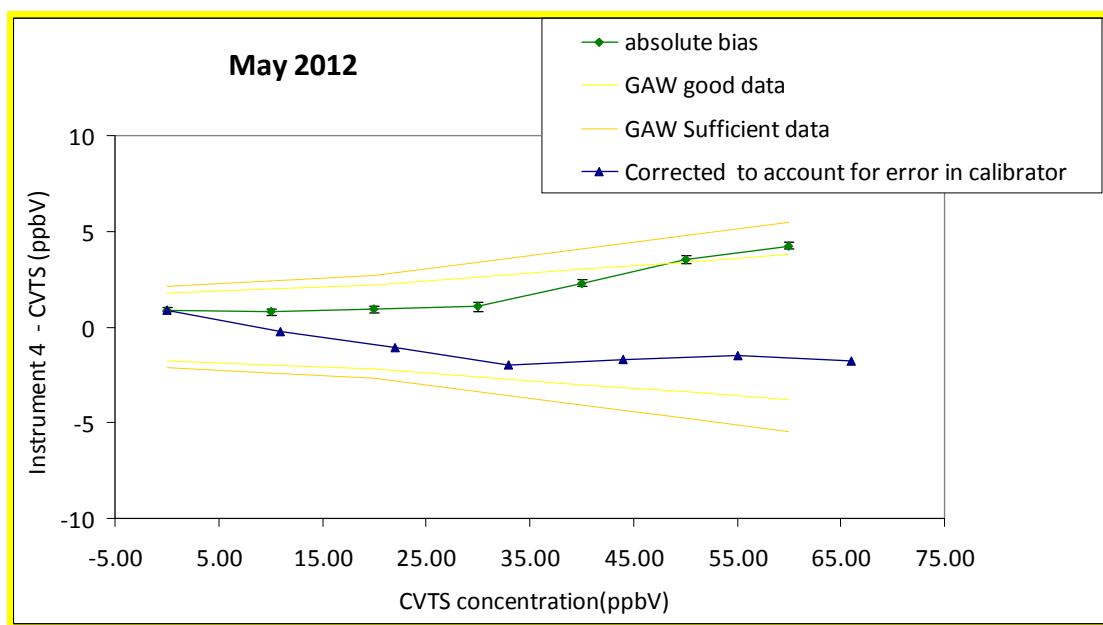
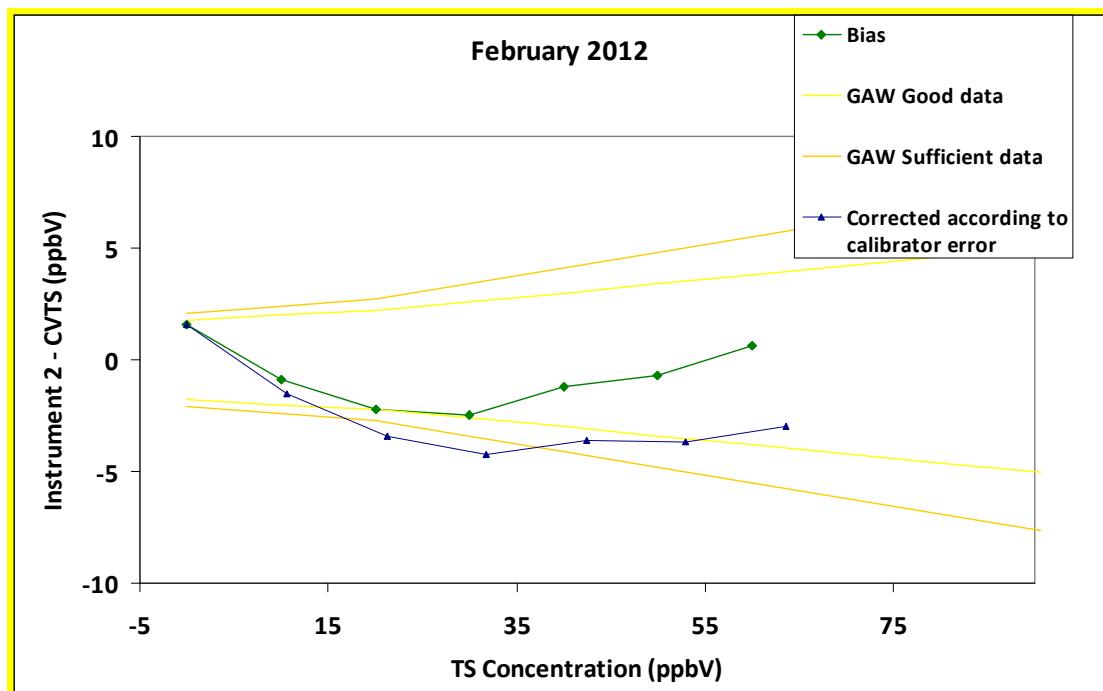
The CVTS was adjusted accordingly (calibration factor changed from 1.48 to 1.35, offset left at 3).

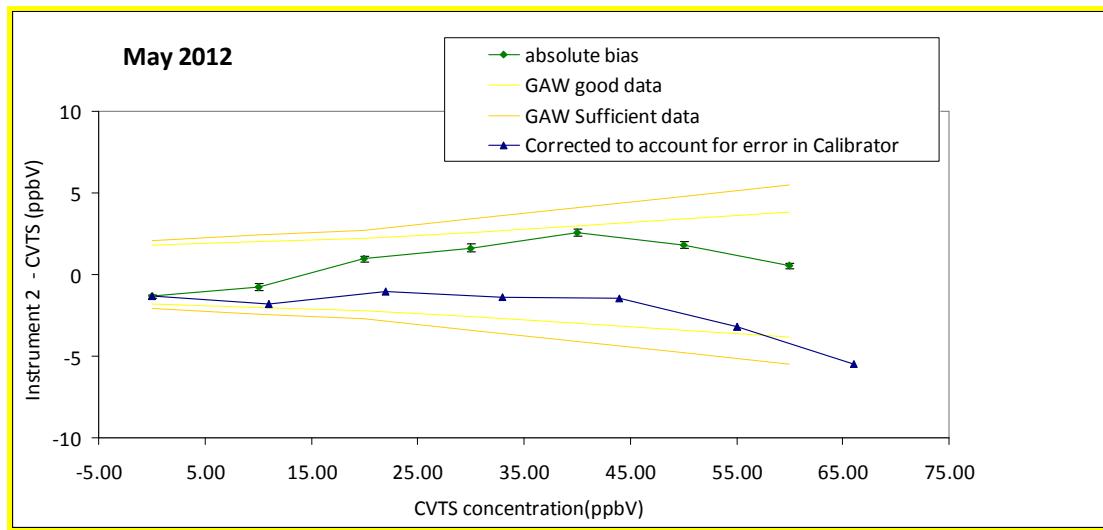
Assuming a linear drift in the calibrator,



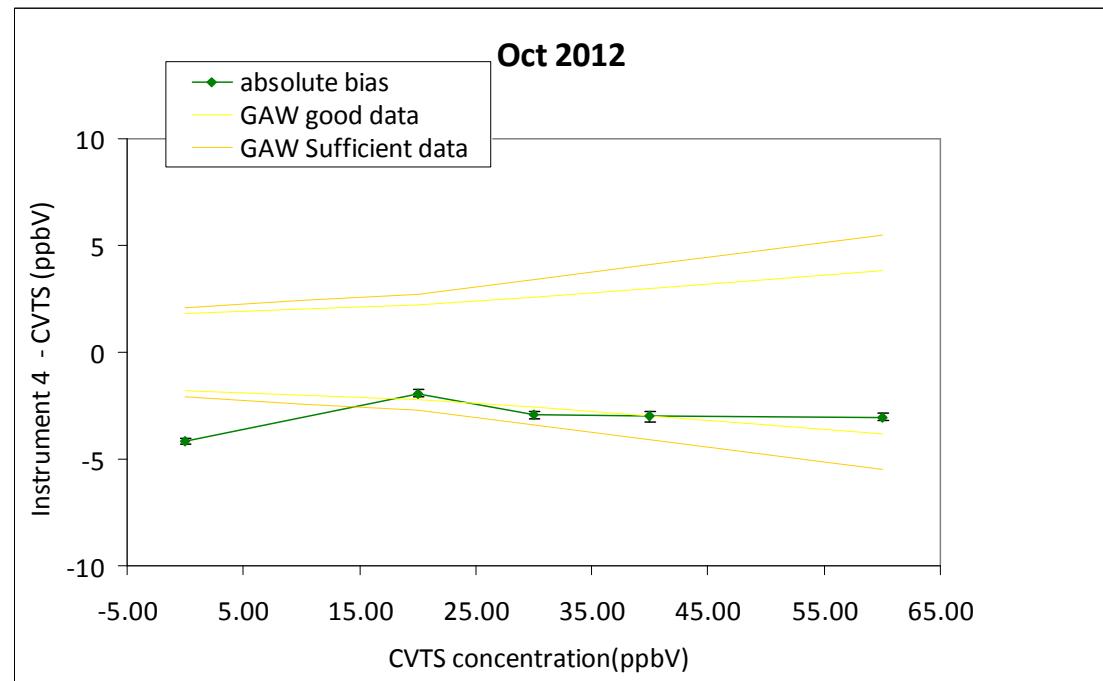
the February and May data was then adjusted to account for this error in the calibrator.

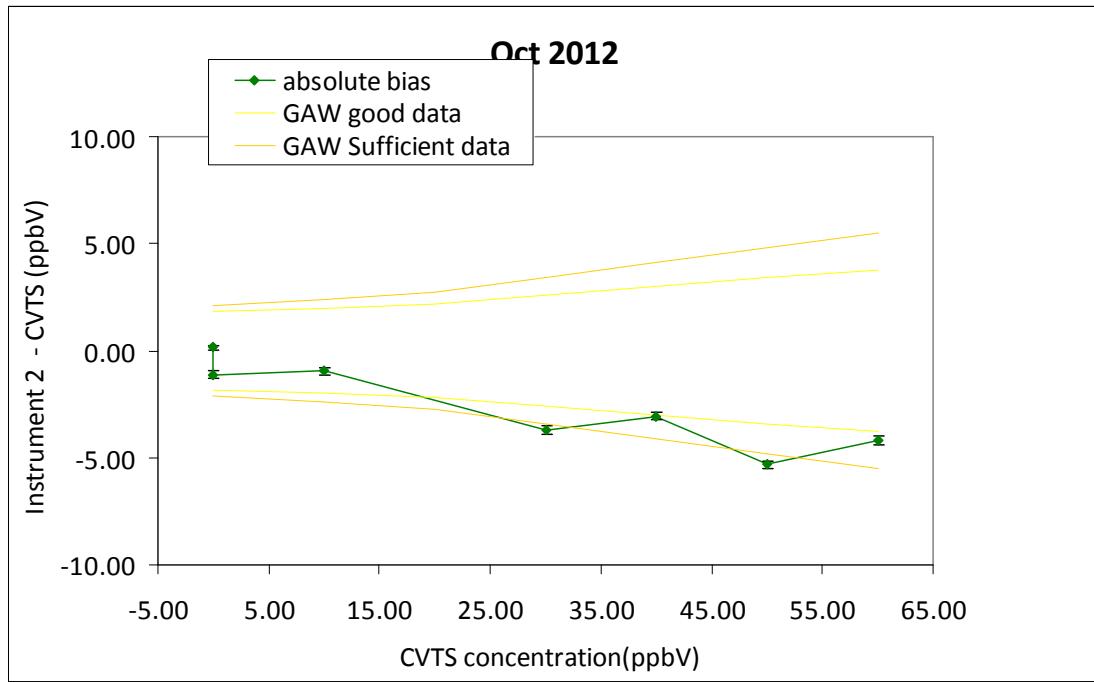




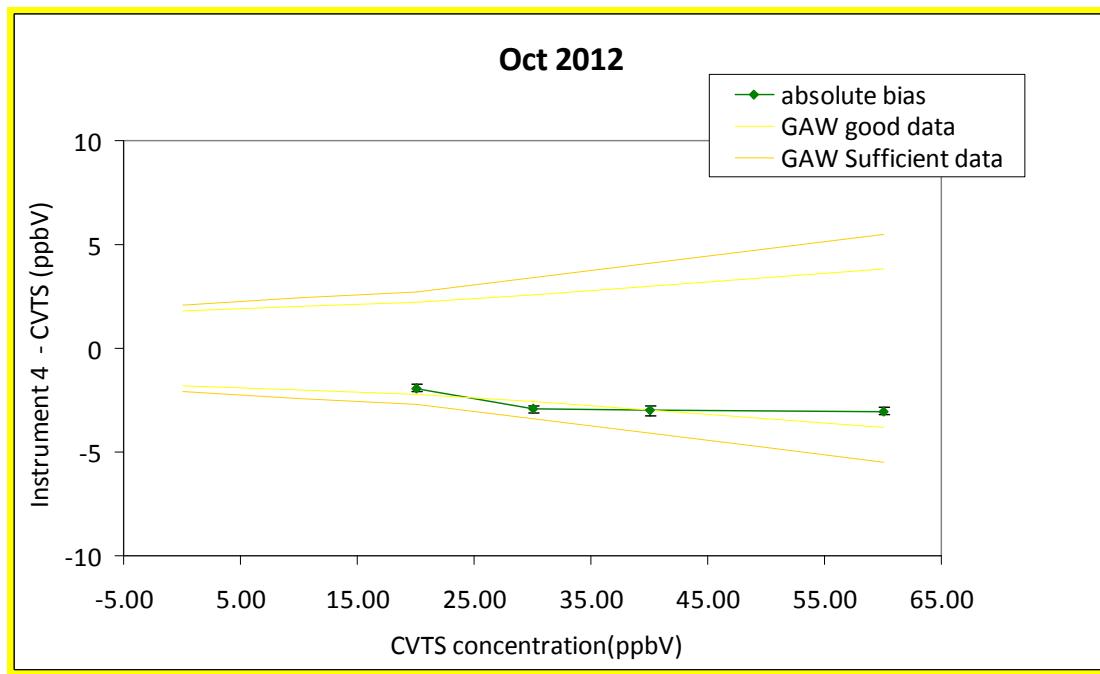


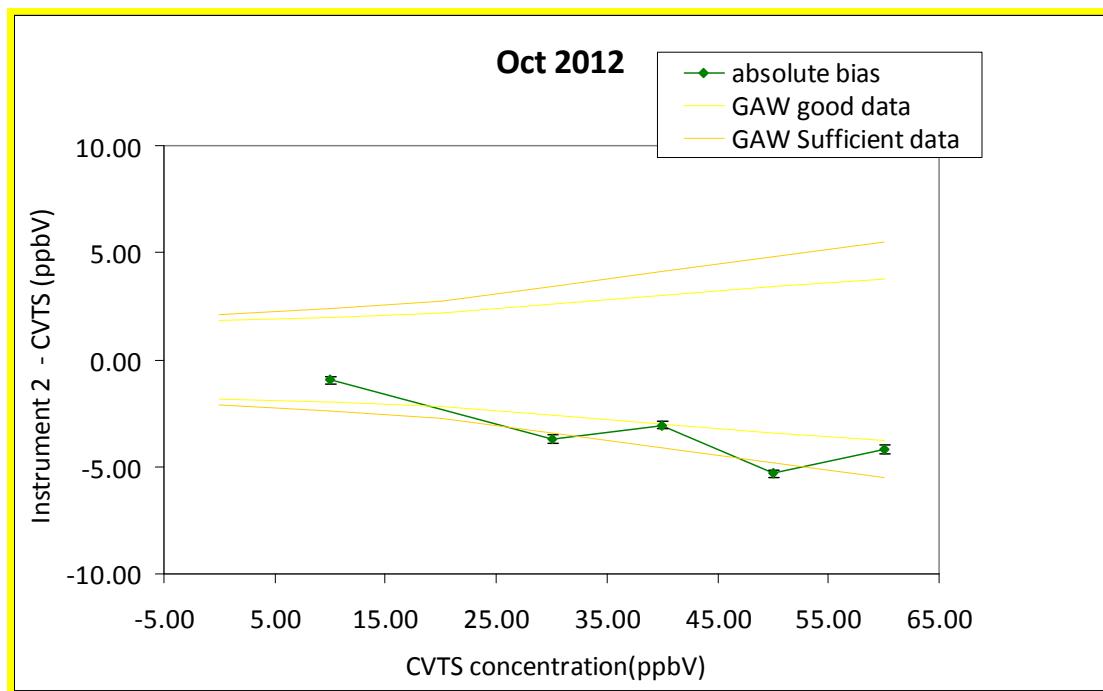
The CVTS was then used to calibrate Instruments 2 and 4 in October 2012. The instruments calibrated well although there was an offset on both instruments of ~-3. This is also observed in the zero data when using an external zero trap but not when running a routine zero on the calibrator.



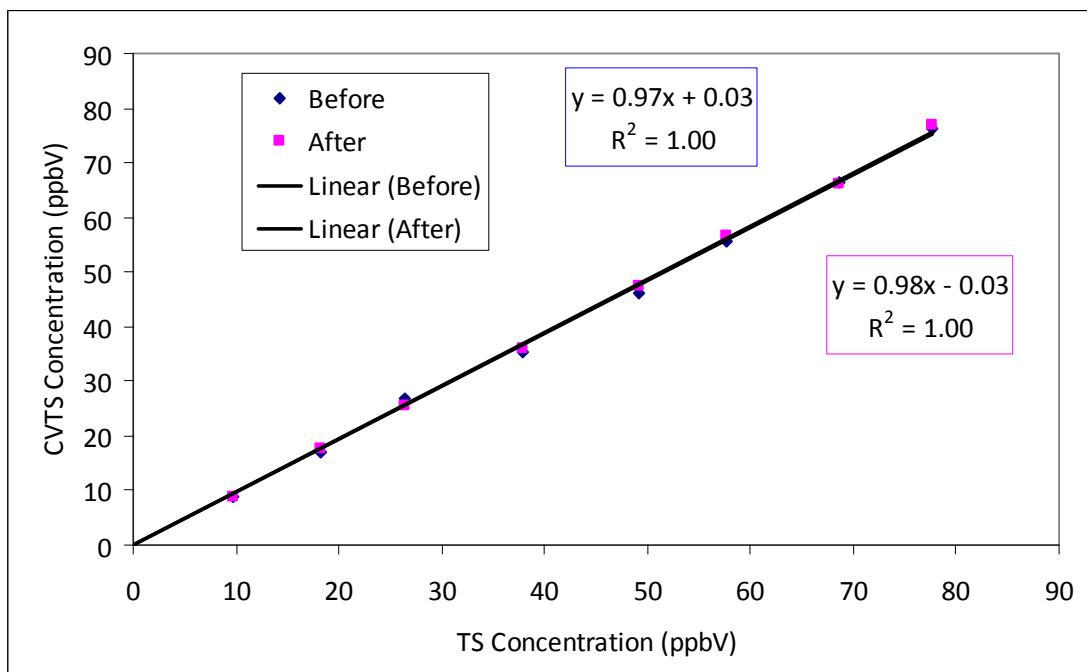


The zero data wasn't logging properly so these calibrations should look like below:-



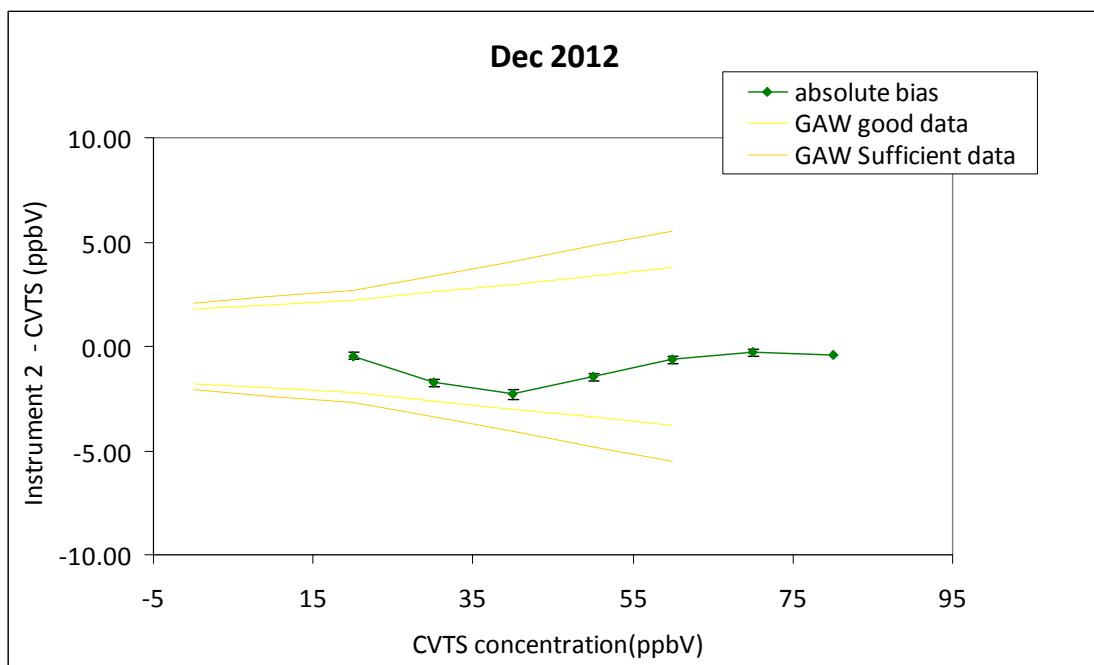
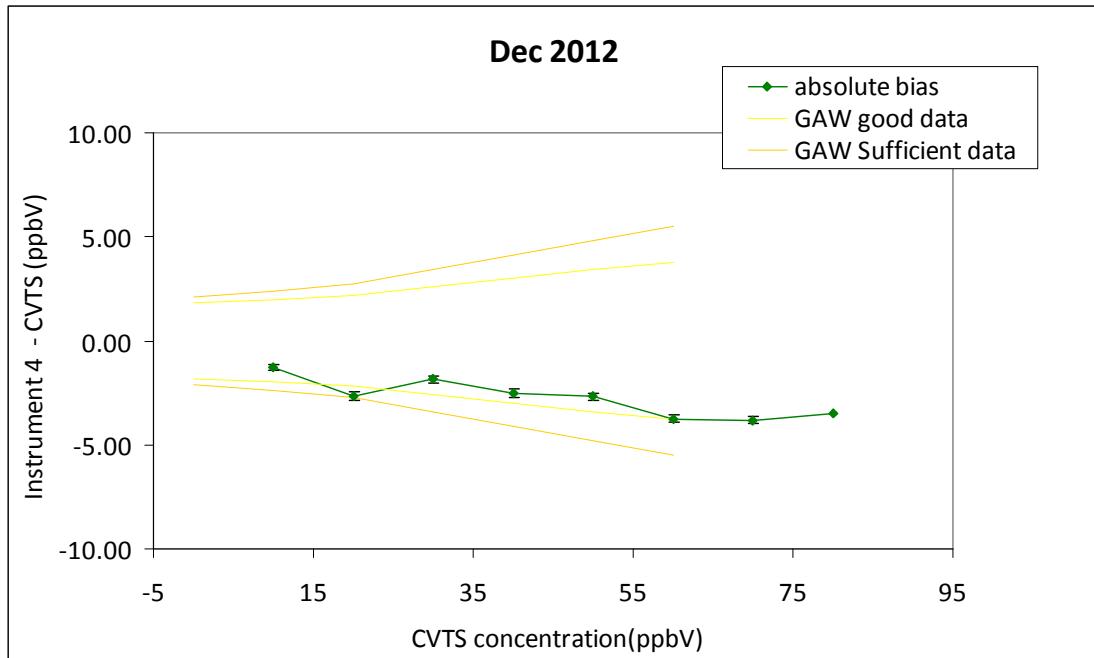


The CVTS was then compared to the TS in November 2012.  
The results are below.



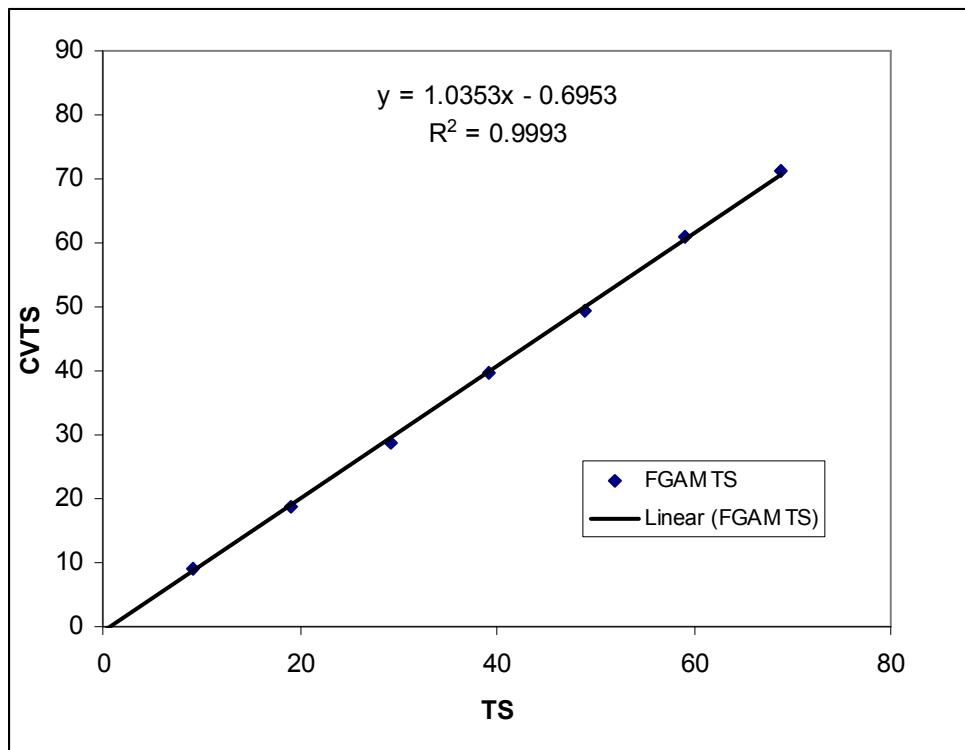
Based on these results the CVTS calibration factor was changed from 1.35 to 1.38. The offset was left at 3 as an offset was not observed in the data compared to the main transfer standard.

The CVTS was then used to calibrate the instruments 2 and 4 again in November.

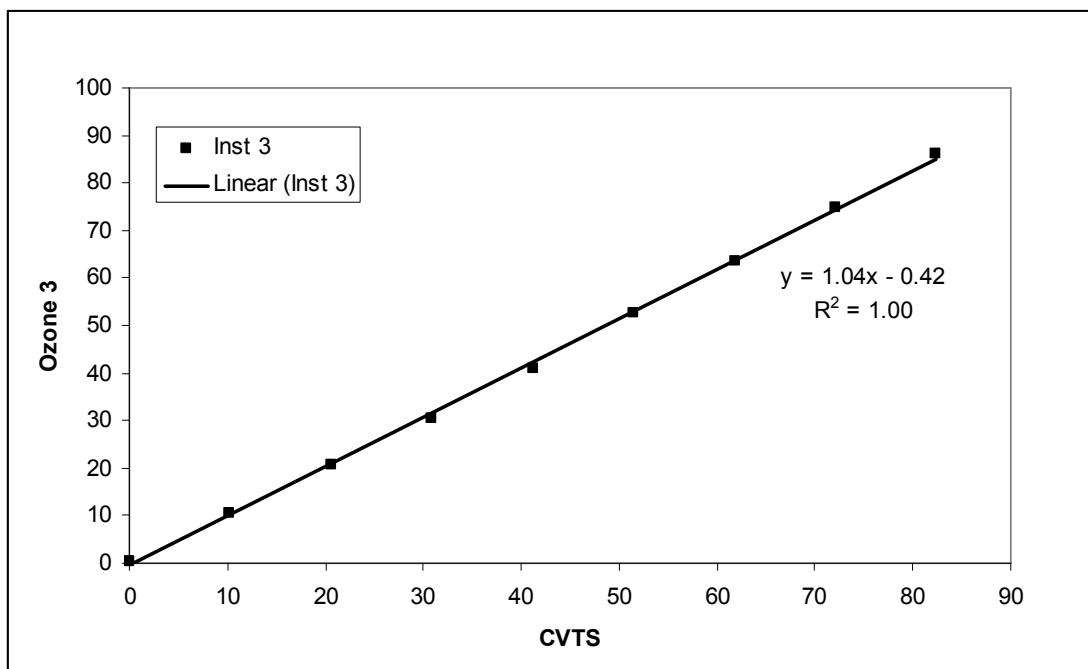


Although both instruments still appeared to calibrate badly, they performed well within the GAW audit. It is suspected that the TS (rather than the CVTS) needs some adjustment. It is due to return to NPL to be calibrated against the PS there at the end of January.

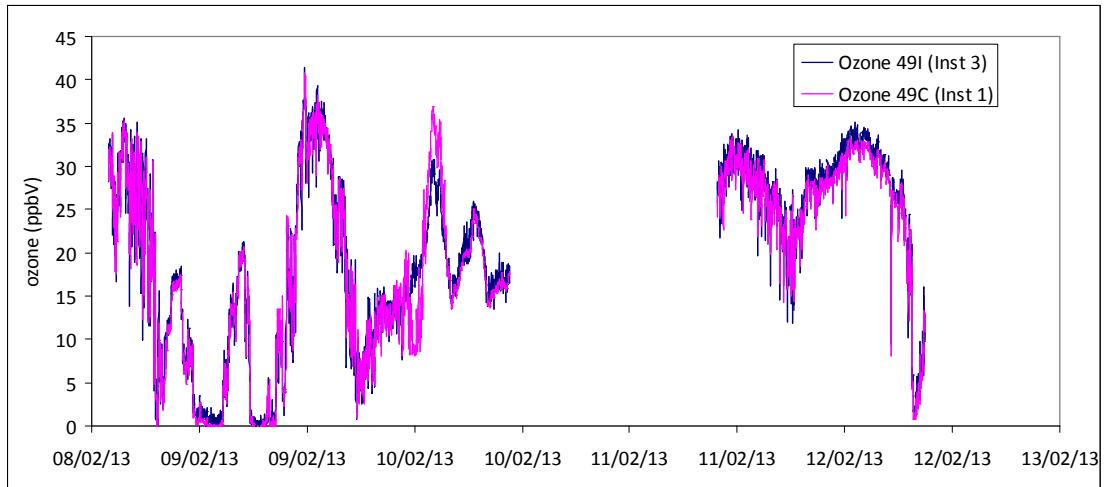
Recalibration against the FGAM calibrator however showed some disagreement with the CVTS at the higher levels. The CVTS was adjusted back down to 1.38 to 1.35.



Instrument 3 was calibrated using the CVTS in Jan 13. Results below.



Instrument 1 and 3 were run together on 5<sup>th</sup> February 2013.



## References

Klausen, J., et al. (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *J. Geophys. Res.-Atmos.*, 108, 4622, doi:10.1029/2003JD003710.