High-resolution Ocean and Atmosphere pCO_2 Time-Series Measurements

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PROJECT SUMMARY

Fossil fuel carbon sources and the growth of atmospheric carbon dioxide (CO_2) are reasonably well known based on economic reconstructions and atmospheric monitoring. Global carbon budgets suggest that over decadal timescales the ocean is absorbing, on average, approximately one third of the CO_2 released from human activity. However, the interannual variability in the ocean uptake and variability in the basic regional patterns of the air-sea CO_2 fluxes are poorly known at this time.

Ocean carbon measurements have shown significant biogeochemical variability over a wide range of timescales from sub-diurnal to decadal periods. In situ measurements are also providing a growing body of evidence that episodic phenomena are extremely important causes of variability in CO_2 and related biogeochemical properties. Year-to-year variations in physics (e.g., upwelling, winter mixing, lateral advection), bulk biological production, and ecological shifts (e.g., community structure) can drive significant changes in surface water CO_2, and thus air-sea flux. Changes in large-scale ocean-atmosphere patterns such as El Niño/Southern Oscillation (ENSO), the Pacific Decadal Oscillation (PDO), and the North Atlantic Oscillation (NAO) appear to drive much of the interannual variability, and this variability is expressed on regional (several hundred-to-thousands of kilometers) rather than basin-to-global scales. The slower, decadal time-scale ocean responses are not as well characterized as the interannual responses, though there is tantalizing evidence for large-scale biogeochemical regime shifts (or perhaps secular trends) and long-term changes in nutrient and carbon distributions. Distinguishing a human-induced, climate-change signal from natural decadal variability on this timescale is often singularly difficult, particularly given the relatively short duration of most oceanographic data records. But model projections suggest that anthropogenic impacts are accelerating and may become more evident in the near future.

Time-series records are essential for characterizing the natural variability and secular trends in the ocean carbon cycle and for determining the physical and biological mechanisms controlling the system. The biological and chemical responses to natural perturbations (e.g., ENSO, dust deposition events) are particularly important with regard to evaluating potential responses to anthropogenic forcing and for evaluating the prognostic models used in future climate projections. Ship-based time-series measurements are impractical for routinely measuring variability over intervals from a week to a month, they cannot be made during storms or high-sea conditions, and they are too expensive for remote locations. Instrumental advances over the past 15 years have led to autonomous moorings capable of sampling properties of chemical, biological, and physical interest with resolutions as good as a minute and duty cycles of a year or more. Although these new technologies are still underutilized, they have been identified as a critical component of the global ocean observing system for climate.

In 2004, the moored CO_2 program was initiated by the Office of Climate Observations (OCO) as part of the ocean observing system. The moored CO_2 network is still in its infancy, but is quickly expanding into a global network of surface ocean and atmospheric CO_2 observations that will make a substantial contribution to the production of seasonal CO_2 flux maps for the global oceans. The long-term goal of this program is to populate the network of OCEAN Sustained Interdisciplinary Time-series Environment observation System (OceanSITES; http://www.oceansites.org/) so that CO_2 fluxes will

become a standard part of the global flux mooring network. This effort has been endorsed by the OceanSITES science team. The moored CO_2 program directly addresses key element (7) Ocean Carbon Network, as outlined in the Program Plan, but also provides a value added component to elements (3) Tropical Moored Buoys and (6) Ocean Reference Stations. Additional information about the moored CO_2 program can be found at: http://www.pmel.noaa.gov/co2/moorings/.

ACCOMPLISHMENTS

Measurements and Network Development

The moored pCO_2 systems collect CO_2 and O_2 data from surface seawater and marine boundary air every three hours. A summary file with each of the measurements is transmitted once per day and plots of the data are posted to the web. In addition to the moored pCO_2 data collected as part of this project, MBARI has been collecting nutrient and chlorophyll measurements on the 125°W, 140°W, 155°W, 170°W TAO cruises. One person participates on these cruises and analyzes samples from the shipboard uncontaminated seawater supply and from CTD casts performed in-between buoy maintenance. These data have proven to be very helpful at interpreting the buoy based measurements and ultimately trying to examine the mechanisms controlling the observed variability in pCO_2.

In FY06, PMEL/MBARI maintained the eight sites from FY05 (Figure 1). There were a total 12 servicing visits to these sites in FY06. To facilitate these service visits, three additional TAO buoy hulls were modified and two new PMEL pCO_2 systems were built. The new pCO_2 systems were needed to replace older systems or systems that were lost at sea earlier in the year.

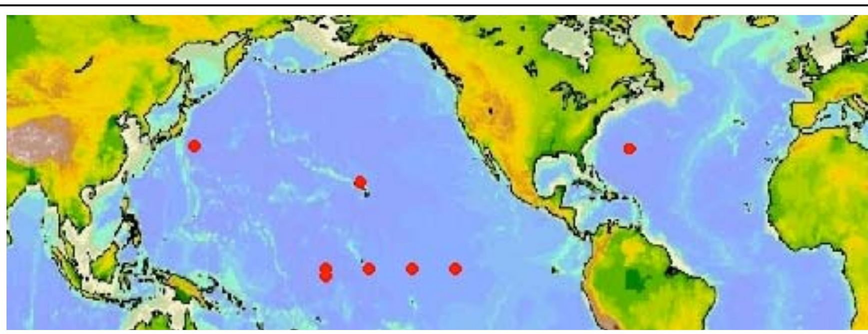

Figure 1. Map of moored pCO_2 systems currently deployed as part of this program.

Instrument/Platform Acquisitions

Here we summarize the deployment schedules and instrument performance over the last year. Systems are grouped into three categories. Five systems are located in the equatorial Pacific on the TAO moorings. Two systems are located in the North Pacific and North Atlantic subtropical gyres on Woods Hole buoys. These systems are co-located with the Hawaii and Bermuda shipboard time-series study sites. One system is located off of Japan in a modified TAO buoy operated by Meghan Cronin (PMEL) as part of an OCO funded OceanSITES flux mooring.

Equatorial Pacific on TAO Moorings:

125°W, 0° - At the beginning of FY06, the PMEL built system at this location collected atmospheric measurements, but lacked seawater measurements due to a valve failure in mid September 2005.

This system was replaced on January 31, 2006. The system functioned well until the buoy went adrift on July 8, 2006. At the time the buoy went adrift, probably due to vandalism, the equilibrator was damaged and the system ceased to collect seawater measurements. The buoy was redeployed on August 31, 2006, but due to deployment error, the equilibrator was jammed above the sea surface and is unable to collect seawater measurements. The system continues to collect good atmospheric measurements. This system is scheduled to be replaced April 2007. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY06: 44% and Lifetime: 52%.

140°W, 0° - This PMEL-built system was recovered and redeployed in late September 2005. The seawater measurements after the redeployment were implausibly high and it is believed that the there was a problem with the installation of the equilibrator. Although the seawater values were compromised, the system collected good atmospheric measurements during the entire deployment. The system was recovered and redeployed on January 16, 2006. The system operated properly until the buoy broke free, probably due to vandalism, on May 14, 2006. A new buoy was deployed on September 23, 2006 and the system is currently fully operational. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY06: 35% and Lifetime: 56%.

155°W, 0° - This MBARI-built system, which was deployed in June 2005 was the first deployment for a system MBARI redesigned to collect the same measurements as the PMEL systems. The system developed leaks in a stainless steel swage fitting allowing water to enter the housing making the system inoperable. The problem could not be identified until the system was recovered in June 2006 and returned to the laboratory for diagnostic testing. Extensive testing and a revision of deployment protocols are being put in place before the next cruise to this location. The percent data return is as follows, FY06: 0% and Lifetime: 35%.

170°W, 2°S - This MBARI-built system, which was deployed in June 2005, was the first deployment for the MBARI redesigned system. The system developed leaks in a stainless steel swage fitting allowing water to enter the housing making the system inoperable. The problem could not be identified until the system was recovered in June 2006 and was returned to the laboratory. The replacement system deployed in June 2006 did not leak, but much of the data quality was poor. The cause of the problem is under investigation. In October 2006, the system was again replaced and appears to be operating properly. The percent data return is as follows, FY06: 20% and Lifetime: 16%.

170°W, 0° - This PMEL-built system was fully operational until the recovery and redeployment on June 24, 2006. During the deployment in June, the surface buoy was dragged across the surface while the anchor was being deployed. This forced water up past the equilibrator into an area of tubing that could not drain properly. This trapped water prohibited the equilibrator from working properly. Although the seawater values were compromised, the system collected good atmospheric measurements during the entire deployment. The buoy was visited by the ship in October 2006 and the system is now operational. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY06: 73% and Lifetime: 87%.

Nutrient and Chlorophyll - Bottle samples are collected and processed by MBARI personnel from the NOAA ship *Ka'imimoana* twice a year on sections at 125°W, 140°W, 155°W and 170°W. Approximately 2000 samples were collected during the cruises in FY06. Approximately 10% of the samples were discarded due to improper sampling and loss during analysis. The percent data return is as follows, FY06: 90%.

HOT/BATS on WHOI designed buoys

MOSEAN buoy at Hawaii Ocean Time-series site (158°W, 22°N) – This system was fully operational for almost all of FY06. The November 2005 scheduled recovery was postponed due to bad weather. Another ship was not available for the recovery/deployment until February 2006. With the unanticipated delay in servicing, the system battery died on January 20, 2006, just 22 days before the successful recovery. The redeployed system is fully operational. The percent data return is as follows, FY06: 93% and Lifetime: 83%.

Bermuda Testbed Mooring (64.2°W, 31.7°N) – A moored pCO_2 system was first deployed on the BTM on October 22, 2005. The system was fully operational for the entire FY06. The system was successfully recovered and redeployed in July 2006. The system is currently operational. The percent data return is as follows, FY06: 100% and Lifetime: 100%.

OceanSITES Flux Moorings

Kuroshio Extension Observatory (144.5°E, 32.3°N) – The mooring at this location was redeployed with a PMEL-built moored pCO_2 system in May 2006. The equilibrator cycle in this system failed on deployment. We believe that water became trapped above the equilibrator during the deployment. The rest of the system, including the atmospheric measurements, is operational.

Logistical Considerations and Improvements

The pCO_2 systems are mounted in buoys that are deployed from a ship. Currently all of our deployments are in conjunction with another project that is covering the buoy deployment and maintenance costs and has already allocated ship time. The pCO_2 systems are typically sent out on a cruise and are set up and deployed by a member of the scientific party as an ancillary task. This arrangement requires about 4 hours for setup and then approximately 10 additional man hours during the cruise. To keep expenses down we generally request that someone already involved in the cruise be trained to deploy the systems so we do not have to pay to send our people to sea for every deployment. As we have learned over the past year, this approach requires that the systems be very robust. Although we have had some problems this past year with inexperienced people deploying the systems, we still believe that this is the most efficient approach and are striving to make the deployment procedures as simple and fool-proof as possible.

During FY06, we had problems with water getting trapped above the equilibrator. Three changes were implemented in the fall of 2006 to prevent this problem from happening in the future. To eliminate the possibility of water being forced up into the equilibrator during the violent times of the buoy deployment and the anchor drop, the systems are now being deployed in stand-by mode. While in stand-by mode, a valve is closed to prevent water from entering the equilibrator. Once the anchor has reached the bottom and the buoy has settled, the system is called via Iridium and put into run mode.

In the event that water does enter the space above the equilibrator, the design of the equilibrator has been modified so that the water will fall back out of the tubing. The equilibrator tubing diameter was increased to allow water to fall more freely out and a tubing guide was added to the buoy tower to ensure that the tubing is properly installed and supported. We have had three deployments since we have implemented these changes and all of them have been successful.

Data Processing

All the PMEL summary files are processed and graphed on a website that is updated daily <http://www.pmel.noaa.gov/co2/moorings/>. The data are currently stored at PMEL and are available from Christopher Sabine at PMEL. The MBARI data are available from Francisco Chavez at MBARI. The carbon data management and synthesis teams are in the process of integrating the moored pCO_2 data together with the underway pCO_2 data from a related OCO project. Ultimately all of the surface CO_2 data will feed into the seasonal CO_2 flux map effort that is currently under development.

All systems are thoroughly tested and calibrated over a range of CO_2 concentrations using WMO traceable standard gases in the laboratory before deployment. The systems are then calibrated with a zero and WMO traceable span gas at the beginning of every three hour measurement cycle during the deployment. We have developed a system for processing the moored pCO_2 data that is collected utilizing automated quality control procedures. Based on the calibration, atmosphere, and seawater information as well as other diagnostic measurements for each identified point relative to the surrounding points, the data point may be flagged as questionable or bad. Typically less than 1% of the data are flagged as questionable or bad. To finalize a dataset, the data are compared to any underway pCO_2 data that are available as well as the Marine Boundary Layer (MBL) atmospheric CO_2 concentrations for a given buoy location as provided by NOAA's GLOBALVIEW-CO_2 network. Based on these comparisons and various diagnostics of the automated system calibration information, the entire data set (air and water values) may be adjusted to match these higher accuracy measurements. Typically these adjustments are less than a couple of parts per million. The data are then merged with sea-surface temperature and salinity data collected by other groups on the same buoy. As all data become available, final calibrated data are archived at the Carbon Dioxide Information Analysis Center (CDIAC) and the National Oceanographic Data Center (NODC) on a yearly basis. As of this report, all PMEL data through January 2006 have been finalized and submitted to CDIAC for public release. We anticipate being able to maintain or improve upon the one year final data release for the foreseeable future.

Analysis and Research Highlights

The moored CO_2 data is providing valuable information on CO_2 variability in surface seawater over a wide range of timescales that have not been fully examined. For example, we are seeing significant differences in the monthly to seasonal variability between the North Pacific and North Atlantic subtropical gyres (Figure 2). As these time-series records grow they will document the full range of differences between these basins. Since both of the sites shown in Figure 2 are co-located with shipboard time-series measurements, these variations can be directly compared to variability in a number of physical and biogeochemical parameters as well as variations in biological composition and activity.

We are also beginning to realize the importance of understanding the biological contributions to CO_2 variability in the equatorial Pacific thanks to the shipboard analyses of nitrate and chlorophyll collected as part of this project. Figure 3 shows a time-series of averaged nitrate and chlorophyll data along the 155°W line. The long-term variations in these parameters correlate very closely with the long-term variations in pCO_2 at this site.

Many publications have focused on CO_2 variability in the equatorial Pacific associated with the El Niño/Southern Oscillation, but the time-series moorings in the equatorial Pacific have shown that

Timescales of Variability	**Range (ppm)**
Long-term (annual rate)	~1.7-2.5
Interannual (ENSO)	~80-100
Seasonal	~20-30
Sub-seasonal (weeks to months)	~50-60
Diurnal	~20-40

variability at other timescales may be nearly as important as the ENSO variability (table 1). Manuscripts are currently in preparation discussing the significance and mechanisms controlling these other timescales of variability.

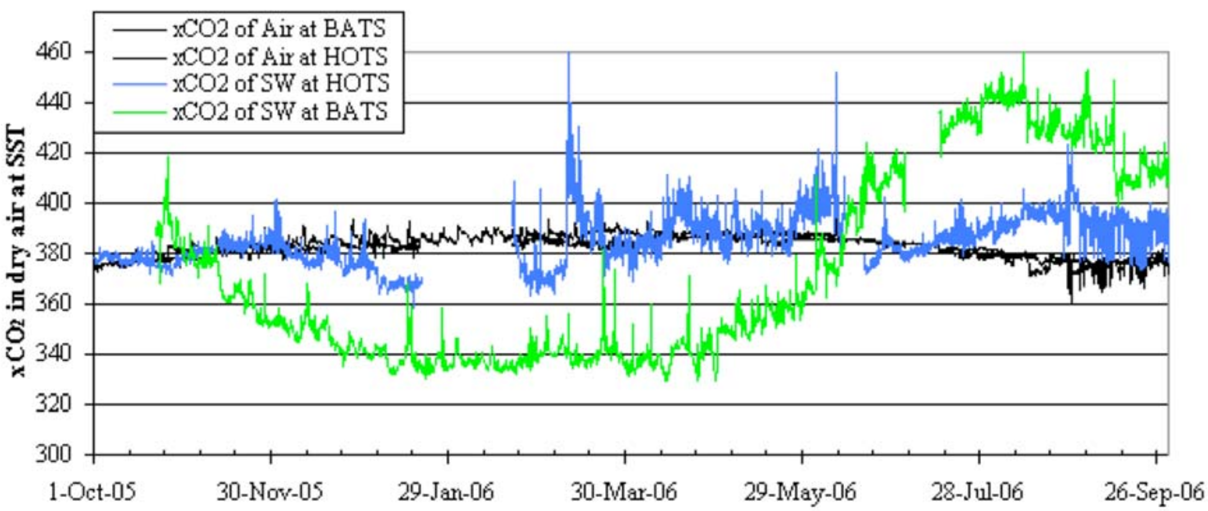

Figure 2. Time-series of CO_2 measurements from the subtropical North Pacific (HOT mooring) and the subtropical North Atlantic (BATS mooring) over the last year.

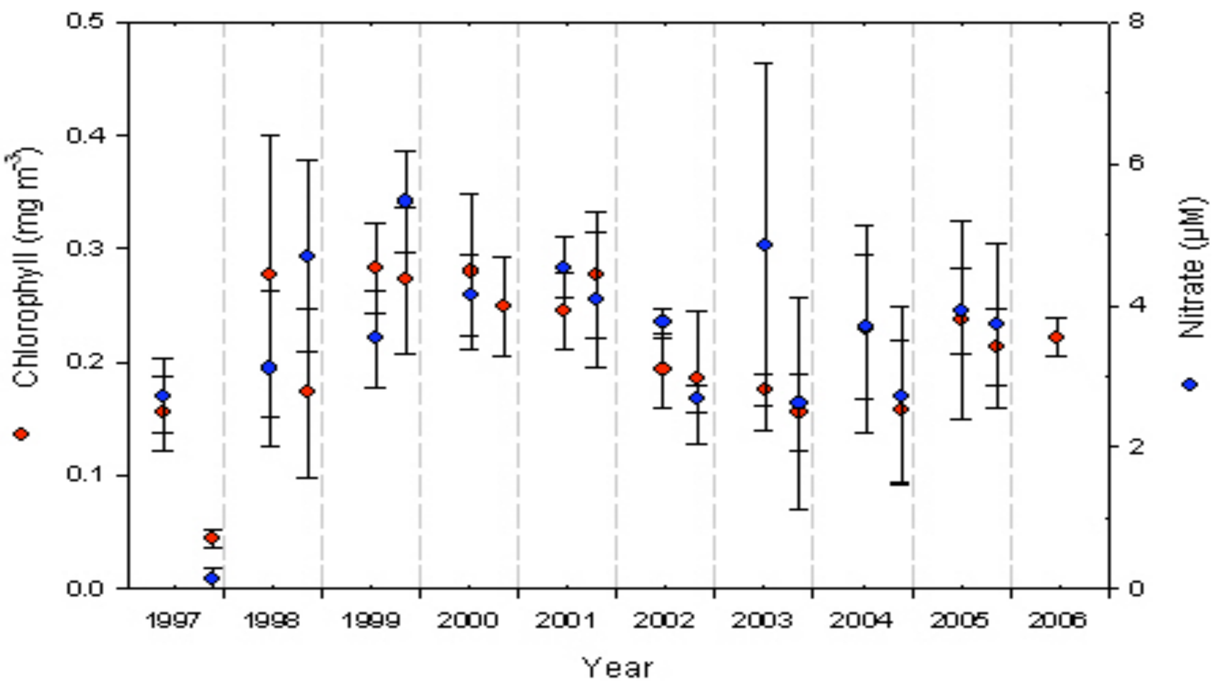

Figure 3. Average sea surface chlorophyll and nitrate levels along 155°W during the spring and autumn cruises from 1997 until 2006.

PUBLICATIONS AND REPORTS

Relevant Publications in FY06

Sabine, C.L. (2006): Global Carbon Cycle. In *Encyclopedia of Life Sciences*, John Wiley & Sons, Ltd., Chichester, http://www.els.net/ (doi: 10.1038/npg.els.0003).

Sabine, C.L., and N. Gruber (2006): Introduction to special section: North Pacific Carbon Cycle Variability and Climate Change. *J. Geophys. Res.*, 111(C7), C07S01, doi: 10.1029/2006JC003532.

Johnson, K. S., L. J. Coletti and F. P. Chavez (2006) Diel nitrate cycles observed with in situ sensors predict monthly and annual new production. *Deep-Sea Research I*, **53**, 561–573.

Ryan, J. P., I. Ueki, Y. Chao, H. Zhang, P. S. Polito, and F. P. Chavez (2006), Western Pacific modulation of large phytoplankton blooms in the central and eastern equatorial Pacific, *Journal of Geophysical Research*, 111, G02013, doi:10.1029/2005JG000084.

Pennington, J.T., Mahoney, K.L., Kuwahara, V.S., Kolber, D.D., Calienes, R., Chavez, F.P. (2006) Primary production in the eastern tropical Pacific: A review. *Progress in Oceanography* 69: 285-317.

Behrenfeld M. J., K. Worthington, R. M. Sherrell, F. P.Chavez, P. Strutton, M. McPhaden and D. M. Shea (2006) Controls on tropical Pacific ocean productivity revealed through nutrient stress diagnostics. *Nature*, 442, 1025-1028.

Relevant Meetings and Presentations in FY06

Sabine:

OCO annual review, Silver Spring, MD, May 10-12, 2006 (invited talk: The Global Ocean Carbon Cycle: Inventories, Sources And Sinks)

ASLO summer meeting, Victoria, BC Canada, June 8-9, 2006 (talk: Temporal Variability In Equatorial Pacific CO_2 Fluxes)

Ocean Carbon and Climate Change Scientific Workshop, Woods Hole, MA, July 10-12, 2006

Chavez:

Invited presentation at Ocean Sites steering committee meeting February 17-20, 2006, Honolulu, Hawaii.

Oral presentations (2) at AGU/ASLO Ocean Sciences meeting February 20-24, 2006, Honolulu, Hawaii. Authored or co-authored 12 abstracts.

Keynote speaker-Consecuencias biologicas de El Niño y El Viejo- at Biannual Mexican Oceanography Conference, 15-19 May, 2006, Manzanillo, Mexico.