



## Greenhouse Gases in the South Atlantic: Testing and Automation of Instrumentation for Long-Term Monitoring

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Understanding ocean uptake of atmospheric CO<sub>2</sub> by the Southern Ocean is important for modelling of future global warming scenarios, particularly since it was recently proposed that this sink was reducing (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: Ascension Island and the Falklands. Flask sample measurements will include CO<sub>2</sub> and CH<sub>4</sub> mixing ratios and the  $\delta^{13}\text{C}$  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  $\pm 0.03$  per mil and  $\pm 0.05$  per mil for CO<sub>2</sub> and CH<sub>4</sub>, respectively (Fisher et al., 2006). A time series of  $\delta^{13}\text{C}$  in CH<sub>4</sub> was maintained for Ascension Island from 2000-2005 and a time series for methane isotopes commenced for the Falkland Islands in autumn 2007.

To meet the continuous monitoring requirements of the new project, three Picarro G1301 CO<sub>2</sub> / CH<sub>4</sub> / H<sub>2</sub>O 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. Initial testing included calibration with NOAA calibrated and target gases, validation of the Picarro-defined H<sub>2</sub>O-correction of CO<sub>2</sub>, and derivation of an H<sub>2</sub>O-correction for CH<sub>4</sub>. Continuing checks on the H<sub>2</sub>O correction are made by having 2 instruments side-by-side taking air from the same inlet, but one having a combined Nafion / Mg-perchlorate drying system that utilizes the analysis system exhaust gas for the reverse flow through the Nafion and maintains water-levels at 0.05% for more than 2 weeks. These instruments are connected to the same air inlet as a GC measuring CH<sub>4</sub> mixing ratio and a LiCor 6252 measuring CO<sub>2</sub> mixing ratio at 30-minute and 1-minute intervals respectively. The third CRDS instrument is connected to a separate airline and can be switched between inlets that are within 1m of grass lawn at ground level or within 5 m of a large oak tree at canopy level.

Flow rates vary between the internal pumps of the CRDS instruments, but 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 speeds up stabilization. Currently the instruments are measuring CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O at 5-second intervals. Precisions (1 SD) of NOAA tanks, based on the final 10 minutes of a 30-minute analysis period are better than  $\pm 0.03$  ppm for CO<sub>2</sub> and  $\pm 0.3$  ppb for CH<sub>4</sub>.

Automated inlets and automated data retrieval will be tested during spring, for deployment on the South Atlantic islands later in 2009.

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