

Atmospheric monitoring and verification of geosequestration at the CO2CRC Otway Project

2007 Annual Report to the CO2CRC

D. Etheridge, R. Leuning, A. Luhar, D. Spencer, S. Coram, L. P. Steele, M. van der Schoot,
S. Zegelin, C. Allison, P. Fraser, L. Porter, C. P. Meyer and P. Krummel

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Meyer and P. Krummel**

**CSIRO Marine and Atmospheric Research, CSIRO Energy Transformed
Flagship and CO2CRC**

August 2007
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Introduction: atmospheric monitoring and verification of geosequestration

The success of geosequestration (carbon capture and geological storage) will be judged by its ability to withhold carbon dioxide (CO₂) emissions from the atmosphere sufficiently well to help control atmospheric concentrations. This requires that any leakage from the storage to the atmosphere is sufficiently slow to avoid losses that would compromise the permanence of the storage and to avoid high CO₂ concentrations near the storage that could impact on health and safety.

Atmospheric monitoring techniques can potentially be applied to geological carbon storage sites (Etheridge *et al.*, 2005; Leuning *et al.*, 2007). Atmospheric monitoring is cost effective, not invasive and continuous and monitors emissions integrated across a number of locations. It is challenging however because atmospheric turbulence and transport mixes the air very effectively thereby reducing the concentration signal from the source relative to the background values. Also, the background atmospheric CO₂ concentration is particularly variable because of natural, agricultural and industrial sources. Sensitive, precise and continuous measurement techniques and a number of modelling methodologies are therefore required to measure the small perturbations in gas concentrations and fluxes that might be caused by the geological storage sources and to distinguish them from background variations. Many of these technologies are available in atmospheric science, though some measurements need developing for remote, unattended field applications. There is no precedent for comprehensive atmospheric monitoring and verification of geosequestration storage.

The CO₂CRC Otway Project atmospheric monitoring and verification program: outline of strategy and aims

The CO₂CRC Otway Project is the first geosequestration project to include a comprehensive atmospheric monitoring program. The monitoring strategy for the Otway Project was based on the effects of hypothetical storage leaks (point and diffuse) simulated by atmospheric dispersion models, over several distance scales at the Otway site. The strategy was designed to provide the optimal chance of identifying and quantifying emissions from a leak, possibly with poorly known location and rate, while using a minimal number of instruments and surveys to reduce cost. A network of atmospheric monitoring equipment has been set up at the site to characterise the background against which anomalous sources of CO₂ or other gases (such as methane or tracers) could be detected. The location and layout of the Otway Project (Figure 1) has some significant advantages for the effectiveness and cost of atmospheric monitoring. It is in a rural region with the coast only 4 km to the southwest. SW winds are prevalent. The short fetch across mainly pasture or lightly forested land minimises the CO₂ concentration variations resulting from ecological exchange. The atmospheric composition at the coast during SW winds can be found from measurements at the Bureau of Meteorology Baseline Air Pollution Station at Cape Grim, NW Tasmania. This provides an upwind boundary condition for the storage site if fluxes within the 4 km fetch of land can be estimated. The potential to reduce the effects of emissions from neighbouring methane and carbon dioxide gas operations (including production wells, pipelines, processing plants and trucking operations), agricultural emissions (primarily from cattle) and the natural CO₂ flux (biological and possibly geological) from the ground, by selecting air trajectories, makes the Otway site a particularly good place to test and develop this technology. The CO₂ source well (Buttress), and other sources of CO₂, and their associated infrastructure, which may release CO₂ and other gases, are likely to be downwind of the geosequestration well during SW winds.

Tracers of the stored CO₂ are proposed for detection in the subsurface and would also aid the atmospheric monitoring. Tracers that have low and steady background atmospheric concentrations, such as SF₆, could be added to the injected fluid to quantify leakage. Carbon dioxide isotopologues that naturally accompany the stored CO₂ could be used if their isotopic values differ significantly from other CO₂ sources/sinks, such as terrestrial ecosystems. Tracers such as carbon monoxide and methane from combustion of fuel or biomass could also be used to distinguish pre-existing CO₂ sources from leakage of stored CO₂.

The demands of monitoring the Otway Project are being met while recognising that this is also a research project for the development and testing of atmospheric monitoring methodologies that could be used for other geosequestration sites that are likely to be larger and in more challenging settings.

Atmospheric monitoring tasks for the Otway Project

The Otway Project atmospheric strategy comprises several tasks supported by CO2CRC involving measurement, interpretation and modelling.

Task 1: CO₂ measurements at the Otway Project. Measure CO₂ concentration near-continuously at an optimum location downwind of the storage site using a CSIRO LoFlo™ CO₂ analyser system. This will provide measurements calibrated to international standards to be directly compared with measurements from other atmospheric networks (especially the LoFlo CO₂ system at Cape Grim and the flask analyses in Task 2). The data stream will be interpreted by models in Task 5 to identify carbon fluxes near the site and estimate the detection threshold for CO₂ leakage.

Deliverables:

- 1.1. Operation and maintenance of the CO2CRC LoFlo CO₂ instrument.
- 1.2. Measure CO₂ concentrations continuously (>80% time) at the Otway Project site before, during and after injection using a precision calibrated system (>0.1 ppm).
- 1.3. Data available as input to Task 5.
- 1.4. Annual report of operations and data.

Task 2: Flask air sampling and analyses at the Otway Project. For concentrations of gases such as CH₄, CO₂ isotopes and tracer compounds such as SF₆, where continuous monitoring technologies for field use are still emerging, sample about 2 times per month, mainly in “baseline” SW wind conditions. This will provide the background variations for a strategy on the use of tracers of CO₂ leakage.

Deliverables:

- 2.1. Concentration and isotope data, up to 30 samples and analyses per year.
- 2.2. Subject to availability of appropriate technology, up to 12 ¹⁴CO₂ samples and analyses per year.
- 2.3. Data available as input to Task 5.
- 2.4. Annual report of operations and data.

Task 3: CO₂ flux monitoring, using flux tower techniques. This task will measure CO₂ fluxes from a characteristic area of the land surface near the site on distance scales of up to about 1 km, using eddy-correlation techniques. The flux data will be used as input to the transport modelling in Task 5 to help explain the measured concentration variations.

Deliverables:

- 3.1. Installation of flux monitoring tower and support equipment.
- 3.2. Collection of CO₂ flux data (>80% time) from the land surface at the nominal scale of 1 kilometre footprint.
- 3.3. Data available as input to Task 5.
- 3.4. Annual report of operations and data.

Task 4: CO₂ flux monitoring, over small scales. This would provide CO₂ fluxes from the terrestrial ecology on smaller scales using soil flux meter techniques at the Otway site. It was proposed as a task to the CO2CRC but not supported in 2006-07. It was however carried out as a fully CSIRO-supported task as it was expected to be necessary to provide information for the carbon fluxes over an additional scale for input into the modelling of the site.

Task 5: Data analysis and modelling. Data from the measurement tasks 1-3 will be collated and interpreted for background variations and to identify any significant variations due to local sources and sinks. The data will be used as input to the CSIRO transport and dispersion model TAPM to help simulate the observed variations.

Deliverables:

- 5.1. Collated data store from project commencement to current date.
- 5.2. Estimation of current detection threshold for CO₂ at the Otway Project facility.
- 5.3. Six monthly presentation of current data analysis and modelling results to CO2CRC.
- 5.4. Annual report detailing results of data analysis and modelling and incorporating any recommendations arising from the monitoring program

In addition there are several research activities, relevant and complementary to geosequestration and the Otway Project, that are funded directly and only by CSIRO Marine and Atmospheric Research through the Energy Transformed Flagship. These include development of new instruments and intelligent sampling techniques, incorporation of the carbon cycle model CABLE into the TAPM transport model, and small scale flux monitoring (including soil flux monitoring at Otway and a controlled release experiment in Canberra). The results of these activities are only briefly mentioned in this report.

Report on deliverables

Overview

Design of the strategy, model simulations of leak dispersion at Otway, and preliminary flask sampling began in late 2005 with routine sampling later in 2006. Flask sampling was done at the corner of Callaghan's and Soda's Roads (about 500 metres north of the final location of the atmospheric module) until January 2007 when access and power to the site were made available. The atmospheric module was installed the first week of January 2007, next to Soda's Road, in the NE corner of the paddock of R. R. and J. A. Brumby, about 600 metres NNE of the CRC-1 injection well (see Figure 1).

The atmospheric module (Figure 2) is an insulated, weatherproof and secure shipping container fitted with electrics, benches and air conditioning. It houses the CO2CRC LoFlo analyser, the flask sampling equipment and the flux station telemetry and data logging equipment. A 10 m tilt-able tower supports the air inlet for LoFlo and flask samples and simple meteorological instruments. The 10 m height places the composition measurements at the same elevation as the lowest modelled level (Task 5). The atmospheric module and tower were made available to the CO2CRC Otway Project on indefinite loan from CSIRO Marine and Atmospheric Research.

The flux station was installed in February 2007 to the west of the atmospheric module. Power and telemetry were connected via trenched cables to the atmospheric module. Flux monitoring began on 8 February 2007.

Latitude, longitude and elevation are 38.52532°S, 142.81065°E, 52 m for the atmospheric module and 38.52501°S, 142.81065°E and 52.5 m for the flux station.

Soil CO₂ flux monitoring (a CSIRO task) involved 3 surveys of randomly selected spots using a small portable soil flux meter concentrated mainly in the paddock of R. R. and J. A. Brumby.

All visits to the site for installation, operations, maintenance and monitoring were made after notifying the CO2CRC and were carried out within CSIRO and CO2CRC guidelines for health, safety and environment to ensure minimal impact on the site, the landowners and their activities.

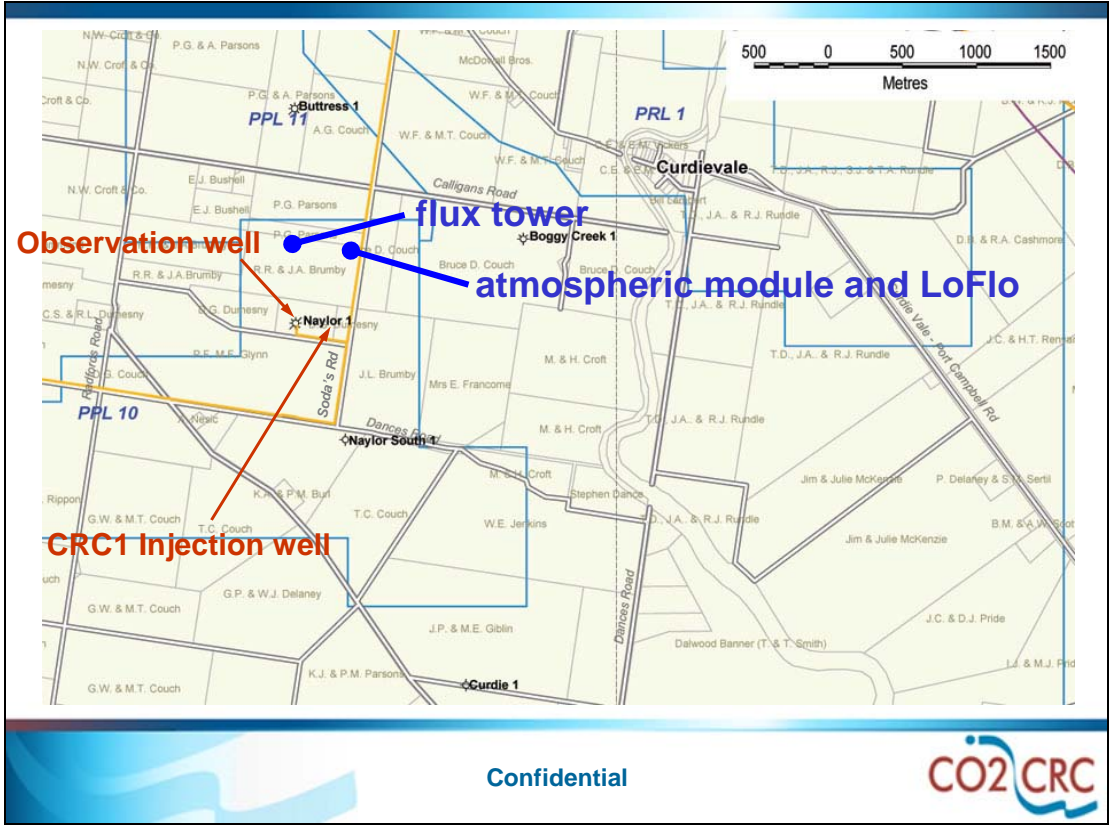


Figure 1. Map of Otway Project site showing wells and atmospheric monitoring installations.



Figure 2. Atmospheric monitoring module and tower.

Task 1. CO₂ measurements at Otway

The LoFlo analyser system (Figure 3) was purchased by the CO2CRC and built, installed, operated and maintained by CSIRO. It comprises an NDIR analyser, a calibration gas suite (6 cylinders each with dedicated TESCOM™ regulators), reference gas tank, inlet system (from the 10 m tower) with Nafion™ dryer, PC with data acquisition and communications (mobile phone dial up modem), and UPS power. Measurements every second are averaged to minute mean CO₂ values with 10 minutes per hour (and about 5 minutes for flow stabilisation) dedicated to reference gas. A calibration run is made every 1-2 months, where the 6 calibration gases are repeatedly measured over a period of about 2 days. Atmospheric CO₂ concentrations are measured to better than 0.05 ppm (parts per million, mole fraction in dry air) precision and are directly traceable to World Meteorological Organisation (WMO) standards and to other CSIRO LoFlo and flask sample measurements (such as at Cape Grim).



Figure 3. LoFlo analyser system inside the module at Otway.

Calibrated CO₂ data, quality controlled and processed to minute and hour means, are stored on CSIRO's server (gl-as) at Aspendale, Victoria and routinely backed up. They are also provided to the CO2CRC for their intranet. The hour mean record is shown in Figure 4. Presently, hour mean CO₂ data are used directly in Task 5.

Maintenance of the LoFlo involves replacement of drying agent and reference gas and running of calibrations, requiring visits about every 4-6 weeks. The only significant periods of downtime were 5 days in April due to a blocked drying tower and 11 days in June due to stalled software that was not readily identified over the phone modem.

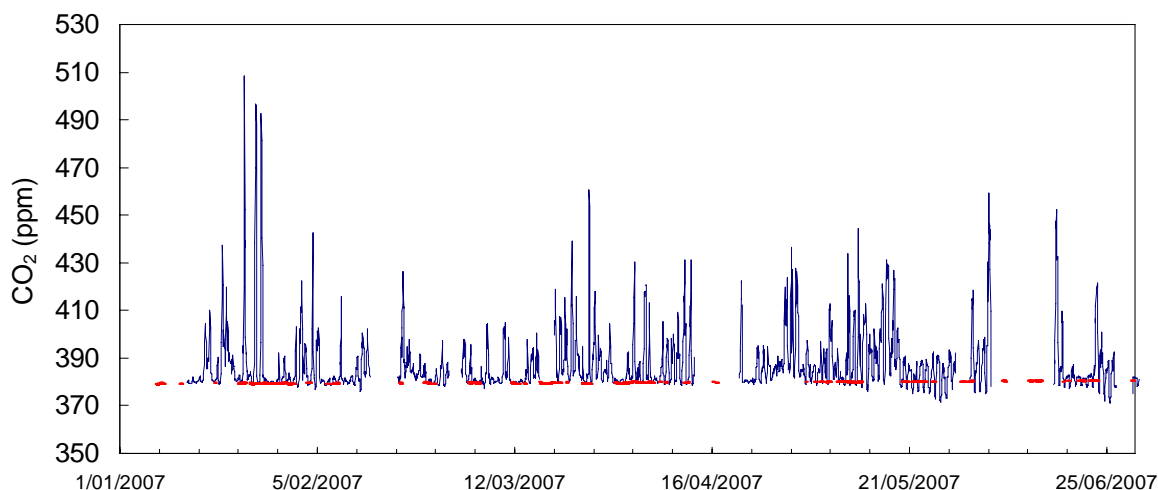


Figure 4. Hour mean CO₂ concentrations from the LoFlo analyser since installation in January 2007. CO₂ measured by the LoFlo at Cape Grim station (hour means, baseline selected) is shown in red.

Task 2. Flask air sampling and analyses at Otway

Air samples were collected in pairs at nominally monthly intervals generally during “baseline” conditions (daytime, moderate to strong winds from the SE to SW sector) using conventional CSIRO sampling techniques. A total of 42 samples in 0.5 L glass flasks were analysed for concentrations of CO₂, CH₄, CO, H₂ and N₂O and for the stable isotopic ratios ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of CO₂. Typical precisions of the CSIRO “GASLAB” concentration measurements are 0.1 ppm, 2.3 ppb, 0.6 ppb, 1.5 ppb and 0.3 ppb, respectively. Precision of the stable isotope ratio measurements are 0.03 ‰ and 0.06 ‰ for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ respectively. The CSIRO measurement scales are traceable to internationally accepted standards (Francey *et al.*, 2003). Two of the site visits collected samples over a diurnal period to quantify effects of respiration and photosynthesis and well-mixed to stable conditions. From this, the CO₂ concentration and $\delta^{13}\text{CO}_2$ measurements were combined to estimate the $\delta^{13}\text{CO}_2$ of the local vegetation exchange to be about -26 per mil, typical of C3 vegetation. Figure 5 shows the CO₂, CH₄, CO and N₂O data of all 0.5 L samples.

Ten air samples were collected at Otway in 3 L stainless steel tanks and analysed for many halogenated trace gas compounds (including SF₆, CFCs, CF₄).

About 14 standard gas samples were transferred to CSIRO sample flasks and sent to ANSTO and NOAA (USA) for measurement of ¹⁴CO₂, to test the suitability of CSIRO sampling equipment for this measurement, and to partake in an international intercalibration exercise. The results will be used to determine what if any modifications would be required to introduce ¹⁴CO₂ into the suite of routine measurements of air samples from the Otway Project for use as a tracer.

Data from Task 2 are stored on the CSIRO Marine and Atmospheric gl-as server at Aspendale, and will be placed the CO2CRC intranet (OBPP file store/Monitoring Atmospheric).

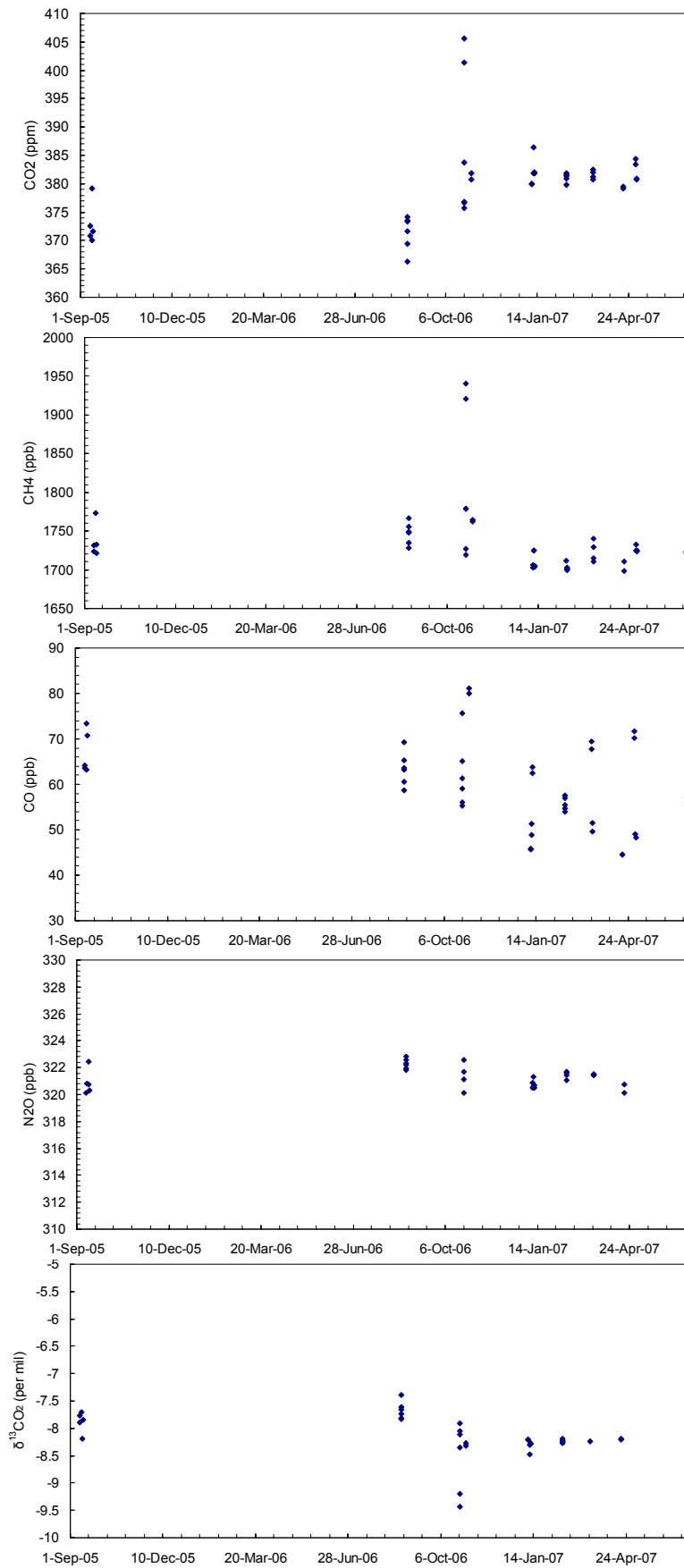


Figure 5. Measurements of CO₂, CH₄, CO and N₂O and δ¹³C of the CO₂ from the flask sampling program at Otway.

Task 3. CO₂ flux monitoring at Otway

The flux station was purchased by CO2CRC and built, installed, operated and maintained by CSIRO. Incoming and reflected solar radiation, net radiation, air temperature, relative humidity, wind speed and direction are measured at 10 m on the mast. Rainfall is measured using a tipping-bucket rain gauge 0.3 m above ground while soil temperature and flux of heat into the soil are measured at a depth of 5 cm. A 3-D sonic anemometer and open-path CO₂ and water vapour analyser were installed at 4.28 m and the fluxes of these quantities are calculated as the covariance of fluctuations in vertical velocity and concentrations of CO₂ and H₂O. Analysis of flux data from the first five months of operation has shown that frequent rain at the site has caused significant problems in measuring the CO₂ and water vapour fluxes required for calibrating the CABLE-TAPM transport and carbon model. This is because water on the lenses of the open-path, optical instrument during and after rain makes it impossible to measure CO₂ and water vapour concentrations accurately during these times. To help overcome these problems, a second, closed-path analyser was installed in early June 2007 and analysis of data from both sets of instruments is progressing. We note that it is only necessary to measure the CO₂ and water vapour fluxes for approximately 25% of the time to calibrate CABLE-TAPM, and we anticipate achieving this goal for the period 8 February until mid July, with improved data recovery thereafter.

Further maintenance of the flux station was necessary in mid July 2007, due to water damage to some of the instruments and the destruction of a second net radiometer by magpies. A new, four-component radiometer has been installed to allow measurement of incoming and reflected solar and thermal radiation. The new instrument should be more resistant to damage by perching birds and will provide data needed to validate the performance of CABLE-TAPM.

Data from Task 3 are stored on the server at CSIRO in Canberra and will be provided to the CO2CRC once final quality control and corrections have been applied.



Figure 6. Setting up the flux station. The atmospheric module is in the distance.

Task 5. Data analysis and modelling for Otway

Data from all measurements have been quality controlled, calibrated and stored on CSIRO's servers. They are used to characterise and assess the causes of background variations in concentrations of many gases and the fluxes of CO₂ at the Otway site.

The CO₂ concentration data for most of the year to date show minimum values very close to the Cape Grim baseline concentrations (Figure 4), consistent with the drought (also evident in the low CO₂ uptake seen in the flux station measurements). Only with rain beginning in May 2007 did the CO₂ concentrations at Otway drop below those at Cape Grim, showing the recovery of vegetation and photosynthesis. CH₄ and N₂O concentrations were often similar to Cape Grim baseline values except when herds of cattle were nearby.

Trajectory modelling (NOAA HYSPLIT) shows that distant sources such as the Melbourne region can have an impact on the atmospheric composition at Otway, as confirmed by elevated measured concentrations of anthropogenic tracers such as SF₆ in some samples. Knowledge of the large scale atmospheric transport, as well as local meteorology, is therefore an important consideration for the Otway Project.

Drill rig operations in March (for the CRC-1 injection well) were detected, when the wind conditions were suitable, as an elevation of about 2 ppm in CO₂, confirmed by CH₄ and CO being also above background ($\delta^{13}\text{C}_{\text{CO}_2}$ is yet to be measured in samples from this event). This gives an indication that the sensitivity of the monitoring is likely to be better than about 6 t CO₂ per day for a point source at this distance from the atmospheric monitoring module, depending on the number of tracers used and the ability to model the atmospheric transport and the natural flux of CO₂.

The CSIRO model TAPM was evaluated for its meteorological performance at the Otway site using the hourly-averaged measurements (wind speed, wind direction and temperature) from the flux station, and it was found that overall TAPM predicts the local near-surface meteorology very well (see Figure 7). As explained above, accurate model representation of atmospheric transport is a necessary link between the surface fluxes (ecosystem and anthropogenic) and the measured concentrations.

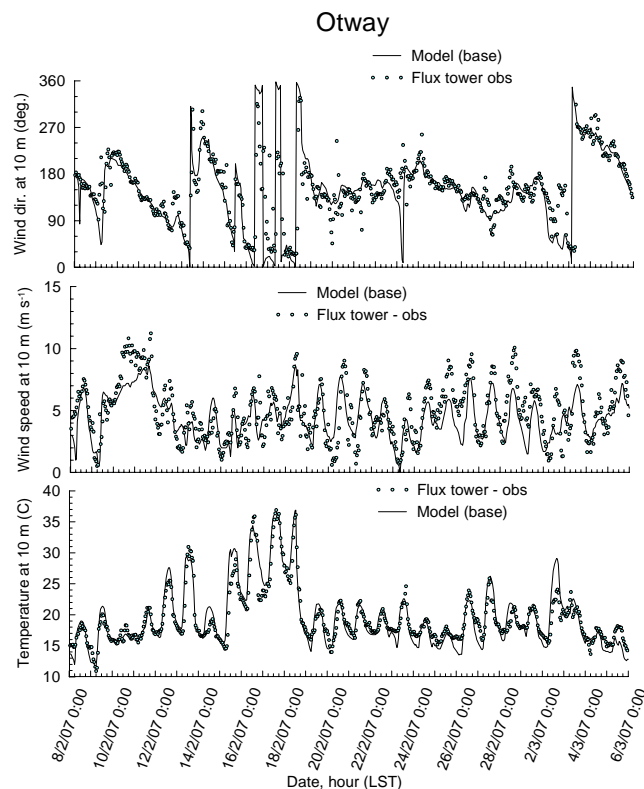


Figure 7. Comparison of the modelled time series of wind direction, wind speed and temperature at 10 m AGL with the measurements at the Otway site.

The coupled model TAPM-CABLE (CABLE is the carbon ecosystem model) was developed for application to the Otway site, as a CSIRO task. It simulates the hourly-averaged LoFlo CO₂ concentrations and the CO₂ flux measurements at the Otway site. The period selected was 8 February – 5 March 2007, which is the (earliest) period for which both LoFlo and flux measurements were available (however, there are some gaps in data during this early period). Prior to the first flux data being available, model runs were also made for part of January 2007 and all of March 2007.

Figure 8a compares the modelled CO₂ concentration time series (black line) with the data. The model underestimates some of the CO₂ peaks, which mostly occur in the middle of the night. This under prediction is perhaps due to the fact the model is underestimating the night time CO₂ flux corresponding to many of these peaks (see Figure 8b). The model also greatly over predicts the magnitude of the daytime photosynthetic uptake (black line in Figure 8b).

TAPM tends to underestimate the frequency of low wind ($< 2 \text{ m s}^{-1}$), and it was suspected that this might be a reason for the model not predicting CO₂ concentrations as high as the observed peaks. To investigate this, we assimilated the 10-m wind data into TAPM and examined the modelled CO₂ concentration time series, with the result that the wind data assimilation does not yield a significantly better prediction. This leads us to believe that the TAPM low wind prediction is not the reason for the model not getting the CO₂ peaks right and that transport processes are not as dominating as the sources and sinks (but there are of course interactions between the two).

CABLE has a number of parameters that need to be tuned based on measurements, and some the inputs to the model (e.g. land use) also need to be examined. It was felt that the Leaf Area Index (LAI) and the values of the parameter $V_{c,max}$ (to do with plant photosynthesis) CABLE uses for different land use types were too high. These values were modified and the model was run again. The results are plotted in Figure 8 (a) and Figure 8 (b). The daytime fluxes reduce greatly with these changes, but they are still too high compared to the measurements. The modelled night time fluxes reduce too, which is not what is desired. These changes do not improve the fit of modelled to measured concentrations during the night time peaks.

Currently we are looking at three CABLE components, namely plant photosynthesis, plant respiration and soil respiration, individually. There are a number of free parameters in these components. TAPM also requires a small modification so that the flux output is not just the net CO₂ flux, but also the three components. Anthropogenic leaks are to be simulated once this fine tuning is over. Recent indications are that distant anthropogenic emissions (Melbourne, Latrobe Valley) are responsible for some of the CO₂ concentration peaks and that the others may be due to a closer CO₂ source. Emissions from the nearby BOC CO₂ production facility are suspected. It will be necessary to obtain actual emission data from BOC to confirm this. The model will also be applied to the more recent measurements, which reflect a seasonal change in the land fluxes.

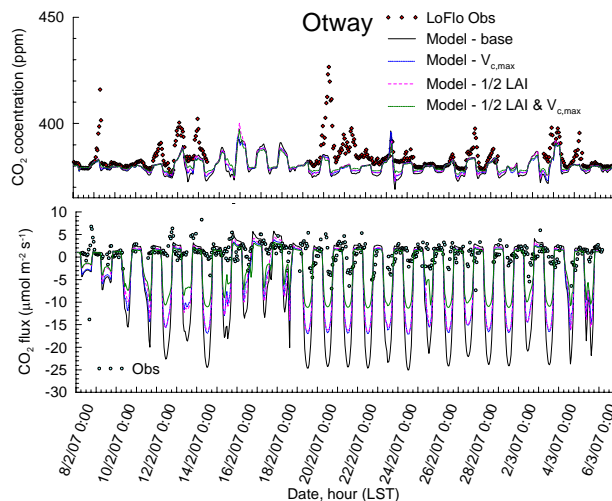


Figure 8. Comparison of the modelled time series of (a, upper panel) CO₂ concentration (b, lower panel) CO₂ flux with the data from the Otway LoFlo and flux station.

Other activities

- EPA regulatory matters. Modelling results and preliminary measurements were made available to the CO2CRC for submission to the EPA for the Otway Project, 2006 and June 2007. With Sharma, Dodds, Berly.
- IEA expert review of monitoring and verification programme at Otway, November 2006. The atmospheric monitoring was assessed and a presentation was made at the meeting. The Otway Project atmospheric strategy was discussed at the site with IEA review group. With Dodds, Sharma, Anderson.
- Soil gas. Advice on sampling and measurement strategy was provided following failure of soil gas sampling bags for analysis of $^{14}\text{CO}_2$ at ANSTO and $^{13}\text{CH}_4$ at NIWA, NZ. With Boreham, Watson.
- Water well gas. The headspace gas of 3 deep water wells in the Otway region was sampled and analysed for the CSIRO suite of trace gases (June 25, 2007). With de Vries, Bernardo, Hennig.
- Anthropogenic CO_2 and CH_4 sources. Estimates of several trace gas sources that could possibly affect the Otway site's atmospheric composition were made and compiled, for use in modelling and interpretation of the atmospheric measurements. A report will be provided after final sample analysis.
- Tracers. Significant input was made to the strategy and planning for tracers to suit the subsurface and atmosphere at Otway. With Undershultz, Stalker, Boreham.
- Media. Atmospheric monitoring by CSIRO and other atmospheric and climate issues reported in:
 - Interview with ABC Warrnambool.
 - Interview with Warrnambool Times.
 - "Drilling for climate change answers" Liz Minchin, *The Age* (Melbourne), February 23, 2007.
 - "Biggest carbon-burial test will hunt for leaks" Rachel Nowak, *New Scientist*, 16 February 2007.
- Attendance at Carbon Capture & Storage And Emissions Trading- Working towards Business opportunities in Australia, UK and Worldwide. A Seminar sponsored by UK Trade & Investment in Cooperation with The Carbon Capture & Storage Association and CO2CRC.
- Guest editor (D. Etheridge), *International Journal of Greenhouse Gas Control*, special issue on geosequestration.

Reports, publications, presentations

Kevin Dodds, David Etheridge, Ray Leuning, Max Watson, Allison Hennig, Ernie Perkins, Anton Kepic, Don Sherlock, Milovan Urosevic, Brian Evans, Bruce Hartley, Chris Boreham, Dirk Kirste, Peter van Ruth and Sandeep Sharma. The Otway Basin Pilot Project (OBPP) Monitoring and Verification Plan, CO2CRC report, September 2006.

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Recommendations

A review of the Otway project atmospheric monitoring and verification program would help ensure that the strategy continues to be appropriate and that the CSIRO/CO2CRC tasks are sufficient and adequately supported to deliver the strategy, especially in the light of the following points.

The ability of the atmospheric monitoring program to detect emissions could be seriously affected if the next stage of the Otway Project resulted in pre-injection processing of the Buttress gas at the Naylor site. The strategy is designed around having no emissions from plant or infrastructure in the vicinity of the injection well or storage site. Any such developments would need to acknowledge the possible impact on the atmospheric program and find ways to minimise or the impact and adapt the monitoring if necessary.

The strategy for tracers needs to be decided upon and the atmospheric monitoring capability made available (eg. continuous monitoring of SF₆).

A landline for communications with LoFlo, flux station and other instruments via the atmospheric module would improve data transfer and would help avoid operating errors by allowing unimpeded remote observation of the instruments.

Information on the emissions (amount, type and location versus time) from the BOC Boggy Creek CO₂ facility must be obtained for use in the interpretation of CO₂ at the Otway Project.

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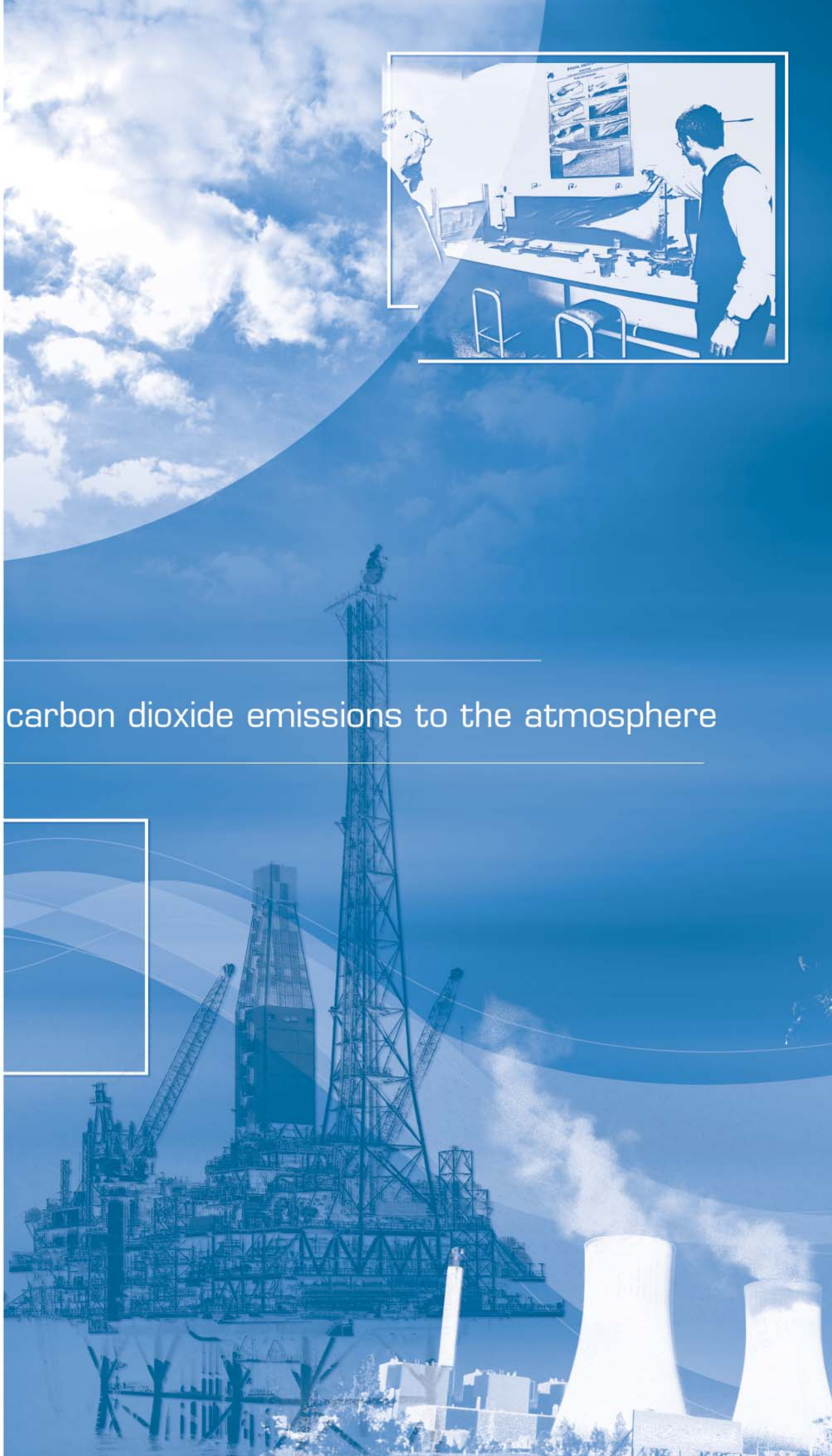
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