"Developing Model Constraints on Northern Extra-Tropical Carbon Cycling Based on measurements of the Abundance and Isotopic Composition of Atmospheric CO<sub>2</sub>"

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Research Objective

The objective of this project was to perform CO<sub>2</sub> data syntheses and modeling activities to address two central questions: 1) how much has the seasonal cycle in atmospheric CO<sub>2</sub> at northern high latitudes changed since the 1960s, and 2) how well do prognostic biospheric models represent these changes. This project also supported the continuation of the Scripps time series of CO<sub>2</sub> isotopes and concentration at ten baseline stations distributed globally.

# Trends in Seasonal Cycle of atmospheric CO2.

A Major outcome of this grant was documenting that large change wide-spread changes in the seasonal of CO<sub>2</sub> have occurred at middle and high latitudes in the Northern Hemisphere since 1960. Thus results was communicated in a high-visibility publication entitled "Enhanced Seasonal Exchange of CO<sub>2</sub> by Northern Ecosystems Since 1960", published in Science Magazine by Graven et al., (2013), which documents an almost explosive increase in this amplitude at middle and high northern latitudes over this period. The paper exploits a coincidental overlap between two extensive airborne CO<sub>2</sub> surveys, widely separate in time. The first, conducted 1960 was led by CD Keeling under the auspices of the International Geophysical Year (IGY), while the second, conducted around 2010, was the Hippers Pole-to-Pole (HIPPO) survey. The IGY/HIPPO comparison allowed changes in the amplitude of the CO<sub>2</sub> cycle to be resolved along a mid-tropospheric transect from 20°N to nearly the North Pole. North of 45N, the amplitude increased by around 50% over the 50-year time frame, while the change from 20 to 45N were in the range of 10%. This pattern is very clearly resolved in the data. Previously, a large increase in amplitude had been documented at only one land station, Barrow Alaska (CD Keeling, Nature, 1996). But the significance of this Barrow record was unclear because of its fragmentary nature and the potential for local artifacts. The Graven et al. paper shows that changes as large as or larger than at Barrow have occurred over a wide expanse of the atmosphere in the Northern Hemisphere. The paper also includes an updated summary of the amplitude changes at Barrow, as shown in Figure 1, where changes in fine features of the cycle can also be seen.

The Graven et al study addressed the project objective to assess prognostic biospheric models by comparing the observations to a series of models from the CMIP5 comparison study. These results show that the existing CMIP5 models typically underestimate the amplitude changes by 50% or more. These models are evidently missing or misrepresenting important processes controlling long-term carbon cycling such as long-term structural changes, and this study motivates improving aspects of the model that relate to the seasonal cycle and continued use of the cycle and its changes as a benchmark test.

By looking at how the amplitude changes varied with latitude, and taking account atmospheric mixing, the Graven et al study showed that

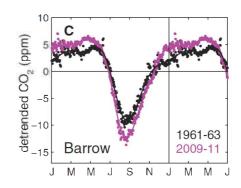


Figure 1. Seasonal cycle in CO2 Barrow Alaska, averaged over years 1961-63 and 2009-2011, showing a large increase in the amplitude.

northern boreal ecosystems were centrally involved in the changes, and that temperate and Arctic ecosystems probably also were important. The large amplitude increase challenges our understanding of how the land biosphere is responding to rising  $CO_2$  and changing climate. The changes probably have implications for the long-term uptake of  $CO_2$ , for atmospheric biosphere interactions influences climate, and thus on forecasts of future climate change and resource availability. But more work is needed to establish these connections. The changes were not anticipated by current earth-system models showing that these models are have fundamental deficiencies relating to changing land surface properties and ecosystem metabolic activity.

Further work, not yet published, on changes in the CO<sub>2</sub> amplitude was also carried out on this award, with an emphasis in the interannual variations of the amplitude at Mauna Loa, as detailed in previous annual reports. The analysis shows that the decadal variations in the seasonal amplitude of CO<sub>2</sub> correlate strongly with the Pacific Decadal Oscillation and that these variations are not explained well by interannual variations in atmospheric transport. We also find that drought in western North America correlates significantly with changes in CO<sub>2</sub> amplitude and PDO over the entire Mauna Loa period, suggesting that land fluxes explain the major changes in the amplitude at Mauna Loa. The study also shows changes have also occurred in the phasing of the Mauna Loa cycle. The causes appear to be complex, involving both changes in transport and land biospheric fluxes.

### Variations in oxygen isotopic composition of atmospheric CO<sub>2</sub>

The project also supported interpretive studies of changes in the isotopic composition of atmospheric CO<sub>2</sub>. While these studies were begun under the previous DOE award DE-FG02-07ER64362, they were brought to fruition and finalized during this award period.

A key finding was reported in a study entitled "Interannual variability in the oxygen isotopes of atmospheric CO<sub>2</sub> driven by El Nino" by Welp et al. (2011). This study showed that the oxygen isotopic composition of atmospheric CO<sub>2</sub> varies with El Nino and that these variations provide a new basis for constraining gross primary production of the land biosphere. The study provocatively suggests that GPP might be as large or larger than 150 Pg C/yr, compared to the

canonically-accepted estimate of 120 Pg C/yr. This higher estimate has subsequently been backed by another recent paper (Koffi, Global Biogeochemical Cycles, 2012) using an independent method. While the dust hasn't settled on this controversy, it already has had implications for climate modelers who have often struggled to tune their models to yield GPP as low as 120 Pg C/yr. The Welp and Koffi papers now suggest that models with GPP of ~150 Pg C/yr might actually be realistic after all.

The project also reported results for measurements of atmospheric radiocarbon in CO<sub>2</sub>, as reported in two companion papers by Graven et al. These radiocarbon data document the impact of global fossil-fuel burning on the radiocarbon trends, and provide constraints on global rates of mixing in the ocean and carbon exchange with the land biosphere. The measurements serve as a backdrop for studies to quantify fossil-fuel emissions using atmospheric measurements in urban or other non-background settings. The data provides the best evidence to date of a quasi-biennial oscillation in atmospheric radiocarbon related to stratospheric tropospheric exchanges and of shifting gradients related to air-sea gas exchange.

## Measurements of CO<sub>2</sub> concentration and isotopes

A major product of this project was continued time series for CO<sub>2</sub> and its isotopes from flasks collected at the ten stations in the Scripps CO<sub>2</sub> network. These data are presented on ScrippsCO<sub>2</sub>.ucsd.edu and echoed on CDIAC. The CO<sub>2</sub> data is incorporated into the NOAA ObsPack product, which is widely used by the CO<sub>2</sub> community.

During this award period, pace of the stable isotopic measurements for the main stations in the program fell due to budget constraints. Because the CO<sub>2</sub> is routinely archived from the flasks, the isotope samples were preserved, and on the basis of additional funding available more recently, some catching up of the analyses has been possible. The stable isotope records from most stations are now caught up through mid-2013.

The project also supported continued archiving of CO<sub>2</sub> extracted from flasks that are set aside for open-ended future applications. This archive has supported a collaboration with Tom Guilderson of Lawrence Livermore National Laboratory to measure radiocarbon as reflected in the publications by Graven et al. (2012), and with Prof. John Eiler of the California Institute of Technology to measure the <sup>17</sup>O excess and the clumped isotopomer (<sup>13</sup>C<sup>18</sup>O<sup>16</sup>O).

Major upgrades in the flask analysis system were carried out: A new Picarro system for analyzing both flasks and reference cylinders was implemented and has been operational since August 2012. We also implemented a fully automated system for extracting CO<sub>2</sub> from flasks and storing the pure CO<sub>2</sub> in sealed glass ampoules for subsequent isotopic analysis.

Operations at our 10 stations ran smoothly with a couple of exceptions, such as detailed in the annual reports.

#### Outreach

The PI was involved in extensive outreach activities related to trends in atmospheric carbon dioxide, as supported by this project, including supporting the development of a new website for providing rapid updates of the Mauna Loa CO<sub>2</sub> record in accessible graphical formats, see

Keelingcurve.ucsd.edu. This website figured prominently in the coverage of the news story when CO<sub>2</sub> concentrations at Mauna Loa first topped 400ppm.

## **Project URLS:**

Main site for data dissemination: http://scrippsco2.ucsd.edu

Mauna Loa updates and additional outreach: http://keelingcurve.ucsd.edu

#### **Publications related to this award:**

Graven, H. D., T. P. Guilderson and R. F. Keeling (2012). "Observations of radiocarbon in CO<sub>2</sub> at La Jolla, California, USA 1992-2007: Analysis of the long-term trend." Journal of Geophysical Research-Atmospheres 117: 1-14.

Graven, H. D., T. P. Guilderson and R. F. Keeling (2012). "Observations of radiocarbon in CO<sub>2</sub> at seven global sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles." Journal of Geophysical Research-Atmospheres 117.

Graven, H. D., R. F. Keeling, S. C. Piper, P. K. Patra, B. B. Stephens, S. C. Wofsy, L. R. Welp, C. Sweeney, P. P. Tans, J. J. Kelley, B. C. Daube, E. A. Kort, G. W. Santoni and J. D. Bent (2013). "Enhanced Seasonal Exchange of CO2 by Northern Ecosystems Since 1960." Science 341(6150): 1085-1089.

Welp, L. R., R. F. Keeling, H. A. J. Meijer, A. F. Bollenbacher, S. C. Piper, K. Yoshimura, R. J. Francey, C. E. Allison and M. Wahlen (2011). "Interannual variability in the oxygen isotopes of atmospheric CO<sub>2</sub> driven by El Nino." Nature 477(7366): 579-582.