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Long-term continuous atmospheric CO_2 measurements at Baring Head, New Zealand

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Abstract

We present a 39-yr record of continuous atmospheric carbon dioxide (CO_2) observations made at Baring Head, New Zealand using a succession of infrared analyser instruments. We include descriptions of the in situ instrumentation, calibration procedures, intercomparison efforts, and data-filtering methods. Located on the southern coast of the North Island, Baring Head is exposed to extended periods of strong air flow from the south with minimal terrestrial influence resulting in low CO_2 variability. The site is therefore well suited for sampling air masses that are representative of the Southern Ocean region. Instrumental precision is better than 0.015 ppm (1-σ) on 1-Hz values and comparisons to over 600 co-located flask samples, as well as laboratory based flask and cylinder comparison exercises, suggests that over recent decades compatibility with respect to the Scripps Institute of Oceanography (SIO) and World Meteorological Organisation (WMO) CO_2 scales has been 0.3 ppm or better.

1 Introduction

Long-term atmospheric CO_2 timeseries measurements have been widely used to infer fluxes of CO_2 between the atmosphere and land or ocean regions (e.g. Enting et al., 1989; Tans et al., 1990; Bousquet et al., 2000), study interannual to decadal variability in these fluxes (e.g. Keeling et al., 1980; Conway et al., 1994; Beaulieu et al., 2012), and diagnose feedbacks between the global carbon cycle and climate change (e.g. Jones and Cox, 2005; Le Quéré et al., 2007). The first in situ continuous measurements of atmospheric CO_2 were made with a high-precision non-dispersive infrared (NDIR) gas analyser by C. D. Keeling in 1958 at Mauna Loa, Hawaii (Keeling et al., 1960, 2001). These data documented for the first time that CO_2 was increasing in the atmosphere and that it was modulated by seasonal changes in photosynthesis and respiration. These results provided the motivation for establishing a global network of observing stations.

The longest-running in situ CO_2 observing programme in the Southern Hemisphere was established in November 1970, through a collaboration between the Department of Scientific and Industrial Research (DSIR), predecessor to National Institute of Water and Atmospheric Research (NIWA) and C.D. Keeling's group from SIO. An NDIR analyser was initially installed at Makara, New Zealand (41°15′ S, 174°41′ E), which is about 15 km northwest of Wellington and 1 km inland from the west coast of the North Island (Fig. 1). Atmospheric CO_2 observations were maintained at the Makara site through March 1972. Because of the significant influence of photosynthetic draw down over local vegetation, in December 1972 the sampling site was relocated to Baring Head (41°25′ S, 174°52′ E) approximately 10 km southeast of Wellington and situated directly on the south facing coastline. The measurements of atmospheric CO_2 at the Baring Head site have continued to the present. DSIR took over the operational responsibility for the programme soon after its installation at Baring Head by SIO, and became part of NIWA in 1992. The Baring Head measurement team has maintained strong links with SIO to the present.

The first four complete years of CO_2 observations from Baring Head were described by Lowe et al. (1979), including aspects of the seasonal cycle and secular trend. Subsequent updates to the dataset and focused analytical discussions are contained in a series of DSIR/NIWA technical reports and meeting reports (Manning and Pohl, 1986, 1987; Manning, 1994; Manning et al., 1994; Gomez, 1997; Brailsford et al., 2011). In this paper, we present the system design and experimental methods used at the Baring Head station, including those used to maintain calibration consistent with the SIO and WMO CO_2 scales and those used for selecting southerly episodes, along with a history of relevant changes. A companion paper will discuss the interpretation and analysis of the record up to the near present (Stephens et al., 2012).

2 Location

The Baring Head site is located on a marine uplift terrace 85 m above the southern coast of the North Island (Fig. 1). The instrumentation is housed in a concrete building with good thermal stability. The area is a regional park with a single residence within a 1 km radius. Wellington city, with a population of 200 000, is located 10 km to the northeast. Wind speeds at the site tend to be high and from either the north or the south. Air masses arriving at the site from the south tend to have trajectories that have not been in contact with land masses or anthropogenic sources of CO_2 for thousands of km and a week or more (Stephens et al., 2012). For this reason, the variability of the CO_2 mole fraction in southerly air flows can be less than 0.1 ppm for periods of days. It is these conditions that were originally targeted for measurement of baseline CO_2 concentrations representative of the mid-latitude Southern Hemisphere, although data are now reported for all wind conditions. Baring Head is part of the WMO Global Atmosphere Watch (GAW) network (GAWSIS ID:BHD), and observations from this site are referenced to the WMO mole fraction scale for CO_2.

3 System design

The Baring Head CO_2 measurement system has operated nearly continuously for over 39 yr. This has been based on a succession of NDIR instruments each measuring the CO_2 mole fraction in cryogenically dried air, referenced to traceable CO_2 scales, and recording data digitally. For perspective, the original data acquisition and control system was built before the advent of personal computers, and included 300 diode plugs and a stepper switch for valve sequencing, voltage-to-frequency converters, digital counters, and a magnetic tape for data storage (Lowe, 1972). Over time there have been many data system upgrades and several changes in the experimental design. We describe the current design of the system, and then include a description of historical changes in Sect. 3.5.

3.1 CO_2 analyser

CO_2 mole fractions are measured with a Siemens Ultramat 3 gas analyser (M52012), which is a dual cell NDIR analyser with a differential full scale of approximately 60 ppm. This analyser has a short-term precision of 0.015 ppm (1-σ in 1-s). To obtain the most stable results, the sensor is temperature controlled above ambient temperatures at 48 °C and the analyser case is flushed with 100 % dry nitrogen gas at a flow rate of 5 $\mathrm{ml\,min^{-1}}$ to keep the electronics dry and to help identify any leaks in the cells. Sample cell gas flow rates are controlled by a mass flow controller (Teledyne Hastings, HFC202) and are set to 150 $\mathrm{ml\,min^{-1}}$ for all gases being measured. A tank with compressed dry ambient air is used as reference gas and is purged through the reference cell of the analyser at a flow rate of 10 $\mathrm{ml\,min^{-1}}$. A single 30 l reference gas cylinder lasts for approximately 9 months.

3.2 Air inlet system

Ambient air is drawn, from a height of 10 m, through two dedicated airlines of polyethylene lined aluminium tubing (Eaton Synflex 1300, ID = 4.6 mm). The path of the air flow from these two lines is selected by a pair of three-way solenoid valves (Parker Hannafin, V54DA1075). One line is directed to a diaphragm pump (KNF Neuberger, N86KTE) then a tee fitting, which directs 150 $\mathrm{ml\,min^{-1}}$ towards the analyser and 3 $\mathrm{l\,min^{-1}}$ to be purged. The sample line not selected is purged at the same total flow rate by a second diaphragm pump, to maintain constant flows and pressures in the inlet tubes. The purge flows are adjusted using needle valves and ball-float flow meters. The flow rate of 3 $\mathrm{l\,min^{-1}}$ translates to a residence time in the inlet tubes of 5 s.

The two inlet lines are alternately selected, nominally every 30 min, and any differences in CO_2 measured on the two lines are used to detect inlet artefacts. To eliminate dilution and pressure-broadening effects of water vapour, the sample air is passed through two drying stages. A glass fridge trap (50 ml volume, 2–6 °C) condenses water on the surface of 3 mm glass beads at an absolute air pressure of 1.8 bar. The condensed water is then removed from the base of the trap by a peristaltic pump (Masterflex, E-07544-01) with a flow rate of 0.21 ml min^{-1}. The second drying stage consists of a stainless steel trap (220 ml volume) filled with 3 mm glass beads to within 3 cm of the top to reduce blockage, which is immersed in a cryogenic ethanol bath at −80 °C. This reduces the water content in the dried air stream to about 1 ppm. The cryo-traps and glass beads are removed and manually dried once per week with hot air.

The gas flowing to the sample cell of the analyser is selected to be either sample or calibration by another three-way solenoid valve. If calibration gases are being analysed, the ambient air flow is vented to the room via a 2-way solenoid valve (Parker Hannafin, B16DA1175), a needle valve, and ball-float flow meter at the same flow rate that is used with the analyser. This ensures a constant pressure and flow regime through the air drying system.

3.3 Calibration gases

A suite of 12 calibration gases with assigned CO_2 mole fractions alternates with measurements of ambient air and up to 4 more cylinders of unknown mole fraction. Eight calibration gases are used as long-term transfer standards, and their CO_2 mole fractions are determined by the WMO Central Calibration Laboratory (CCL), with an estimated uncertainty of ±0.07 ppm (1-σ) with respect to the WMO scale. Another 4 calibration gases and the reference tank are used as short term working standards and are prepared at Baring Head. The remaining four gases are unknowns to be determined, either working gases in preparation or comparison gases like the WMO Round Robin gases (see Sect. 6). A comprehensive calibration using all 12 gases is nominally performed every 2 weeks to characterise the detector response and the 4 working standard mole fractions. Since the cylinders of calibration gas are dried chemically to better than 2 ppm of water vapour upon filling, they are not passed through the cryogenic trap for drying. Comparative measurements demonstrated no bias when calibration gas was analysed directly or dried cryogenically. This substantially reduces the flushing volume when switching between different calibration gases. To ensure long-term stability and longevity of the calibration gases, high pressure aluminium gas cylinders (30 and 50 l) with high purity stainless steel or brass pressure regulators have been used. A mass flow meter (Tylan Co. FM-360) installed in the flow path of the calibration gases monitors for flow mismatch with the mass flow controller to ensure valve function and a leak free flow path.

3.4 Data acquisition and control

A LabView program (Gomez, 1997) is used to drive the solenoid valves, monitor temperatures and flows, and collect the output of the CO_2 analyser. To conserve reference and calibration gases, each analysis period of a calibration gas is monitored. When the standard deviation of the 1 Hz data is within 0.02 ppm for 1 min, the gas jog, or measurement, is accepted as stable, and the mean value and standard deviation for that last minute is logged before analysing the next gas. This typically leads to calibration gas analysis periods of 4 min. Sample gas readings following a valve switch are ignored until a cumulative cell flush of 200 ml is achieved, typically within approximately 80 s. Averages and statistics are calculated on the subsequent sample data over 5 min intervals.

3.5 Significant changes to the system

Though the general architecture of the CO_2 system shown in Fig. 2 has remained unchanged since initial installation at Makara in 1970, several modifications have been made over the years to improve different aspects of the setup. The original system used a single polyethylene line, but in 1976 this was changed to two 316 stainless steel lines, and later changed to Synflex in 2011, these changes were undertaken with comparison of airlines to ensure data integrity. Also in 1976 the effective dew point of the cryo trapping system was reduced from −30 °C to −50 °C, then reduced again to its current value of −80 °C in 1998. Prior to 1982, calibration gases were mixtures of CO_2 in nitrogen, but have been CO_2 in air since (see Sect. 4). The system originally used a URAS-1 (Hartmann and Braun Instruments) infrared analyser, switched to a URAS-2T in 1976 (Lowe et al., 1979), and to the current Siemens Ultramat 3 in 1985 (Manning and Pohl, 1987), each instrument change involved rigorous comparisons to ensure continuity. In 1987, the total number of calibration gases was increased from 8 to 12, with 4 additional lines added in 1999. Prior to 1993, the calibration gases also went through the cryogenic dryer. Before to the removal of the dryer, the system had 10 µm inline particle filters with polycarbonate bowl and manual drain located at the inlet to the pump. In 2012, 10 µm inline type Teflon filters (Headline Filters, type 117-G) were added immediately before the inlet lines enter the building to reduce salt and dust particles.

The provider of WMO transfer standards was changed from SIO to the National Oceanic and Atmospheric Administration (NOAA) in 1994. Prior to this, all calibration and working gases had originated from SIO, and after that working tanks were prepared at NIWA. To conserve data storage, the system originally recorded 30 min average values and statistics, but in 1997 this was changed to 5 min values, and the system now also saves 1 s values for additional diagnostics. From 2001 on, the system used pressure relief valves instead of needle valves on the sample and purge pump lines, but these were returned to needle valves in 2010 allowing condensation to pass better.

Further information on specific aspects of the historic measurement programme can be obtained from laboratory reports (Manning and Pohl, 1986, 1987; Manning, 1994; Manning et al., 1994; Gomez, 1997; Brailsford et al., 2011). The DSIR/NIWA reports are available through the NIWA library (http://www.niwa.co.nz/news-and-publications).

4 Calibration protocols

The control program is designed to minimise gas usage while maintaining a high degree of precision through the selection of appropriate calibration cycles. These cycles are constructed so that the sequence of gas jogs varies, helping to detect and remove possible biases caused by incomplete flushing or surface recovery from running a previous gas. The nominal “Cycle 1” is used to monitor the variability of the CO_2 mole fraction in the sample air and to track analyser drift. It uses a suite of 4 working gases, 3 of which are selected to be measured every 2 h in a cycle that measures each selected gas twice. The analyser determines if the ambient CO_2 mole fractions have a standard deviation over a 4-h period of 0.2 ppm or less. If this stability criterion is met, then a “Cycle 2” of 3 working gases twice each is run every hour. This ensures that the instrument response is more accurately determined over these periods, which are used to define background CO_2 trends. Prior to 1998, Cycle 1 measured 3 working gases every 3.5 h, and Cycle 2 measured 3 working gases every 1.5 h. Transfer tanks that have CCL calibrations are nominally measured every 2 weeks in a “Cycle 3” that typically includes 8 CCL tanks and the 4 working tanks, and may include additional working tanks in preparation or tanks being measured for other purposes.

For Cycle 3, the system first flushes the regulators on all tanks to be analysed for approximately 8 min each before the measurements are made, and then cycles through all cylinders 7 times varying the cylinder order. This cycle is designed to characterise slowly changing aspects of the instrument response and to define the mole fractions of the working and other cylinders. Using these procedures, the life of 30 l working tanks is approximately 9 months and the life of 30 l calibration transfer gases is in excess of 15 yr. Transfer gases are managed in suites of 4, typically arranged to cover a mole fraction range of 30 ppm centred on steady interval air CO_2 mole fractions. All calibration transfer gases are assigned mole fractions at the WMO CCL prior to use in New Zealand and are returned to the CCL at the end of their life for recalibration to check for drift. When possible and especially in cases when drift was suspected, the cylinders have been returned to the CCL for more frequent recalibrations.

The processing of the calibration gas measurements also solves for errors in individual cylinder assignments (Manning and Pohl, 1987). By tracking these apparent offsets, excessively drifting cylinders can be identified and removed from the analysis procedure if necessary. The reassignment of a transfer gas mole fraction only occurs if a CCL recalibration shows it to have changed composition, in which case a linear trend is applied between the measurements. When working gases have been found to be drifting in CO_2 mole fraction, we also assign their values based on a linear trend over the drifting period. Cylinder drift is typically less than 0.2 ppm over the life of the cylinder as found elsewhere (Kitzis, 2009; Langenfelds et al., 2005), but there have been several cases of cylinders that drifted by as much as 2 ppm.

The Baring Head measurements were initiated before the so-called "carrier-gas effect" (Bischoff, 1975; Pearman and Garratt, 1975) was understood. This refers to the importance of the balance of N_2 and O_2 in the calibration gases. Until 1978 measurements were made using calibration gases of CO_2 in N_2. After the discovery of the carrier-gas effect, a combination of CO_2 in N_2 and CO_2 in natural air standards were used during the period 1978–1992, allowing the sensitivity of the analyser to this effect to be characterized, and time- and concentration-dependent corrections, on the order of 3 ppm, were applied to the CO_2 in N_2 cylinder mole fractions (Manning and Pohl, 1987).

5 Data processing

Raw CO_2 analyser signals and diagnostic parameters are transmitted back to NIWA on a daily basis. We then use customized software routines to screen the data for problems, plot various diagnostics, calculate fits to calibration measurements, and apply these calibrations to the final measurements. Historically, these tasks were performed by a series of manually executed Fortran, IDL, MS Access, and MS Excel routines that made timely production of calibrated data and propagation of retroactive changes to primary reference scales difficult. Recently, we have replaced this legacy system with a series of automated scripts in the free statistical software R (http://www.r-project.org), that achieve the same tasks with greater transparency, ease of use, and ability to handle calibration scale changes. The new data processing system has been designed and checked to be functionally consistent with the earlier procedures documented by Manning and Pohl (1987), and applies the most current scales to the calculations. For the transfer cylinders calibrated by SIO prior to 1995 the SIO 08A scale is applied and for the transfer cylinders calibrated by NOAA starting in 1994 the WMO X2007 scale is applied.

Throughout our data processing, we propagate error estimates for our measurements that are reported along with the final data. These error estimates are the combination of errors associated with short-term signal variability, drift in the analyser between calibration intervals, and errors in the working tank mole fraction assignments. The contribution from short-term variability is estimated from the standard deviation within the 30-min or 5-min averaging periods. Early in the record, these standard deviations were calculated on 1-min values within the longer average time period, but have more recently been calculated on 1-s measurements. In practice, the variability over 5- or 30-min periods is dominated by relatively slow changes in either actual mole fractions or instrument response, such that standard errors calculated using 1-s or 1-min values are usually very similar.

The error contribution from drift in analyser response between calibrations is typically 0.05 ppm, and the error in the working tank mole fraction assignments is assumed to be 0.2 ppm. We sum these two error contributions, and the contribution from short-term variability, geometrically to generate final error estimates that are nominally 0.3 ppm on 5- to 30-min measurements during stable CO_2 conditions. It is important to note, however, that most contributions to errors in atmospheric CO_2 measurements are systematic and not random in nature, and a rigorous assessment of compatibility between any two different measurement records or laboratory programmes can only be achieved through intercomparison activities (WMO, 2011, see also Sect. 6).

CO_2 mole fraction data are recorded for all wind conditions, but certain data are selected to represent baseline air that is well mixed and free from recent terrestrial influences. Baseline air data are identified through a filtering process that takes into account the variability in atmospheric CO_2 and meteorological conditions that indicate the site is sampling clean air that recently passed over the Southern Ocean (Stephens et al., 2012). Data are considered only if the standard deviation of measured values from a single inlet line over a six hour period is 0.1 ppm or less, allowing for data gaps with calibrations or other instrument down time of up to 2 h. Multiple overlapping periods of steady data are then combined to form steady intervals, such that CO_2 can trend significantly within a several-day steady interval as long as 6-hourly sub-periods still satisfy the variability criteria. The steady intervals are further selected for southerly wind conditions only, as strong northerlies can show terrestrial influence but also have low CO_2 variability. Finally, a filter is imposed to exclude data that corresponds to air flow over the South Island land mass. This is achieved by ensuring the atmospheric pressure at Christchurch on the east coast is 1 hPa or greater than that at Hokitika on the west coast at the time of data collection (Manning and Pohl, 1986). Steady interval data that meet these criteria are combined to form a baseline air dataset for the site (Fig. 3). The fit and trend lines in this figure are calculated using the Seasonal-Trend Decomposition procedure by Loess (STL) (Cleveland et al., 1990), a filtering procedure that decomposes timeseries data into trend, seasonal and residual components. A trend window of 25 months was used in this calculation. In addition to the steady interval data, a dataset is compiled of all mean hourly values. These data include all wind directions, and are reported along with wind speed, wind direction, and within-hour CO_2 variability, to allow for subsequent filtering. These data are available via ftp (ftp://ftp.niwa.co.nz/tropac/), or from the World Data Centre for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdcgg/).

6 Intercomparisons

In addition to the continuous measurements of CO_2, we also carry out several flask collection programmes at Baring Head. These flasks serve the dual purposes of providing an important independent comparison to the continuous analyser and allowing for a number of additional gas species and isotope ratios to be measured. Since 1977, evacuated 5 l glass flasks have been manually collected on average every 3 weeks and returned to SIO for measurement of CO_2 mole fractions, with stable isotope ratios of

$^{13}C/^{12}C$ and $^{18}O/^{16}O$ in CO_2 also measured since 1985. Also, starting in 1999, we have collected pairs of 2.2 l glass flasks biweekly, using an automated system, for analysis by NOAA of CO_2, CH_4, CO, N_2O, SF_6, and H_2 mole fractions, and the stable isotope ratios in CO_2. Between 2000 and 2002, a flask collection was carried out in collaboration with CSIRO in Australia, and currently we are in the initial stages of a co-located CSIRO LoFlo (Francey and Steele, 2003) instrument deployment that will allow comparison of two continuous analysers operating at Baring Head simultaneously. Finally, a cavity ring down spectroscopy instrument (Picarro Inc, G2301) has been under assessment since 2011 as a successor instrument to the Siemens NDIR.

Additional quality control is provided by results from WMO round-robin cylinder intercomparison exercises. These comparisons are designed to assess the ability of a laboratory to maintain the WMO mole fraction scale by determining the CO_2 mole fraction in a suite of unknown cylinders as compared to internal laboratory calibration gases. NIWA has participated in all five of these round-robin exercises to date, with differences between DSIR/NIWA measurements and assigned CCL values on 2 to 3 cylinders per comparison are typically ~ 0.08 ppm with a maximum deviation of 0.20 ppm (Table 1).

Figure 4 shows the results of the SIO, NOAA, CO_2 intercomparison efforts at Baring Head. The automated flask system is programmed to collect NOAA flasks during southerly stable-CO_2 conditions, allowing for a lower influence of atmospheric variability on the comparison with the in situ instrument. For the manual SIO flask collections, efforts are made to collect flasks during southerly conditions, but because of the constraint of field visits only once per week this is not always possible. A significant part of the variability in the flask in situ comparisons, in particular those to SIO flasks, is likely due to real atmospheric variability and the difficulty in sampling the same air. Despite this variability, the biennially-smoothed difference curves shown in Fig. 4 provide valuable information on potential systematic biases in the different methods on several-year timescales.

These indicate that over the early part of the record, systematic differences between Baring Head in situ and Scripps flask measurements could be as large as 0.8 ppm, but that over the more recent period, the comparisons of the continuous measurements to Scripps, NOAA, and NIWA flasks are generally 0.3 ppm or better. The recent intercomparison results are generally consistent within the combined in situ and flask error estimates, and we find whole population medians (±1-σ) for the SIO and NOAA intercomparisons of 0.16 ± 0.52 ($n = 271$) and 0.05 ± 0.42 ($n = 113$) ppm, respectively. The variability in these values is significantly larger than the long-stated WMO goal of 0.05 ppm compatibility between laboratories in the Southern Hemisphere, but is not dissimilar from values found in other intercomparison programmes (WMO, 2011; Richardson et al., 2012; Masarie et al., 2001, 2011). Uncertainties in comparing atmospheric CO_2 data from different sites and measurement programmes limits the ability to make conclusions about CO_2 fluxes, in particular in the Southern Ocean (Law et al., 2008; Monfray et al., 1996, Stephens et al., 2012), and improving the quality and intercomparability of on-going measurements remains a high priority at Baring Head and for the community as a whole.

7 Conclusions

Baring Head is the longest running in situ CO_2 monitoring station in the Southern Hemisphere. Back trajectory analysis demonstrates that during southerly conditions Baring Head is exposed to air that has most recently passed over the Southern Ocean (Stephens et al., 2012). This region has been of great interest to the carbon cycle community in recent years due to findings that suggest the efficiency of the Southern Ocean carbon sink may be slowing in response to climate and chemistry change (Wetzel et al., 2005; Lovenduski et al., 2007; Le Quéré et al., 2007).

The consistent operation of the Baring Head CO_2 observations has provided a valuable data set in a data-sparse region. We have presented atmospheric CO_2 mole fractions in baseline air representative of the mid- to high-latitudes of the Southern Hemisphere. As the region is dominated by ocean, the seasonal amplitudes are small compared to Northern Hemisphere stations that see strong terrestrial signals. The trend over the time series is consistent with those observed at other stations. The strengths of this measurement programme are that it has generated a time series over four decades that is homogeneous and directly tied to CCL reference scales and that the high time resolution in situ record allows for sophisticated filtering for various analytical needs. The redundancy built in to the calibration procedure allows for the possibility of detecting drifting gases that can be compensated for, ensuring robustness to the data analysis. This is particularly critical for mid to high latitude Southern Hemisphere stations, where the atmospheric CO_2 variations that need to be detected are small.

The importance of intercomparison within a measurement programme has been demonstrated with the flask intercomparison and WMO round robin programmes. These have been a feature of the Baring Head measurements, with both providing information regarding the comparability of the CO_2 observations. We are evaluating recent advances in instrumentation for the measurement of atmospheric CO_2 and plan to operate the site with the best-available technology, while still maintaining strong links to the CCL and the earlier calibration in the long-term record.

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References

Beaulieu, C., Sarmiento, J. L., Mikaloff Fletcher, S. E., Chen, J., and Medvigy, D.: Identification and characterization of abrupt changes in the land uptake of carbon, Global Biogeochem. Cy., 26, GB1007, doi:10.1029/2010GB004024, 2012.

Bischof, W.: The influence of the carrier gas on the infrared gas analysis of atmospheric CO_2, Tellus, 27, 59–61, 1975.

Bousquet, P., Peylin, P. Ciais, P., LeQuèrè, C., Friedlingstein, P., and Tans, P. P.: Regional changes in carbon dioxide fluxes of land and oceans since 1980, Science, 290, 1342–1346, 2000.

Brailsford, G. W., Sherlock, V., Gomez, A., Riedel, K., Smale, D., Kotkamp, M., Stephens, B., Robinson, J., Connor, B., and Mikaloff Fletcher, S. E.: In situ and ground-based remote sensing measurements of atmospheric CO_2 in New Zealand, in: 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, edited by: Brand, W., WMO TD No. 1553, 58, Jena, Germany, 2011.

Cleveland, R. B., Cleveland, W. S., McRae, J. E., and Terpenning, I.: STL: a seasonal-trend decomposition procedure based on Loess, J. Official Stat., 6, 3–33, 1990.

Conway, T. J., Tans, P. P., Waterman, L. S., Thoning, K. W., Kitzis, D. R., Masarie, K. A., and Zhang, N.: Evidence for interannual variability of the carbon cycle from the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory Global Air Sampling Network, J. Geophys. Res., 99, 22831–22855, doi:10.1029/94JD01951, 1994.

Enting, I. G. and Mansbridge, J. V.: Latitudinal distribution of sources and sinks of atmospheric CO_2: direct inversion of filtered data, Tellus B, 41, 111–126, 1989.

Francey, R. J. and Steele, L. P.: Measuring atmospheric carbon dioxide-the calibration challenge, Accred. Qual. Assur., 8, 200–204, 2003.

Gomez, A. J.: The CO_2 remote control system at Baring Head, in: Report of the Ninth WMO Meeting of Experts on Carbon Dioxide Concentration and Related Tracer Measurement Techniques, edited by: Francey, R., WMO TD No. 952, Aspendale, Australia, 1997.

Jones, C. D. and Cox, P. M.: On the significance of atmospheric CO_2 growth rate anomalies in 2002–2003, Geophys. Res. Lett., 32, L14816, doi:10.1029/2005GL023027, 2005.

Keeling, C. D.: The concentration and isotopic abundances of carbon dioxide in the atmosphere, Tellus, 12, 200–203, 1960.

Keeling, C. D., Whorf, T. P., Wahlen, M., and van der Plicht, J.: Interannual extremes in the rate of rise of atmospheric carbon dioxide since 1980, Nature, 375, 666–670, doi:10.1038/375666a0, 1980.

Keeling, C. D., Piper, S. C., Bacastow, R. B., Wahlen, M., Whorf, T. P., Heimann, M., and Meijer, H. A.: Exchanges of atmospheric CO_2 and $^{13}CO_2$ with the terrestrial biosphere and oceans from 1978 to 2000, I. Global aspects, SIO Reference Series, No. 01–06, Scripps Institution of Oceanography, San Diego, 2001.

Kitzis, D.: Preparation and stability of standard reference air mixtures, available at: http://www.esrl.noaa.gov/gmd/ccl/airstandard.html (last access: August 2012), 2009.

Langenfelds, R. L., van der Schoot, M. V., Francey, R. J., and Steele, L. P.: Modification of air standard composition by diffusive and surface processes, J. Geophys. Res., 110, D1330730, doi:10.1029/2004JD005482, 2005.

Law, R. M., Matear, R. J., and Francey, R. J.: Comment on “Saturation of the Southern Ocean CO_2 sink due to recent climate change”, Science, 319, 570, 2008.

Le Quéré, C., Rödenbeck, C., Buitenhuis, E. T., Conway, T. J., Langenfelds, R., Gomez, A., Labuschagne, C., Ramonet, M., Nakazawa, T., Metzl, N., Gillett, N., and Heimann, M.: Saturation of the Southern Ocean CO_2 sink due to recent climate change, Science, 316, 1735, doi:10.1126/science.1136188, 2007.

Lovenduski, N. S., Gruber, N., Doney, S. C., and Lima, I. D.: Enhanced CO_2 outgassing in the Southern Ocean from a positive phase of the Southern Annular Mode, Global Biogeochem. Cy., 21, GB2026, doi:10.1029/2006GB002900, 2007.

Lowe, D. C.: Automatic atmospheric CO_2 monitoring equipment, DSIR, Institute of Nuclear Sciences, Lower Hutt, New Zealand, available at: http://webcat.niwa.co.nz/documents/INS-R-112.pdf (last access: August 2012), 1972.

Lowe, D. C., Guenther, P. R., and Keeling, C. D.: The concentration of atmospheric carbon dioxide at Baring Head, New Zealand, Tellus, 31, 58–67, 1979.

Manning, M. R.: Status of New Zealand CO_2 measurement programme, in: Report of the Seventh WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, 7–10 September 1993, edited by: Pearman, G. I. and Peterson, J. T., WMO TD No. 669, Rome, Italy, 1994.

Manning, M. R. and Pohl, K. P.: Atmospheric carbon dioxide monitoring in New Zealand, 1971–1985, DSIR, Institute of Nuclear Sciences, Lower Hutt, New Zealand, available at: http://webcat.niwa.co.nz/documents/INS-R-350.pdf (last access: August 2012), 1986.

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Manning, M. R. and Pohl, K. P.: A review of analyser calibration gas mixtures used in the New Zealand CO_2 monitoring program, DSIR, Institute of Nuclear Sciences, Lower Hutt, New Zealand, 1987.

Manning, M. R., Gomez, A. J., and Pohl, K. P.: Atmospheric CO_2 record from in situ measurements at Baring Head, in: Trends'93: A Compendium of Data on Global Change, ORNL/CDIAC-65, edited by: Boden, T. A., Kaiser, D. P., Sepanski, R. J., and Stoss, F. W., Oak Ridge, Tenn., USA, 1994.

Masarie, K. A., Langenfelds, R. L., Allison, C. E., Conway, T. J., Dlugokencky, E. J., Francey, R. J., Novelli, P. C., Steele, P. L., Tans, P. P., Vaughn, B., and White, J. W. C.: The NOAA/CSIRO flask-air intercomparison program: a strategy for directly assessing consistency among atmospheric measurements derived from independent laboratories, J. Geophys. Res., 106, 20445–20464, 2001.

Masarie, K. A., Petron, G., Andrews, A., Bruhwiler, L., Conway, T. J., Jacobson, A. R., Miller, J. B., Tans, P. P., Worthy, D. E., and Peters, W.: Impact of CO_2 measurement bias on CarbonTracker surface flux estimates, J. Geophys. Res.-Atmos., 116, D17305, doi:10.1029/2011JD016270, 2011.

Monfray, P., Ramonet, M., and Beardsmore, D.: Longitudinal and vertical CO_2 gradients over the subtropical/subantarctic oceanic sink, Tellus, 48, 445–456, 1996.

Pearman, G. I. and Garratt, J. R.: Errors in atmospheric CO_2 concentration measurements arising from the use of reference gas mixtures different in composition to the sample air, Tellus, 27, 62–65, 1975.

Richardson, S. J., Miles, N. L., Davis, K. J., Crosson, E. R., Rella, C., and Andrews, A. E.: Field testing of cavity ring-down spectroscopy analyzers measuring carbon dioxide and water vapor, J. Atmos. Ocean. Tech., 29, 397–406, doi:10.1175/JTECH-D-11-00063.1, 2012.

Stephens, B. B., Brailsford, G. W., Gomez, A. J., Riedel, K., Mikaloff Fletcher, S., Nichol, S., and Manning, M.: Analysis of a 39-year continuous atmospheric CO_2 record from Baring Head, New Zealand, Biogeosciences, in preparation, 2012.

Tans, P. P., Fung, I. Y., and Takahashi, T.: Observational constraints on the global atmospheric CO_2 budget, Science, 247, 1431–1438, 1990.

Wetzel, P., Winguth, A., and Maier-Reimer, E.: Sea-to-air CO_2 flux from 1948 to 2003: a model study, Global Biogeochem. Cy., 19, GB2005, doi:10.1029/2004GB002339, 2005.

WMO: Report of the 15th WMO/IAEA Meeting of Experts on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques, edited by: Brand, W., WMO TD No. 1553, Jena, Germany, 2011.

Table 1. Results from WMO round robin intercomparisons, tabulated as the ppm differences between the DSIR/NIWA determined values and the central calibration laboratory assigned values (L. Zhou, personal communication, 2009–2011).

Comparison date	CCL determined mole fraction			Difference NIWA – CCL		
1991–1992	341.50	348.89		−0.11	−0.12	
1995–1997	342.21	358.90	376.79	0.02	0.10	0.20
1999–2000	349.89	364.50	381.30	0.05	0.03	0.09
2002–2006	353.60	366.28	383.31	−0.08	−0.08	−0.09
2009–2011	373.92	387.55	401.66	−0.00	−0.03	−0.07

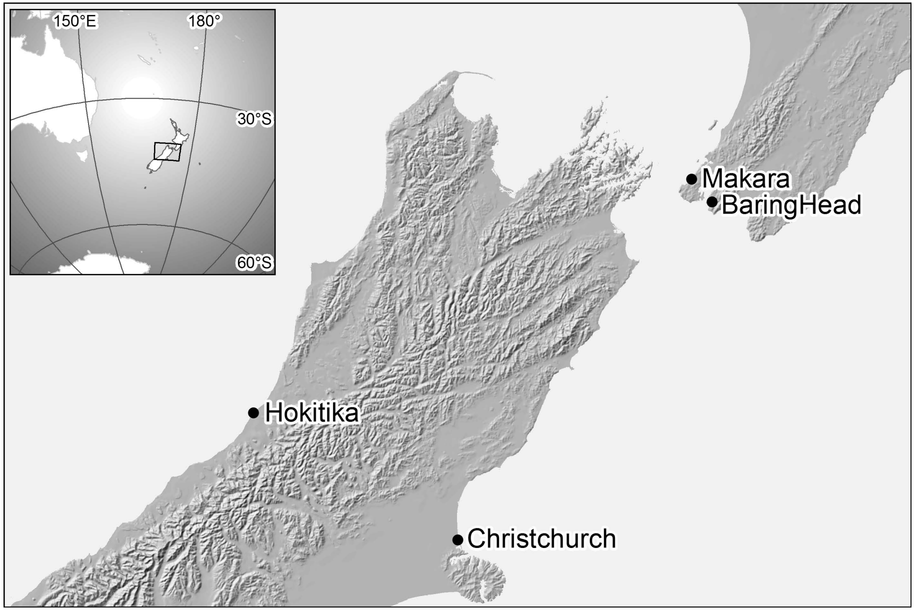

Fig. 1. Map showing the location of Baring Head station. The mountain range between Hokitika and Christchurch allows for the identification of atmospheric pressure differentials that ensure air arriving at Baring Head has not been in contact with the South Island land mass.

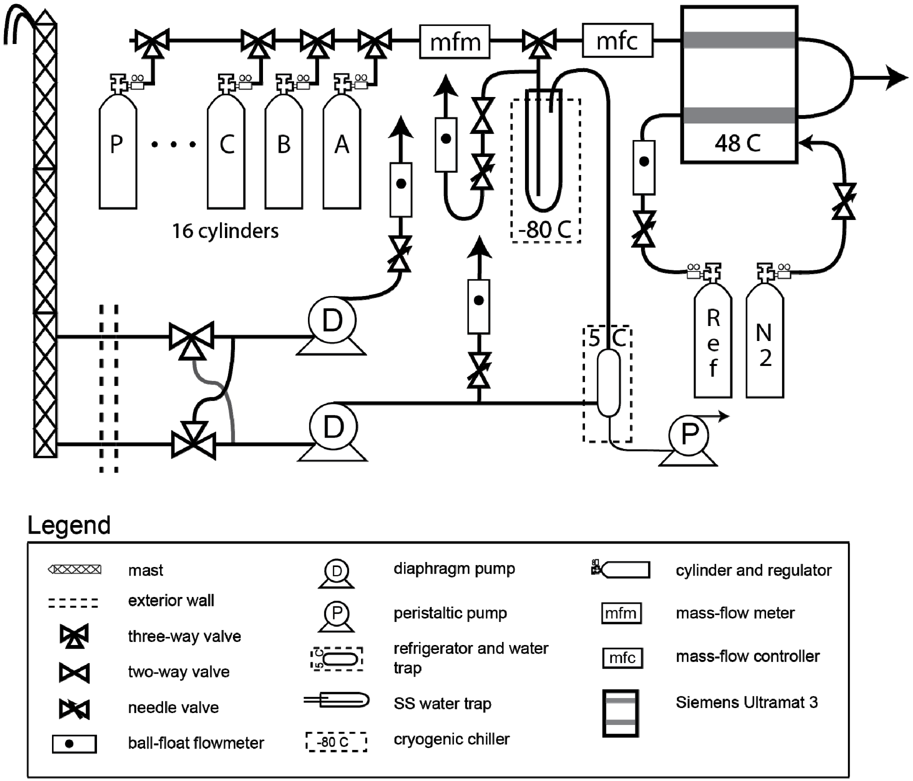

Fig. 2. Schematic of the Baring Head CO_2 system. Components include two alternating inlet lines, pumps, needle-valves, mass flow meter, mass flow controller, solenoid valve, fridge and cryo water traps, a Siemens Ultramat 3 CO_2 analyser, and reference gases for calibrating with respect to the WMO CO_2 scale.

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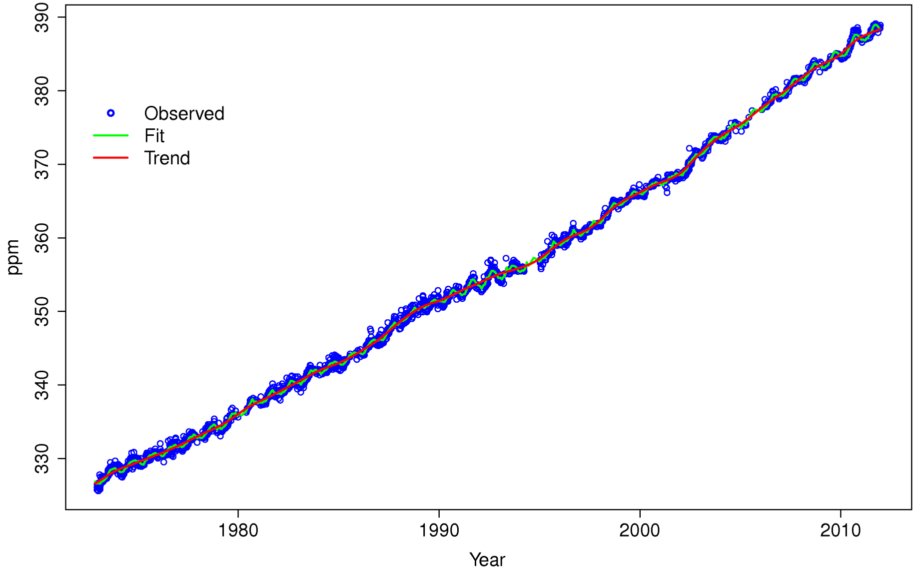

Fig. 3. Baring Head southerly interval CO_2 timeseries. The steady interval observations are plotted (blue) with a fit to the observations (green) and deseasonalised trend (red) calculated using STL.

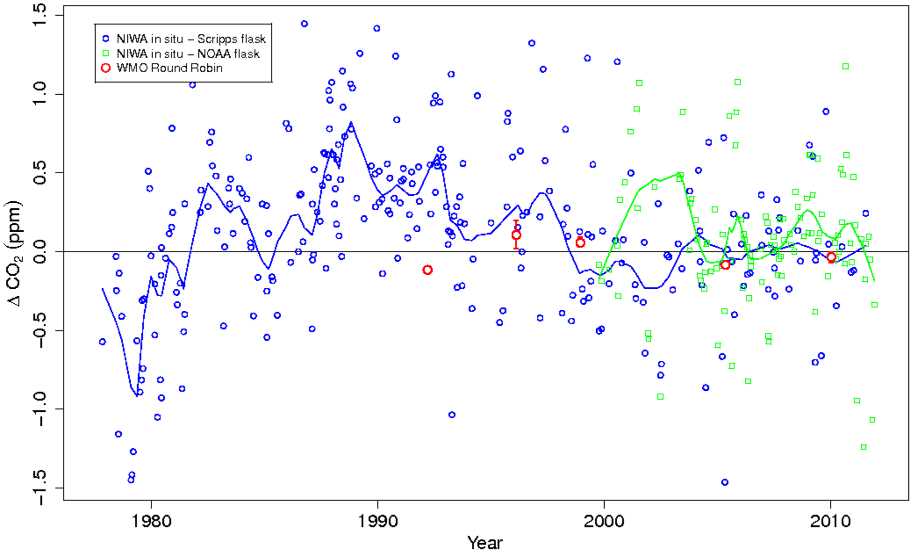

Fig. 4. Intercomparison results shown as the difference between in situ Baring Head measurements and Scripps flasks, NOAA flask pairs, and WMO round-robin cylinders, respectively. Comparisons have been filtered for a minimum time difference of 30 min, a maximum standard deviation on in situ CO_2 over a centred 2-h period of 0.75 ppm, and to exclude outliers $> 3\sigma$. Lines represent loess filters to each data set using a 2-yr smoothing window.

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