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Travel report for Queen Elizabeth II Technicians study award

Travel period: 02.November – 26. November 2016

Summary:

I received the QE II Technicians study award in order to receive training at CSIRO in Melbourne, Australia, on state-of-the-art laser instrumentation to measure isotope ratios in atmospheric carbon dioxide (CO_2). NIWA is considering the purchase of a similar instrument with the idea of deploying the instrument in remote areas during field campaigns. This study award enabled me to get hands-on experiences on such instrumentation (QCL laser instruments) under the supervision of world-recognized experts in the field. CSIRO is operating two QCL instruments in Melbourne (Fig. 1). Under the supervision of CSIRO scientists, I could follow through the steps of bringing a QCL instrument into service, followed by training on running it independently, e.g. at remote study sites. The first goal was to learn the necessary basics to operate such instrumentation, ranging from basics on operating software to instrument plumbing and performance. The next step was to learn about what it takes to make fully calibrated measurements of highest possible data quality. A further outcome of the visit to CSIRO was that I was able to make some small experiments on the QCL instrument to learn about the variation of the instrument performance. Finally, I had the opportunity to learn about the specialised software that CSIRO uses to manage the resulting large data streams. This training was an extremely valuable learning experience for me and positions NIWA well for future work with such instruments.

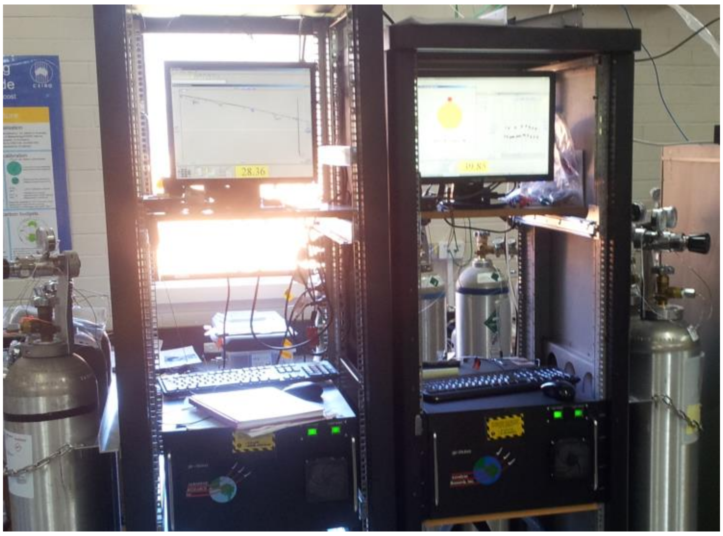

Figure 1: Two Aerodyne QCL instruments at CSIRO in Aspendale. The left system is for measurements of N_2O and CO mixing ratios, the system on the right is for measurements of CO_2 concentrations and isotope ratios.

1. Software and hardware basics to operate the QCL instrument

Dr. Loh of CSIRO introduced me to technical operator knowledge that is required to understand what the instrument is doing and why that is the case. Above all, this includes a basic understanding of the software of the QCL instrument (TDL Wintel). TDL Wintel is a very complex software, which allows the operator to control and optimise wide range of crucial instrument parameters. The level of operator knowledge and skills that is required to run an Aerodyne QCL instrument exceeds that of similar instruments made by other manufacturers by far, but it comes with the opportunity to further optimise the system in order to achieve a superior performance. The introduction to TDL Wintel probably took almost two weeks at CSIRO and continued to be a large learning component during the entire training period. During this period, we encountered a problem with the auto-start function in TDL Wintel. For a yet unknown reason, the instrument tunes itself into an erroneous state upon a system start, in which it monitors wrong absorption peaks and it doesn't produce an optimal fit. This problem required regular Skype meetings with the U.S.A. based manufacturer and could not be permanently solved at the time. I value that this provided me with very deep insights into TDL Wintel, however, it also reduced the time that was available for further training on the QCL instrument at CSIRO. After all, I evaluate this as one of the more valuable experiences, as it showed the risk of facing instrument down time due to its outstanding complexity.

2. Optimising the instrument configuration for automated measurements and calibrations

Before my training started, Dr. Loh set the instrument configuration back to a state that is similar to when such a system is delivered by the manufacturer. The goal of this exercise was to put me in the situation as if I had received a newly ordered instrument and was now in the process of bringing into its first service. One of the first steps to optimise the instrument configuration was to install an additional inlet valve to plumbing of the system and to integrate it into the TDL Wintel software. This valve can now be used to switch between measurements of atmospheric air and a range of calibration and diagnostic gases, either by manually pushing a button in the software interface or automatically, based on an operator-defined measurement schedule. A measurement schedule can be used to repeat sequences of air and reference gas measurements (Fig. 2). This is useful when the system is operated in a continuous measurement mode, for example during long-term field deployment. We also used measurement schedules to run the system over night, when we were not working on it. The supplied gases include two cylinders with natural air that contain CO_2 with different isotopic composition. These two gases were used as calibration gases in order to control the isotopic span in the measurements. Furthermore, we included regular measurements of CO_2-free air to determine the baseline (true zero CO_2) of the instrument. Another gas we connected to the instrument was a cylinder of CO_2-free air to flush the instrument housing. The purpose of this gas was to eliminate the potential for measurement artefacts due to laboratory air including exhaled CO_2 to enter the open path of the optical measurement system (Sect. 3.2). Using all these gases is necessary to achieve the physical minimum configuration that enables measurements of CO_2 isotope ratios in air with highest possible accuracy. This configuration is suitable for field deployment, as it can operate for several days or weeks without the need for a system operator.

Figure 2: Photograph of the QCL instrument screen showing TDL Wintel during an automated measurement sequence. The absorption spectrum is shown in the left window, with absorption peaks for each of the main isotopologues (626, 636, 628). The window to the right shows the trace of 626 measurements, when the system alternates between measurements of outside air and reference gases in a defined measurement schedule. The bottom panel shows additional instrument parameters, for example a cell pressure of ~40 Torr indicated in the yellow window (Sect. 3.1).

3. Experiments to improve the performance of the QCL instrument

After the completion of the above mentioned steps, I took the opportunity to run a few simple experiments to optimise the instrument performance.

3.1 Pressure dependence

In the optical cell, the QCL system measures the abundance of CO_2 isotopologues (molecules of same material but different isotopic composition). More specifically, it measures the absorption of mid-infrared radiation at different wave lengths, where different isotopologues of CO_2 absorb mid-infrared radiation on isotopologue specific wave lengths. This results in a measurement of the abundance of each isotopologue. The signal to noise ratio of the measurement can be improved by increasing the number of CO_2 molecules in the optical cell, which can be achieved by i) increasing CO_2 concentrations in the measured gas or ii) increasing the sample pressure inside the cell. Because we measure ambient air and are also interested in its CO_2 concentration, it is against our interest to increase the CO_2 concentration in the sample (e.g. by pre-concentration). This leaves us with the option to increase the sample pressure in the optical cell, which we varied between 30 and 80 Torr (39 and 106 mbar) in our experiments. As expected, the precision of the measurements improved significantly with increased pressure from 0.08 to 0.04 ‰ for carbon isotope ratios. However, we also observed a significant pressure broadening effect on the peaks in the absorption spectrum, which is an unwanted effect that we could observe but were unable to quantify with the experiments made. Thus, we chose an intermediate operating pressure of 40 Torr (53 mbar).

Another important pressure effect resulted in a systematic variation of CO_2 isotope ratios. The isotopic composition of the same sample gas changed significantly with different cell pressures. Therefore, precise control of cell pressure is important for two reasons, i) measurement stability and ii) referencing accuracy. The stability of a single measurement can be affected when the pressure of the delivered sample varies throughout the measurement. This will increase the noise of each measurement and limit the precision of the measurements. The referencing accuracy can be affected systematically when sample and reference gases are delivered to the instrument with different pressures. Because CSIRO has the goal to develop the QCL analyser towards a capability for measurements in flask samples with different pressures and limited amount of air, precise pressure control is vital. In order to save sample gas, it is furthermore important to implement a pressure control system that reacts very fast and precise. We started with some experiments to control the cell pressure with available equipment but were limited with time. The current configuration is suitable for measurements of ambient air and air samples from high pressure cylinders.

3.2 Using CO_2-free air to flush the analyser

The QCL instrument is operated inside a laboratory facility to measure outside air and gas mixtures in high pressure cylinders. It is therefore important that the measurements are independent of the CO_2 in the laboratory air. The optical section of the QCL instrument is isolated from laboratory air by an internal housing. However, we found that this housing only reduces the exchange of air between the inside of the instrument and the laboratory. Because the exchange of air is slow, the effect of people working in the laboratory on the measurements is not immediate, which made it difficult to identify. In order to be unaffected by variations in the concentration and the isotopic composition of CO_2 in the lab air, we installed a CO_2-free air flow that permanently flushed the optical unit of the analyser. The permanent flushing of the instrument stabilised the measurements considerably.

4. Software to manage large data streams

Dr. Loh introduced me to the software package (GC-Werks) that CSIRO uses to manage the data streams from their continuous analysers. For example, GC-Werks can ingest the 1 Hz data from the QCL and furthermore include additional data from the measurement schedule. This enables GC-Werks to identify blocks of air, reference gas and other measurements. GC-Werks can then be configured to perform all correction and calibration calculations, including updates thereof when new reference gases are installed. Uploading a complete data set including these calculations takes seconds for years of data. GC-Werks can be used for a comprehensive but fast data quality analysis. Because GC-Werks can also be merge measurement data with other data of interest, e.g. meteorological data, GC-Werks allows for a first interpretation of the QCL data. For example, GC-Werks is capable can be linked to atmospheric transport model data, in order to select greenhouse gas data for specific meteorological conditions. The wide range of applications make GC-Werks an interesting software for NIWA's applications, it was great to have the opportunity to learn about it.