Long-term Performance of Picarro Instruments Prior to South Atlantic Remote Deployment

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1. Introduction

Understanding ocean uptake of atmospheric CO_2 by the South Atlantic Ocean is important for modelling of future global warming scenarios, particularly since it was recently proposed that this sink was decreasing (Le Quéré, et al., 2007). To help our understanding of this problem a new project aims to flask sample air from 5 South Atlantic sites and set up continuous monitoring at the 2 most accessible of these. Flask sample measurements will include CO_2 and CH_4 mixing ratios and the $\delta^{13}C$ measurement of both of these gases using the rapid continuous flow trace gas analysis system at Royal Holloway, University of London (RHUL). Routine precisions are ±0.03 ‰ and ±0.05 ‰ for CO_2 and CH_4, respectively (Fisher et al., 2006).

References

Fisher, R. et al. (2006) Rapid Comm. Mass. Spec. 20, 200-208.
Le Quéré, C. et al. (2007) Science 316, 1735-1738.

2. Current and Past Monitoring of Greenhouse Gases by the RHUL group in the South Atlantic Region

The Royal Holloway, University of London (RHUL) atmospheric group has previous experience of sample analysis from South Atlantic sites, having analysed $\delta^{13}CH_4$ and carbon gas mixing ratios on pressurised 22-litre SS tanks collected by Meteorological Office staff on Ascension Island between 2000 and 2005 (Fig.1) and carried out isotopic intercomparisons with NOAA for this site. This sampling stopped due to lack of isotopic evidence for African burning emissions, with the exception of 1 sample in 5 years. Now that RHUL has the capability to analyse $\delta^{13}CH_4$ to high precision on small 100 ml samples, the isotopic time series will be restarted as part of this project.

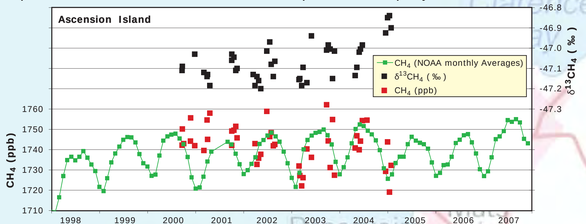
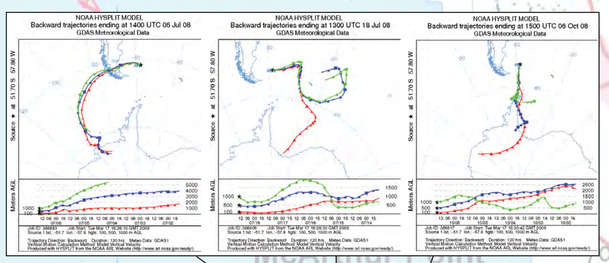


Fig. 1 - Comparison of RHUL flask sampling for Ascension Island from 2000 - 2005 with NOAA flask monthly mean methane mixing ratios

Preliminary bi-monthly sampling using 5-litre Tedlar bags commenced on the Falkland Islands in October 2007 thanks to island resident Louise Taylor. These were analysed for CH_4 and $\delta^{13}CH_4$ (Fig.2). Since the beginning of 2009 sampling has switched to 3-litre SS flasks for more complete analysis of carbon-bearing gases. So far the airmass trajectories on sampling days have been mostly from the South Pacific and the Antarctic Peninsula (Fig.2). The value of this site for understanding of the South Atlantic Ocean will only be realised after a sustained period of continuous monitoring.



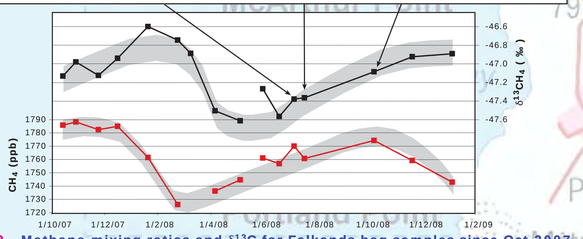


Fig. 2 - Methane mixing ratios and $\delta^{13}C$ for Falkands bag samples since Oct 2007

The closest long-term sampling site for greenhouse gases are the bi-weekly flask samples from Tierra del Fuego (S. Argentina) as part of the NOAA network. Preliminary data suggest a higher CH_4 mixing ratio for the Falklands, and more local and South American source influence (Fig.3).

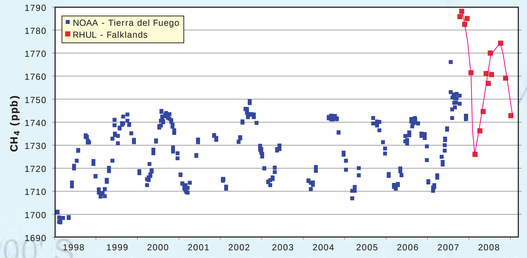


Fig. 3 - Methane mixing ratios for Falkands bag samples compared with NOAA 1998-2007 Tierra del Fuego data

3. Planned Flask Sampling and Continuous Monitoring of Greenhouse Gases in the South Atlantic Ocean

A transect of sites (Fig. 4) is required to better understand the behaviour of CO_2 and CH_4 sources and sinks in the South Atlantic. Ascension Island and the Falkland Islands have the best communications (regular flights) and have been selected as locations for continuous monitoring with the Picarro CRDS instruments. It is hoped that bi-monthly flask sampling can be initiated on St. Helena and the remote islands of Tristan da Cunha and South Georgia, although access to those would be on a six-monthly basis.

- Planned Picarro continuous monitoring sites for CO_2 and CH_4
- Planned bi-monthly flask sampling sites for CO_2 and CH_4
- Current NOAA bi-weekly flask sampling sites

Fig. 4 - Map of the South Atlantic showing current and proposed sampling sites

Flask sampling at all 5 sites will allow analysis of CO_2, O_2 and CO at UEA, and CO_2, CH_4, H_2 and $\delta^{13}CO_2$ and $\delta^{13}CH_4$ at RHUL.

The Falklands site has to be best situated to provide power supply and possible networking and be close to the SE and E coast to avoid sampling of local sources on the occasions when the air is arriving directly from the S Atlantic oceanic sector. The old communications hut close to Stanley Airport (Figs. 5 and 6) provides the best compromise of location, access and potential.

Fig. 5 - Planned sampling site on the Falklands already has power supply and a mast a) interior, b) exterior, c) distance from airport

Fig. 6 - Current flask sampling and proposed continuous monitoring sites near Stanley Airport, Falkland Islands

4. Development of an Automated Air Inlet for the Picarro G1301

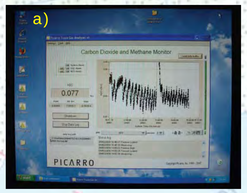
To meet the continuous monitoring requirements of the new project, three Picarro G1301 CO_2 / CH_4 / H_2O Cavity Ring Down Spectrometers (CRDS) were installed at RHUL in October 2008 for testing, calibration and the development of an automated air inlet system suitable for analysis of calibration gases at the remote sites. Two of these instruments are connected to the same air inlet as a GC measuring CH_4 mixing ratio and a LiCor 6252 measuring CO_2 mixing ratio at 30-minute and 1-minute intervals respectively. The third CRDS instrument is connected to a separate airline which is further away from potential local anthropogenic sources, but only 10m from a large oak tree.

Flow rates vary between the internal pumps of the CRDS instruments, but are within the range 260-300 cc/min when inlet valves are fully opened. Controlling flows below 200 cc/min significantly increases stabilisation time for cylinder gases. Likewise setting outlet pressures for NOAA and target gases at 4 psi and allowing the instrument pumps to control flow into the cavity speeds up stabilisation. Currently the instruments have user-defined logging of CO_2, CH_4 and H_2O at 10-second intervals. Precisions (1 SD) for five NOAA-calibrated tanks, based on the final 10 of a 30-minute analysis period are between ±0.025 and ±0.035 ppm for CO_2 and ±0.18 and ±0.25 ppb for CH_4.

Fig. 7 - Picarro 2 with Nafion drier on the inlet line which tees off from the Dekoron airline seen in the background

Between October 2008 and March 2009, one of the instruments sharing the same air inlet had a Perma Pure MD-110-144P-4 Nafion Dryer (as used by NOAA for field monitoring) on the inlet (Fig. 7). The reverse flow utilises the exhaust flow from the CRDS with an inline Mg-Perchlorate / Drierite drying tube. This maintains the H_2O content at 0.05 to 0.08% for 2 weeks, at which point the drying tube is changed. At this low level the H_2O content is directly correlated with the DAS temperature of the instrument (measured near the air inlet) and this correlates with the cycles of the lab air conditioning unit (Fig. 8a). During April 2009 two Nafion driers were used in tandem (Fig. 8b). This reduced the H_2O content to 0.03 to 0.05% and extended the lifetime of the chemical drying tube on the exhaust line. An alternative for the field would be to use a more expensive chiller system that requires ethanol replenishment. Drying units are essential as they greatly reduce the stabilisation time of the dry calibration gases and reduce the effects of any inaccuracies inherent in water vapour corrections.

Software development to control an automated inlet and data retrieval is currently nearing completion at UEA. This will allow switching between ambient air flow and a suite of reference, target, long-term and zero gases (Fig. 9). It is planned that each calibration-gas analysis will take out only 30 minutes of the ambient air record, preceded by 5 minutes of calibration-gas venting, allowing regulator and line flushing and stabilisation. Minutes 18-28 will be utilised to calculate standard values, before switching to allow 2 minute stabilisation time for ambient air. An additional flag for data rejection is based on cavity pressure, values becoming unstable outside a 140 ±0.1 mbar window.



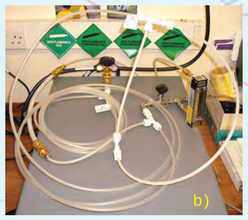


Fig. 8 - a) Water vapour cycling due to air conditioning activity, b) Nafion driers in tandem on inlet with curved Cajon-fitted chemical drier on the reverse exhaust flow line

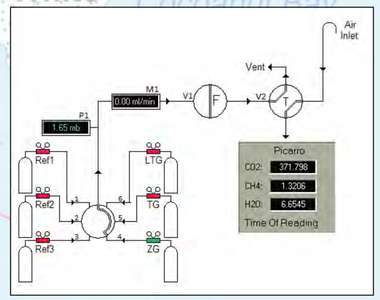


Fig. 9 - Screen shot of software being developed at UEA for automated flow control, standard analysis and data retrieval

5. Calibration and Testing of the Picarro G1301

Initial testing of the instruments has included calibration with NOAA-calibrated and target gases, validation of the Picarro-defined H_2O-correction of CO_2, and derivation of an H_2O-correction for CH_4. This has been enabled by having two instruments side-by-side taking air from the same inlet and one having the air-stream dried. The corrected CO_2 data is within analytical error for instruments measuring 0.07 and 0.70% H_2O (Fig. 10a). Our calculated correction is 6.952 ppm / 1% H_2O for CO_2 and 0.02579 ppm (25.79 ppb) / 1% H_2O for CH_4. This is clearly visible for the uncorrected data (Fig. 10b) with a difference of 18 ppb CH_4 for the two instruments before and after applying the water vapour correction (Fig. 10c).

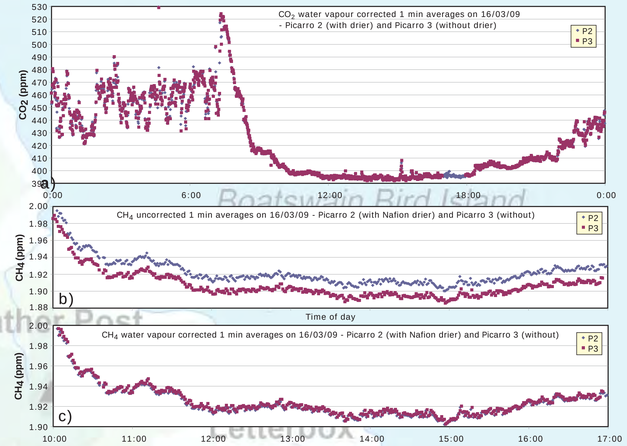


Fig. 10 - Water vapour corrections applied to data for Picarro 2 (dried air) and Picarro 3 (undried), a) application of factory CO_2 correction, b) and c) before and after application of the RHUL CH_4 correction.

A second concern was the long-term drift of the instruments. After adding our own approximate slope correction to the instrument software after initial tests, it has remained unchanged since Nov 2008. Drift has been checked since then using our NOAA 5 calibration gas. No obvious drift has been recorded for CO_2, although the values vary within a range of ±0.1 ppm of the known (Fig. 11a). CH_4 is drifting upward (Fig. 11b) at a rate between 0 and 0.1 ppb / month (Nafion-dried) and between 0.4 and 0.5 ppb / month (undried). This information will be used to select time intervals between calibration-gas analyses.

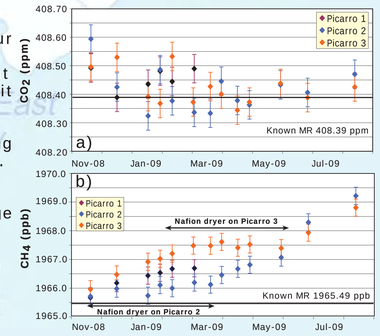


Fig. 11 - Drift of our NOAA 5 standard on all instruments between Nov 08 and Aug 09 for a) CO_2, and b) CH_4.

Linearity of all instruments was checked during Feb to Aug 2009, by measurement for at least 30 minutes of each of five NOAA calibration gases (CO_2 range 380 - 420 ppm, CH_4 range 1830 - 2030 ppb) on the same day. The residuals generated by the best fit line through these points are better than ±0.02 ppm for CO_2 and ±0.2 ppb for CH_4 (Fig. 12), better than the analytical precision obtained for these species. Smallest residuals are achieved after applying a $^{13}C_{CO2}$ correction to the data. This is because recent NOAA calibration gases contain CO_2 depleted in ^{13}C by up to 28 ‰ relative to ambient air and CRDS measures only $^{12}C_{CO2}$.

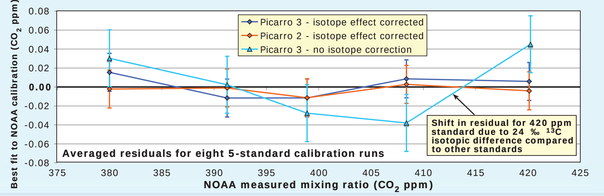


Fig. 12 - Five point calibration using NOAA cylinders to test instrument linearity