Final Technical Report

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

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Introduction.

The primary goal of our research program, consistent with the goals of the U.S. Climate Change Science Program and funded by the terrestrial carbon processes (TCP) program of DOE, has been to improve understanding of changes in the distribution and cycling of carbon among the active land, ocean and atmosphere reservoirs, with particular emphasis on terrestrial ecosystems. Our approach is to systematically measure atmospheric CO_2 to produce time series data essential to reveal temporal and spatial patterns. Additional measurements of the $^{13}C/^{12}C$ isotopic ratio of CO_2 provide a basis for distinguishing organic and inorganic processes. To pursue the significance of these patterns further, our research also involved interpretations of the observations by models, measurements of inorganic carbon in sea water, and of CO_2 in air near growing land plants.

This DOE grant ran concurrently with grants from NSF (ATM91-21986, ATM97-11882, and ATM01-20527), from NASA (NAGW-2987, NAG5-3528, and NAG5-11217), and from DOE DE-FG03-93ER61543. This grant is not officially coordinated with the NSF, NASA, or other DOE grant but the four programs are closely related, and all grants shared a common goal to advance understanding of the global carbon cycle.

This study called for continued atmospheric measurements at an array of ten stations from the Arctic Basin to the South Pole and at 2 vegetated sites in North America. Air was collected in flasks brought back to the laboratory for analysis, except at Mauna Loa Observatory, Hawaii, where continuous measurements were also carried out. The NSF grants funded atmospheric measurements as well as measurements of sea water from oceanographic vessels coordinated with oceanographic work included in the other DOE grant for the World Ocean Circulation Experiment (DEFG03-93ER61543). The NASA grants focused on using models to predict measurements of atmospheric CO_2 concentration and $^{13}C/^{12}C$ ratio, and thereby to establish how sources and sinks of atmospheric CO_2 have been influenced by climatic change and human activities.

This DOE grant ER62075 was originally for 3 years. However, we applied for new grants in 1998 and 2001 which were accepted, each extending support for 3 additional years under Grant ER62075. Progress was synthesized and set forth in the DOE

grant proposals in 1998 and 2001, as well as in a grant proposal in 2004 that resulted in funding under a new DOE grant DE-FG02-04ER63898. In addition, progress during the grant period was reported in technical reports dated 30 May 1996, 6 May 1997, 7 June 1999, March 2000, 29 May 2002, 28 April 2003, and 8 June 2004. A no-cost extension of Grant ER62075 set the termination date at 31 July 2005.

Description of Work Accomplished.

For atmospheric CO_2 our analytical methods were essentially as described by Keeling et al. [1989]. Isotopic measurements during this reporting period were carried out until 2000 on a VG Prism II mass spectrometer in the laboratory of Professor Martin Wahlen at SIO, and from 2000 to present on a VG (now GV) Optima mass spectrometer in our own laboratory. The analyst at all times was Alane Bollenbacher of our research group. During the transition period near 2000, a detailed overlapping of data was carried out to provide long term stability of the records.

Direct measurements of the concentration of atmospheric CO_2 and its $^{13}C/^{12}C$ ratio at 10 observing stations in a nearly pole-to-pole array have been extended for 9 more years, continuing the longest existing dataset of simultaneous measurements of these two indicators of global and regional change in the Earth's carbon cycle. Substantial net exchanges of CO_2 between the atmosphere and terrestrial vegetation are directly revealed on the global scale. When atmospheric transport of CO_2 is accounted for by using a tracer transport model, our data also reveal substantial variations in net exchanges of CO_2 separated into tropical, temperate, and boreal zones. Our data indicate that vegetation in the extra-tropical zones in both hemispheres have been a net sink for atmospheric CO_2, whereas the tropical zone is a net source. All zones show interannual variability, especially the tropics where we consistently find a marked correlation with strong El Niño events [Piper et al., 2001; Keeling et al., 2001; Keeling et al., 2005].

We decompose the carbon cycle at the global scale by a double deconvolution procedure that divides the non-industrial global net exchange flux into terrestrial and oceanic components [C. D. Keeling et al., 1989, 2005].

Climatic impacts on the carbon cycle are evident on the global scale. Rates of change in globally-averaged atmospheric CO_2 data show a striking relation to the Southern Oscillation Index lagged by 6 months. Times of prominent minima in SOI correspond to maximum rates of rise in concentration and fall in $^{13}C/^{12}C$ ratio.

The global net terrestrial ecosystem CO_2 flux (NEE) determined by double deconvolution shows a similar pattern to the global atmospheric CO_2 patterns, while the corresponding oceanic flux shows lesser variability tending to be opposite in phase.

With the global fluxes and the observed north-south gradients in CO_2 and $^{13}C/^{12}C$ as constraints, we calculate zonal terrestrial and oceanic net fluxes by the inverse method [Piper et al., 2001]. We divided global NEE into four zonal terrestrial regions: boreal, northern temperate, tropical, and southern temperate. (The southern polar zone has negligible terrestrial vegetation). Results of our analysis identifies strongly varying terrestrial exchanges of CO_2 with the atmosphere, which tend to correlate with seasonally adjusted land surface temperature, especially in the tropics.

Rhf (heterotrophic respiration plus other non-industrial terrestrial releases of CO_2 release including CO_2 from fire) was calculated as the difference between NEE from our inverse calculations and NPP derived from radiometric satellite data (e.g. Nemani et al., 2003). Globally, NEE varied more than NPP, so that temporal patterns of Rhf and NEE tend to be similar. Rhf, more so than NPP, tends to correlate with global average land temperature.

In the boreal zone, NEE, on average, tended to be small, and therefore NPP and Rhf nearly equal, except near 1990 where there was a prominent peak in Rhf accompanied by a more moderate peak in NPP. The preceding years of rising NPP and Rhf were accompanied by increasing boreal temperature and amplitude of the seasonal cycle of atmospheric CO_2, the latter seen in a remotely-sensed vegetative-index sensitive to NPP [Myneni et al., 1997].

In the northern temperate zone, NPP showed little variation and exceeded Rhf in all years, so as to produce a strong persistent terrestrial CO_2 sink. NEE and Rhf varied, but with little correlation with zonal temperature.

In the tropics, Rhf accounted for most of the variation in NEE, both showing strong correlations with zonal land temperature. During three strong El Niño events [C. D. Keeling et al., 2005], accompanied by peak land temperatures and strong minima in the SOI, Rhf was high and NPP was low. At the time of a moderate SOI minimum in 1992, accompanied by the eruption of Mt. Pinatubo, Rhf and NPP were both low. In the southern temperate zone, NPP shows no significant variability, while NEE shows an increasing sink accompanied by a small temperature rise. In summary, we find little evidence in any zone, that NEE and NPP co-varied systematically.

Our atmospheric data show remarkable changes in amplitude of the seasonal cycle of atmospheric CO_2 which correlate with zonal land temperature anomalies and satellite vegetation index data [C. D. Keeling et al., 1996; Myneni et al., 1997]. In the Northern Hemisphere outside of the tropics, a large annual cycle in atmospheric CO_2 is observed, which provides a sensitive measure of changing seasonality in the terrestrial carbon cycle. Data from our program for two widely separated polar stations, Alert and Point Barrow, show a persistent amplitude increase in the 1980's to over 40% above the average of the 1960's, a dip in the mid-1990's, and thereafter a return to high amplitudes. These changes tend to correlate with average land temperature north of 47 degrees north. In the north temperate zone (23.5-47.0 degrees N), temperature increases of about 1.2 degrees C since 1975 have been accompanied by amplitude increases of about 35%, much of it since the early 1990's. In the tropics, a lesser but significant increase in temperature is observed since 1980, accompanied by a small but significant delayed amplitude increase. The increase was accompanied by a progressively earlier response of land plants to spring warming [Keeling et al., 1996; Myneni et al., 1997; Myneni et al., 1998]. The oceanic contribution to seasonal variability, as confirmed by $^{13}C/^{12}C$ data [Whorf, 1996], is small. From our analysis of fluxes, described above, it is evident that seasonality in both NPP and Rhf has increased markedly.

We compared interannual trends in the difference in CO_2 concentration and the $^{13}C/^{12}C$ ratio between pairs of stations of our array with the rate of emissions from fossil fuel combustion. These comparisons extend from the late 1950s to the present,

during a period of time in which fossil fuel combustion approximately tripled, producing striking differences in the isotopic ratio and concentration differences between stations. By an extrapolation procedure, we deduced residual profiles of the north-south gradient in both concentration and isotopic ratio that would exist if no fossil fuel CO_2 had entered the atmosphere. The residual for concentration is in close agreement, but rendered in greater detail, than a profile deduced earlier by Keeling and Heimann [1986]. Evidently, the concentration of CO_2, over the past 45 years on average, would have been about 1 part per million lower in the Northern Hemisphere than in the Southern in the absence of fossil fuel combustion. The isotopic residual shows a similar pattern except that an equatorial peak, seen in the concentration profile, is absent, as expected if this concentration peak is of oceanic origin. By comparing the evolution up to the present of the two profiles, caused mainly by fossil fuel combustion, we hope to gain a firmer understanding of the time-varying terrestrial biospheric sinks over nearly half a century using inverse modeling procedures. By comparing these evolving north-south CO_2 concentration and isotopic ratio gradients with predictions of process-models such as BIOME-BGC, as we pan to do, it should be possible to broaden our understanding of the long-term role of terrestrial vegetation in the global carbon cycle.

We continued a site-specific study to document the $^{13}C/^{12}C$ ratio of atmospheric CO_2 exchanged with forests and grasslands, this ratio derived from the covariance of concentration and isotopic ratio over diurnal cycles [C. D. Keeling, 1958, 1961; Lancaster, 1990]. The northern station in Alberta, Canada shows no appreciable trend in the $\delta^{13}C$ of CO_2 emitted into the air other than expected in response to a change of -0.4‰ in the $^{13}C/^{12}C$ ratio of ambient atmospheric CO_2 from 1987 to 2003. The southern station in Montana, however, shows a negative trend until the mid-1990's and then a gradual return to nearly the same ratio as in 1987, if the -0.4‰ ambient CO_2 change is allowed for. Changes in water stress, with drier conditions near the beginning and end of the record, more likely at the southern station than the northern, are a likely cause of the swings in ratio only seen there. Thus, neither record shows evidence of a secular increase in plant discrimination as seen from 1958 to 1987 [Lancaster, 1990], suggestive of a stimulation in photosynthesis caused by rising ambient CO_2 [Lloyd and Farquhar, 1994].

In summary, our data show that recent variability in the carbon cycle has produced changing patterns and substantial imbalances in the sources and sinks of atmospheric CO_2, discoveries so far mostly unanticipated by modeling studies. Unexpected behavior is not surprising because multiple factors, both human and natural, evidently affect both assimilation and release of CO_2 by terrestrial ecosystems, and all must be correctly prescribed if changes in the distribution and cycling of carbon among the active carbon reservoirs are to be adequately understood.

In a recent extension of our program, we have contributed to measurements of the radiocarbon (carbon-14) content of atmospheric CO_2, through a collaboration with Dr. Thomas Guilderson of Lawrence Livermore National Laboratory. Dr. Guilderson has pioneered the capability of making accelerator measurements of the $^{14}C/^{12}C$ ratio to the unprecedented precision of 1 to 2‰ on samples as small as those obtained from our 5-liter air samples. This capability has recently been demonstrated on samples archived from the SIO program. The data exhibit a long-term trend which reflects the

continued "relaxation" towards a baseline of the atmospheric excess from the bomb tests in the 1950's and 1960's.

The new $^{14}C/^{12}C$ data exhibit seasonal and interannual variations, and gradients with latitude (higher values at the low-latitude stations) with greater clarity than in the most careful previous work [Levin and Hesshaimer, 2000]. The $^{14}C/^{12}C$ content of CO_2 is sensitive to exchanges of CO_2 with the oceans and terrestrial biosphere, and also is a powerful tracer of fossil-fuel emissions, the latter devoid of carbon-14. The $^{14}C/^{12}C$ ratio is an underutilized tracer which potentially has several important applications: (1) constraining turnover-times of the size of the terrestrial biosphere [Randerson et al., 2002], (2) constraining rates of ocean mixing and ventilation [Hesshaimer et al., 1994; Levin and Hesshaimer, 2000], and (3) constraining rates of fossil-fuel burning [Levin et al., 2003].

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The next four articles were accepted for publication in *Global Biogeochemical Cycles* after peer review. The editor recommended that they be published as a monograph. A proposal to the American Geophysical Union to publish these four articles as a separate monograph was recently approved. They are available on the internet as submitted to Global Biogeochemical Cycles (http://cdrg.ucsd.edu/articles.html), as well as reformatted for easier readability at http://repositories.cdlib.org/sio/reference/01-6 and 01-7, -8 and -9.

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