

## FINAL REPORT

A Study of the Abundance and  $^{13}\text{C}/^{12}\text{C}$  Ratio of Atmospheric Carbon Dioxide to Advance the Scientific Understanding of Terrestrial Processes Regulating the GCC.

This is the final report for Grant DE-FG02-04ER63898, which provided three years of support, starting Sept. 2004. This grant, together with continuing grants from the National Science Foundation, provided the core support for the Scripps CO<sub>2</sub> program over the grant period. The DOE effort has been continued under a more recent DOE grant (DE-FG02-07ER64362) which started in Sept 2007.

### OBJECTIVES AND APPROACH:

The main objective of this project was to continue research to develop carbon cycle relationships related to the land biosphere based on remote measurements of atmospheric CO<sub>2</sub> concentration and its isotopic composition. The project continued time-series observations of atmospheric carbon dioxide and isotopic composition begun by Charles D. Keeling at remote sites, including Mauna Loa, the South Pole, and eight other sites. The program also included the development of methods for measuring radiocarbon content in the collected CO<sub>2</sub> samples and carrying out radiocarbon measurements in collaboration with Tom Guilderson of Lawrence Berkeley National Laboratory (LLNL). The radiocarbon measurements can provide complementary information on carbon exchange rates with the land and oceans and emissions from fossil-fuel burning. Using models of varying complexity, the concentration and isotopic measurements were used to establish estimates of the spatial and temporal variations in the net CO<sub>2</sub> exchange with the atmosphere, the storage of carbon in the land and oceans, and variable isotopic discrimination of land plants.

### OPERATIONAL ACTIVITIES:

#### Remote Sampling

The most extensive activity under this grant has been the continuation of time-series measurements of the concentration and  $^{13}\text{C}/^{12}\text{C}$  and  $^{18}\text{O}/^{16}\text{O}$  isotopic ratios of atmospheric carbon dioxide CO<sub>2</sub> at an array of remote sites, extending from Alaska to the South Pole. At all stations, samples of air are collected in 5-liter glass flasks and returned to our instrument laboratory for analysis. At Mauna Loa Observatory, Hawaii, and at La Jolla, CO<sub>2</sub> concentration is also measured continuously with on-site analyzers. Flask sampling frequency is once per week except at the three southernmost stations, where it is approximately half as often or less: Raoul I. in the Kermadec Islands, Baring Head, New Zealand, and the South Pole. Samples were also collected in collaboration with Seoul National University, South Korea, and El Centro de Investigacion Cientifica y de Education Superior de Ensenada (CICESE) of Baja California. The stations are, respectively: Cheju-Do Island near Korea (1990 to present) and on the coast of Mexico

near La Paz (1997 to present). The Korean effort provides Seoul National University with intercomparisons with our data, but does not furnish an especially useful data set for our program. The second effort, however, has furnished data to be added to that of our present station array.

### **Sampling in vegetated areas.**

We have also continued the program to study gas exchange in vegetated areas by collecting and analyzing air samples over the diurnal cycle in the summer (~ August 1<sup>st</sup>), extending time-series going back to 1987 at two forest sites: Hamilton, Montana in the United States and Rock Lake in Alberta, Canada.

### **Archiving of CO<sub>2</sub>**

Under this grant we have continued to archive CO<sub>2</sub> samples in glass ampoules from flasks collected at the remote sites. A subset of this archive has been used for radiocarbon measurements in collaboration with LLNL.

## **CAPACITY BUILDING:**

### **Radiocarbon measurements**

A significant achievement in this funding period was the completion of the Ph.D. thesis of Heather Graven. This project involved a close collaboration with Guilderson of LLNL to improve the capability for making high precision radiocarbon measurements and to apply this capability to measure archived CO<sub>2</sub> samples from the Scripps CO<sub>2</sub> program, thus producing long-term high quality time series at the Scripps sites. The resulting data are shown in Figure 1. Results from all sites show an irregular seasonal cycle and a long-term decreasing trend. The results, which comprise the most comprehensive large-scale dataset for <sup>14</sup>C variability, are qualitatively similar but more precise than most previous observations. The data contain useful constraints on ocean circulation, gas exchange, and fossil-fuel burning. Heather's thesis can be downloaded from [http://bluemoon.ucsd.edu/publications/heather/thesisHG\\_050708.pdf](http://bluemoon.ucsd.edu/publications/heather/thesisHG_050708.pdf)

### **Instrumentation Upgrades**

Under this grant we completed an upgrade in the instrumentation used at Mauna Loa, replacing the original Applied Physics Corporation (APC) analyzer used since the 1950s with a modern Siemens Ultramat 6 instrument. This transition included a ~1 year overlap period that demonstrated consistency between the two analyzers to a high level, as summarized in a technical report prepared by Stephen Walker.

### **Data reduction**

Under this grant we also carried out an upgrade in the processing of the data streams from flasks and continuous measurements. These streams were previously maintained by Tim Whorf, using an approach that combined Fortran programs with manual flagging of outlier data and manual handling of intermediate data files. The new approach, developed by Stephen Walker, automates the entire process, under control of a Matlab “shell” program, that variously invokes the original Fortran routines as well as invoking

new routines for flagging and handling of intermediate files. The new approach has been applied to all data since 2001, with Tim's results retained for previous years. On the basis of several years of overlap, we have verified that the new algorithms satisfactorily duplicate the methods used by Tim without introducing biases, thus ensuring uniform time series over the transition. Despite the automation, visual inspection of recent results is still carried out on a regular basis by Stephen Walker as an additional quality check.

### **CALIBRATION ACTIVITIES:**

Under this grant and a parallel grant from NSF, work continued to bring about a coordination of measurements at Scripps with those at the Global Monitoring Division (GMD) of NOAA (formerly NOAA-CMDL) based on manometric determinations of reference gases at both institutions. This work required bringing back into operation the constant volume mercury manometer (CMM), used at Scripps since ~1960 and shut down temporarily in 1999 as the result of a building refurbishment.

We completed manometric analyses of CO<sub>2</sub> in air from nine high pressure tanks, prepared and analyzed manometrically by NOAA. The measurements were at done at Scripps on the CMM as well as on a newer electronic manometer developed at Scripps principally for seawater work. The results showed good agreement between NOAA and the Scripps electronic manometer but showed a concentration-dependent offset with the original Scripps manometer of up to several tenths of a ppm. Additional work was carried out to assess possible sources of systematic error, including recalibration of the mercury thermometers used on the CMM, an independent assessment of the CMM pressure measurements by calibration against a dead-weight tester, an evaluation of possible temperature gradients induced by lamp illumination, and an assessment of possible drift in the "plenums" used to assess the volumes on the CMM and electronic manometers.

An important finding, confirming earlier suspicions, is that the volumes of the glass "plenums" used to calibrate the volumes on the CMM have not remained constant, but decreased very slightly over time since they were brought into use in the early 1970s. This drift evidently reflects small distortion of the glass over time. Pending the complete analysis of these and other test results, we have "frozen" the Scripps CO<sub>2</sub> scale to yield constant values for particular set of reference gases (so-called "white stripes"), without regard for whether these gases may have drifted. Although we believe any such drift is small, the fact that the recent data are not closely tied to a manometric calibration is clearly undesirable. Until we decide on the proper interpretation of the manometric calibration data (including measurements extending back two decades), it is premature to make adjustments to our results. We continue to work to resolve this issue.

### **INTERPRETATIONAL ACTIVITIES AND FINDINGS:**

#### **Anomalous CO<sub>2</sub> growth**

Measurements of CO<sub>2</sub> and <sup>13</sup>C/<sup>12</sup>C at all stations in our network provided the basis for analysis of regional and global variations of atmospheric CO<sub>2</sub>. A global average was formed by weighting station data according to surface area in zones extending halfway (in latitude) to each neighboring station. As shown in Figure 2, atmospheric CO<sub>2</sub> and <sup>13</sup>C/<sup>12</sup>C continue to vary in close concert with each other and in synchrony with the Southern Oscillation Index, up through the latest 'warm' event in late 2005. The pattern shows that the land biosphere continues to be the main cause of variations of atmospheric CO<sub>2</sub> on the El Niño time scales.

We have continued studies to assess whether recent increases in the atmospheric CO<sub>2</sub> growth rate are anomalous relative to the expected response to fossil-fuel burning and the ocean and land sinks on decadal time scales. Measurements by the Scripps program at Mauna Loa and other sites show that the CO<sub>2</sub> concentration achieved record levels in 2008, as they have in nearly all prior years, reflecting the unabated global rise. Recent media coverage of this rise, as reported also based on independent NOAA CO<sub>2</sub> data, has emphasized that the recent rise has been unexpectedly rapid, fueling fears that the natural sinks for CO<sub>2</sub> are slowing or saturating (e.g. U.K. Guardian, 12 May 2008).

These accounts overlook the continuing very close relationship between the rise and global fossil-fuel emissions. A best fit of fossil fuel emissions to the Mauna Loa CO<sub>2</sub> record from 1958 to present gives 0.57 for the 'airborne fraction' – i.e. 57% of fossil fuel emissions remain airborne. This fraction varies from year to year, but has held fairly constant when the record is viewed in 5-year increments. The last year for which CDIAC lists fossil emissions is 2005 at 7.985 PgC. Assuming conservatively that fossil emissions have grown at a rate of 2.5% per year since 2005, we get 8.39 PgC for 2007. If mixed uniformly in the atmosphere, this would yield a rise of 2.27 ppm atmospheric increase expected for 2007. The observed rise over the past year was around 2.1 ppm, very close to the expectation from this simple calculation. On this basis, it appears that the recent rise in atmospheric CO<sub>2</sub> is very consistent with past rises, reflecting growth in fossil-fuel emissions and a generally proportional rise in the sinks. The data, by themselves, offer no compelling evidence for slowing or saturation of the sinks.

This perspective draws support from a manuscript which we have recently submitted to the journal *Tellus* by L. E. Rafelski, S.C. Piper, and R.F. Keeling entitled “Climate effects on atmospheric carbon dioxide over the past century”. L.E. Rafelski is a graduate student under the supervision of the principal investigator. The manuscript is essentially an update of C. D. Keeling et al (*Nature* **375**, 666-670, 1995), using explicit modeling of land temperature effects on land biota to investigate the causes of decadal fluctuations in growth rate seen in the ice core and modern CO<sub>2</sub> records. The analysis suggests that slowing of growth of CO<sub>2</sub> from 1940-1955 and the sustained growth in CO<sub>2</sub> after 1980 (despite a decrease in the growth of fossil-fuel emissions) may both be caused by temperature effects on land biota.

### **Seasonal Variations**

We continue to investigate causes of changes in the amplitude of the CO<sub>2</sub> seasonal cycles in the northern hemisphere in the context of changes in land biota metabolism, as

described in previous annual reports. This work was not brought to completion under the subject grant, but is continuing under the more recent renewal grant.

### **Regional radiocarbon measurements**

As an offshoot of her thesis project to measure radiocarbon in atmospheric CO<sub>2</sub>, Heather Graven also participated in an effort to assess the feasibility of using radiocarbon to assess regional fossil-fuel emissions. This work involved airborne sample collections (for radiocarbon analysis) as well as in situ airborne measurements of CO<sub>2</sub> and CO concentrations, and relied on partial support from this grant for extractions and isotopic analyses and extractions. A manuscript from this project, submitted to *Tellus*, demonstrates the feasibility of using radiocarbon to distinguish land biospheric and fossil-fuel contributions to the nocturnal CO<sub>2</sub> buildup.

### **Gradients and hemispheric source/sink relationships**

Work continued under this grant to advance towards publication two manuscripts that were in preparation at the time of Dave Keeling's passing, as described in the previous annual reports. The first of these involves an analysis of the long-term changes in the interhemispheric gradients in CO<sub>2</sub> concentration and <sup>13</sup>C/<sup>12</sup>C ratio, and second involves an interpretation of these changes on shorter time scales (e.g. associated with El Nino phenomenon). These projects are continuing under the more recent DOE grant.

## **DELIVERABLES**

### **Project Web Page**

A group website ([scrippsco2.ucsd.edu](http://scrippsco2.ucsd.edu)) serves as the primary outlet for data and graphical materials from the program. The target audience includes students, the public at large, the media, and the scientific community. This web site, which was substantially developed under support from this grant, displays updated high-quality plots of the Mauna Loa record and other "classic" plots from the program. The site also includes tabulated data available for download and discussion of the major program elements and their significance. The site continues to be refined and updated in response to user suggestions.

We continue also to submit our data to CDIAC.

### **Publications**

Hashimoto, H., et al., El Nino-Southern Oscillation-induced variability in terrestrial carbon cycle, *Journal of Geophysical Research*, 109, D23110, doi:10.1029/2004JD004959, 2004.

Keeling, C. D., et al., Atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> exchange with the terrestrial biosphere and oceans from 1978 to 2000: observations and carbon cycle implications, in *A History of Atmospheric CO<sub>2</sub> and its Effects on Plants, Animals, and Ecosystems*, editors, Ehleringer J. R., T. E. Cerling, M. D. Dearing, Springer Verlag, New York, 2004.

Keeling, C. D., S. C. Piper, R. B. Bacastow, M. Wahlen, T. P. Whorf, M. Heimann, and H. A. Meijer, Exchanges of atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> with the terrestrial biosphere and oceans from 1978 to 2000. I. Global aspects, SIO Reference Series, No. 01-06, 2001.

Piper, S. C., C. D. Keeling, M. Heimann, and E. F. Stewart, Exchanges of atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> with the terrestrial biosphere and oceans from 1978 to 2000. II. A three-dimensional tracer inversion model to deduce regional fluxes, SIO Reference Series, No. 01-07, 2001.

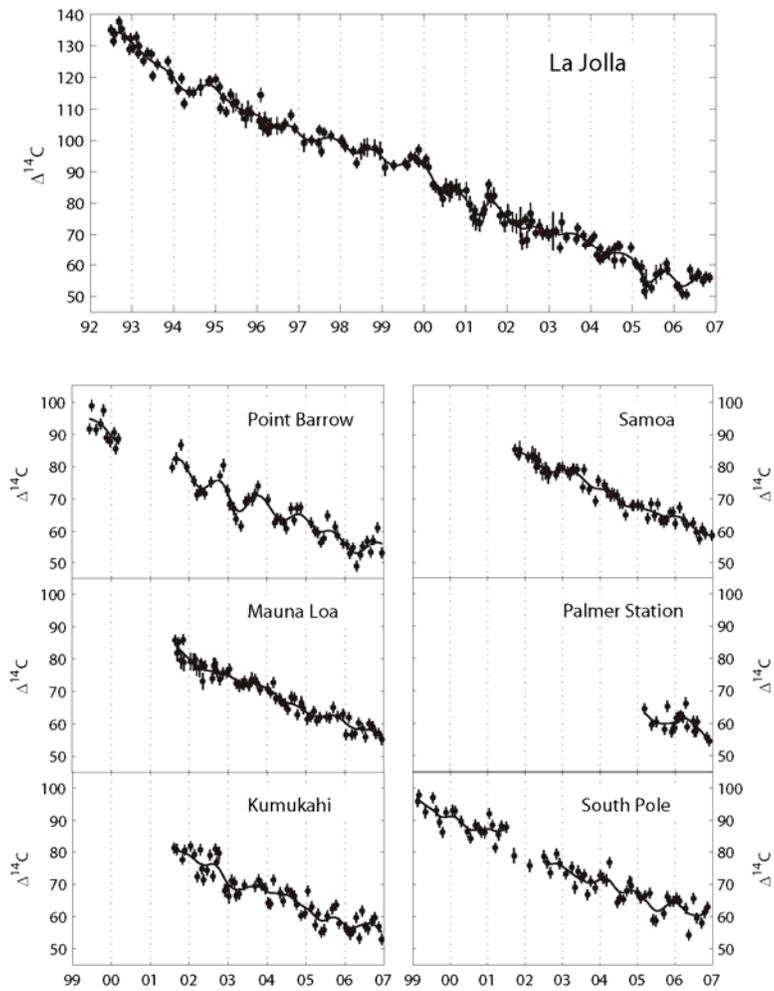
Piper, S. C., C. D. Keeling, and E. F. Stewart, Exchanges of atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> with the terrestrial biosphere and oceans from 1978 to 2000. III. Sensitivity tests, SIO Reference Series, No. 01-08, 2001.

Keeling, C. D., and S. C. Piper, Exchanges of atmospheric CO<sub>2</sub> and <sup>13</sup>CO<sub>2</sub> with the terrestrial biosphere and oceans from 1978 to 2000. IV. Critical overview, SIO Reference Series, No. 01-09, 2001.

Graven, H. D. 2008. Advancing the use of radiocarbon in studies of global and regional carbon cycling with high precision measurements of <sup>14</sup>C in CO<sub>2</sub> from the Scripps CO<sub>2</sub> Program. Ph.D. . Department, University of California, San Diego, La Jolla.

Graven, H. D., B. B. Stephens, T. P. Guilderson, T. L. Campos, D. S. Schimel, J. E. Campbell, and R. F. Keeling, Vertical profiles of biogenic and fossil fuel-derived CO<sub>2</sub> from airborne measurements of DELTA<sup>14</sup>C and CO<sub>2</sub> above Colorado, submitted to Tellus B, 2008.

Rafelski, L. E., Piper, S. C. and Keeling, R. F. Climate effects on atmospheric carbon dioxide over the last century. Submitted to Tellus B, 2008.



HDG 12/07/07

Figure 1. Measurements of the radiocarbon content of atmospheric  $\text{CO}_2$ , based on  $\text{CO}_2$  samples that were previously extracted from flasks in the Scripps network and archived in sealed glass ampoules.

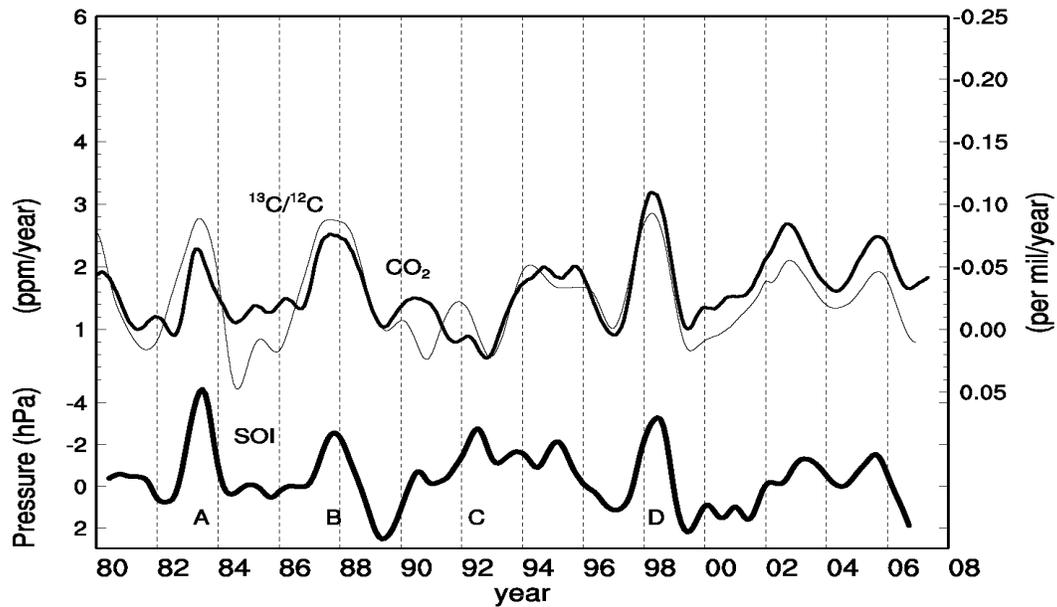


Figure 2. Rates of change of globally averaged atmospheric CO<sub>2</sub> concentration, in ppm (thick line), and delta<sup>13</sup>C, in per mil (thin line). For comparison, the Southern Oscillation Index (SOI) is shown, calculated as the difference of atmospheric pressure at Darwin, Australia and Tahiti. The SOI is shown inverted and lagged 6 months. Vertical lines labeled "A", "B", "C", and "D" indicate times of minima in the Southern Oscillation index lagged by 6 months.