High-Resolution Ocean and Atmosphere pCO_2 Time-Series Measurements

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1. 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/.

2. ACCOMPLISHMENTS

2.1. Measurements and Network Development

The PMEL built moored pCO_2 systems ($MAPCO_2$) 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 and plots of the data are posted to the web once per day. MBARI also operates moored pCO_2 systems at two equatorial sites. In addition to the moored pCO_2 data, MBARI has been collecting nutrient and chlorophyll measurements on the 155°W and 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 FY08, PMEL/MBARI maintained eight of the sites from FY07. A ninth CO_2 mooring site was located off of Bermuda at the Bermuda Atlantic Time Series (BATS) station, but the mooring at that location (BTM; Tommy Dickey) had to be pulled near the beginning of FY08 due to lack of funding. There were a total 13 servicing visits to these sites in FY08. New pCO_2 systems were needed to replace older systems or systems that were lost at sea earlier in the year.

The long term goal of this program is to populate 50 OceanSITES flux reference moorings with pCO_2 systems (Figure 1). With eight moorings currently fitted with pCO_2 systems (plus the Papa mooring currently funded by NSF), we are currently at 18% completion of the open ocean moored CO_2 program goal.

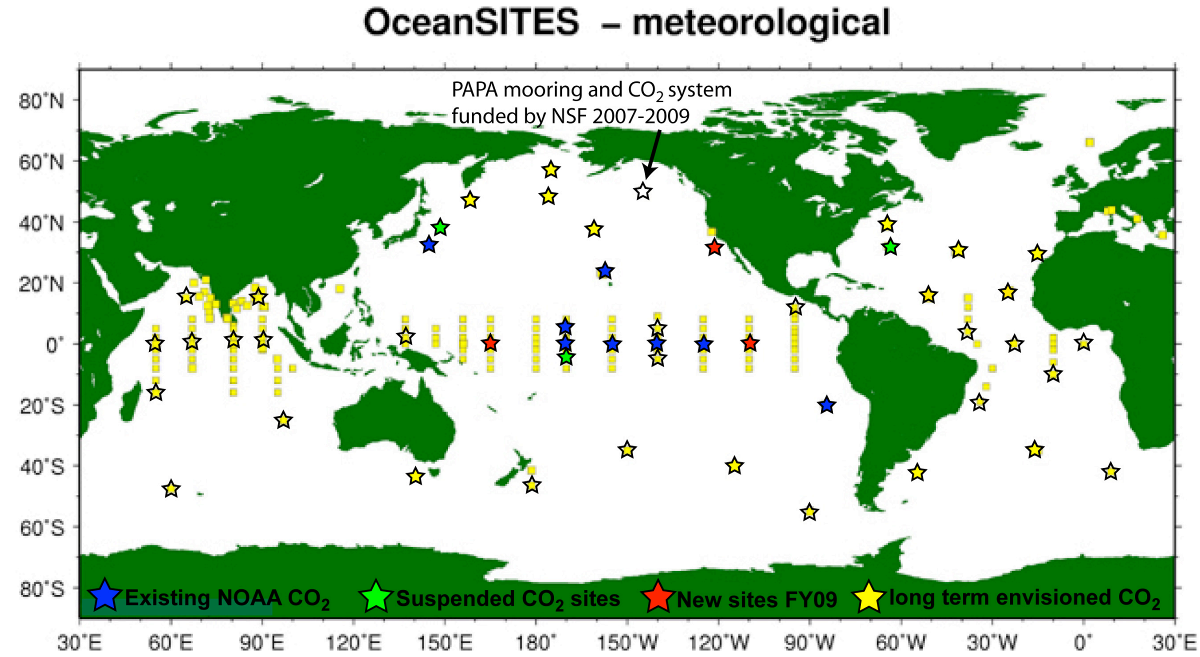


Figure 1. Map of moored pCO_2 systems currently planned and deployed as part of this program.

2.2. 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. Three systems are on Woods Hole buoys located in the North Pacific subtropical gyre, North Atlantic subtropical gyre and in the South Pacific upwelling region off of Chile. Two of the Woods Hole buoys are co-located with shipboard time-series study sites at Hawaii and Bermuda. One system is located off of Japan in a high-latitude 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 start of FY08, the mooring originally deployed at this location was adrift. On October 16th, a new buoy was deployed. This $MAPCO_2$ system has not yet been recovered and the system is still fully operational. The data are still preliminary, but they indicate that this system operated well the entire year. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY08: 96% and Lifetime: 57%

140°W, 0° - This $MAPCO_2$ system was functional at the start of FY2008. The detector was somewhat noisy, but the data can be cleaned up with post recovery processing of the data. On September 30, 2007, NDBC made an attempt to replace the system during a buoy ride, but due to rough conditions, the replacement system was damaged. On November 20th, the buoy went adrift. While adrift, the system continued to collect atmospheric pCO_2, but the seawater readings were compromised. On May 9, 2008 a new buoy was deployed and the system was fully operational for the remainder of the year. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY08: 54% and Lifetime: 53%

155°W, 0° - This MBARI-built system lost its battery pack during a vandalism incident in September 2007 thus was not working at the beginning of FY08. The buoy was not serviced until February 2008. Once the system was replaced, the instrumentation worked well until the buoy was recovered in September 2008. Currently the system is collecting atmospheric values, but there is a problem with the equilibrator and the seawater data are not useable. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY08: 52% and Lifetime: 35%

170°W, 2°S – Moved to 170°W, 2°N in July 2007.

170°W, 2°N - This MBARI-built system was moved to this location from the historic 170°W, 2°S in July 2007 when NDBC was not able to deploy this buoy at 170°W, 2°S. This system was fully operational from the beginning of the fiscal year until August when the system was recovered and redeployed. Currently the system is collecting atmospheric values, but there is a problem with the equilibrator and the seawater data are not useable. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY08: 90% and Lifetime: 95%

170°W, 0° - This MAPCO_2 system was operational the entire year. On November 29th, the calibration gas delivery pressure decreased by 50% which, over the course of the remaining deployment caused the detector to drift. The wells which house the pCO_2 calibration cylinder on this buoy were defective and seawater was able to penetrate inside. The regulator on the calibration gas became corroded and had begun to fail. This system was just returned to the lab, but preliminary data returns suggest that the detector was reading 12 ppm low by the time it was recovered. Once the data are re-processed, it is reasonable to expect that this drift can be corrected. This system was recovered and a new system was deployed on August 20, 2008. This system was fully operational the remainder of the year. The percent data return (only counting times when both seawater and atmospheric measurements were considered good) is as follows, FY08: 100% and Lifetime: 81%

Nutrient and Chlorophyll - Bottle samples were collected and processed by MBARI personnel from the NOAA ship *Ka'imimoana* during the two occupations of the 155°W lines and during the summer occupation of the 170°W line. Approximately 280 chlorophyll and 224 nutrient samples were collected and analyzed. The percent data return is as follows, FY08: 100%.

WHOI designed buoys

MOSEAN at Hawaii Ocean Time-series site (158°W, 22°N) – The MOSEAN buoy was pulled by Tommy Dickey's group at UCSB due to lack of funding in July 2007. A MAPCO_2 system was deployed on this buoy for three years. The percent data return is as follows, Lifetime: 88%.

WHOI Hawaii Ocean Time-series Station (WHOTS) (157°W, 22°N) – The WHOTS mooring was co-located with the MOSEAN mooring, so when we found out that MOSEAN was being pulled in 2007 we put a MAPCO_2 system on WHOTS to continue the time series. The CO_2 system at this location was operational for all of FY08. The system ceased to transmit daily data in late February, but it continued to run and store data internally. In June, the buoy and MAPCO$_2$ system were recovered and a fresh buoy and MAPCO$_2$ were deployed. The percent data return is as follows, FY08: 100% and Lifetime: 100%.

Bermuda Testbed Mooring (BTM) (64.2°W, 31.7°N) – This mooring was pulled by Tommy Dickey's group at UCSB in early October 2007 due to lack of funding. We are communicating with several investigators that are working hard to re-establish a mooring at this important time series site. We are hopeful that a new mooring will be deployed in FY09 and are prepared to place our CO_2 system on whichever platform becomes available. The percent data return is as follows, Lifetime: 100%.

Stratus (19.7°W, 85.5°N) – The MAPCO$_2$ system was fully operation for the entire fiscal year at this location. In October, the buoy and MAPCO$_2$ system were recovered and a fresh buoy and MAPCO$_2$ were deployed. The percent data return is as follows, FY08: 100% and Lifetime: 100%.

OceanSITES Flux Moorings

Kuroshio Extension Observatory (144.5°E, 32.3°N) – This past year was the first successful deployment at this location. Previous KEO deployments used an ATLAS type buoy and our CO_2 system did not operate properly in that buoy configuration under the high current and wave conditions of the North Pacific. In September 2007, a high latitude mooring replaced the Atlas style mooring at this location. The MAPCO$_2$ system deployed at the KEO site was operational for most of FY08. In mid August 2008 the equilibrator readings became very noisy. In September, the site was serviced and a new buoy and MAPCO$_2$ system were deployed. Recovery of the old system indicated that the equilibrator had become jammed by a piece of debris, but only one month of data were lost. Preliminary data returns from the new system suggest that it is operating well. The percent data return is as follows, FY08: 91%.

Japanese Kuroshio Extension Observatory (146.5°E, 38°N) – In February 2007, when this buoy was first deployed, the KEO system was not operational. We decided to add a MAPCO$_2$ system in an effort to begin the data collection in the region. The MAPCO$_2$ system at this site was operational during the remaining part of FY07. In October of FY08, an attempt was made exchange the MAPCO$_2$ system during a buoy ride. The attempt resulted in a faulty installation of the MAPCO$_2$ system. While we were able to collect atmospheric pCO_2, we were unable to collect seawater pCO_2 data. The PMEL buoy was recovered in the winter and a Japanese buoy was deployed in its place. Since the MAPCO$_2$ was operational at the KEO, a new MAPCO$_2$ was not deployed at JKEO.

2.3. 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 FY08, upgrades were made to the MAPCO$_2$ software giving more control via satellite to the personnel at PMEL. During every deployment, someone from the PMEL CO$_2$ group is standing by to remotely turn on the system after the buoy is deployed and to ensure that is running properly before the ship leaves the site. In addition to being able to turn the system on and off, several parameters can be changed remotely to optimize data collection.

The majority of the MAPCO$_2$ system failures are due to the breakdown of the equilibrator portion of the system. The TAO buoys are often the target of fishing and vandalism and on many occasions the equilibrator pipe was found bent when it was serviced. Biofouling continues to be a problem in highly productive areas. To make the MAPCO$_2$ easier to service on the buoy, we designed and manufactured a quick disconnect that goes in between the electronics package and the airblock/equilibrator assembly. With this quick disconnect, personnel can easily swap out the equilibrator assembly during a buoy ride. We have been searching for a quick disconnect that is both robust enough, yet affordable for the last three years. The quick disconnect assembly is a mix of off the shelf and customized parts. The first quick disconnect was deployed this summer. By next year, we hope to have a quick disconnect at all locations.

In September 2007, the Atlas-style mooring at the KEO site was replaced with a mooring designed by PMEL to withstand the conditions at high latitudes. This is also the first successful year with the MAPCO$_2$ system at KEO. It is hard to say for certain, but deploying on the more stable platform in this high current, typhoon-laden area may have been the key to successfully collecting data with the MAPCO$_2$ system.

2.4. Data Processing

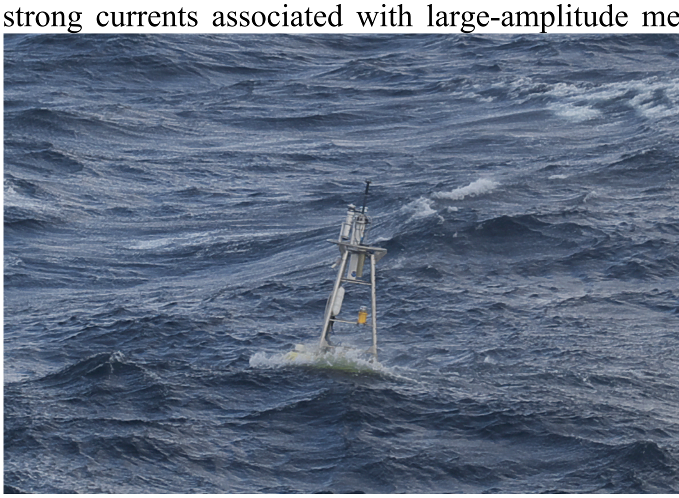
All the PMEL summary files are processed and graphed on a website that is updated daily <http://www.pmel.noaa.gov/co2/moorings/>. The data are currently stored at PMEL and are available from Christopher Sabine at PMEL. The MBARI data are available from Francisco Chavez at MBARI. The carbon data management 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. During the field season it is difficult to keep up with the data processing, but now that the season has ended we are on target to have all the data through March 2008 finalized and submitted to CDIAC for public release by February 2009. We anticipate being able to maintain the one year final data release from the date of recovery for the foreseeable future.

2.5. Analysis and Research Highlights

The highlight of this past fiscal year was the successful collection of the first full year of CO_2 data from the Kuroshio Extension Observatory (KEO). Excess heat received in the tropics is carried poleward by strong western boundary currents—the Gulf Stream in the North Atlantic, and the Kuroshio in the North Pacific. In particular, the Kuroshio Extension carries warm water at a rate of nearly 140 million cubic meters per second (140 Sv) into the North Pacific. As cold dry air of continental origin comes in contact with this warm water, heat and moisture are extracted from the surface, resulting in deep convection and rainfall. This excess heat from the tropics is then carried further poleward in the atmosphere through the action of storms, thereby maintaining a global balance of heat. The regions of intense air-sea heat fluxes in the Gulf Stream and Kuroshio Extension are also characterized by intense uptake of CO_2, while regions of strong upwelling, such as in the eastern equatorial Pacific, are characterized by CO_2 outgassing. Without the oceans to absorb significant amounts of the CO_2 released from human activity, the climate change would be much more pronounced. Thus air-sea heat and carbon dioxide flux measurements, particularly within western boundary current regions, are a critical element of the global earth observing system of systems (GEOSS).

The challenges of mooring a surface buoy in a western boundary current regime are considerable. Water depth in the Kuroshio Extension (KE) region is nearly 6000 m. In the core of the KE jet, current speeds can exceed 3 knots at the surface and 0.5 knots in the bottom 3000 m, placing significant strain on the mooring. Typhoons and winter storms can generate damaging winds and waves. Additionally, surface buoys can be vulnerable to shipping traffic and fishing vandalism. To survive the strong currents associated with large-amplitude meanders in the KE jet, PMEL leveraged the design experience gained from equatorial Tropical Atmosphere and Ocean (TAO) moorings and Deep ocean Assessment and Reporting of Tsunami (DART) moorings, making changes specific to the KE conditions. The buoy used for the first few KEO deployments was based on the tropical ATLAS design. While this design generally worked for the meteorology instruments during normal conditions, the buoy did not appear to have sufficient flotation and stability for the CO_2 systems to operate properly and was clearly not stable under extreme conditions (see picture to left). Thus, in FY08 the KEO ATLAS buoy was replaced with a larger PMEL high latitude buoy design. With the new, more



stable buoy, the $MAPCO_2$ system was able to function properly and we were able to get a first high resolution assessment of the CO_2 concentrations in the Kuroshio Extension.

Figure 2 shows the FY08 seasonal cycle of CO_2 and temperature at KEO. Surface water CO_2 values are below atmospheric for all but one month out of the year making this area a significant sink for atmospheric CO_2. The drop in surface water CO_2 during the winter months is primarily driven by the drop in sea surface temperature. In the spring, however, biological productivity continues to keep the CO_2 values low even as sea surface temperature begins to rise. The seasonal range in surface water CO_2 is approximately 100-120 ppm.

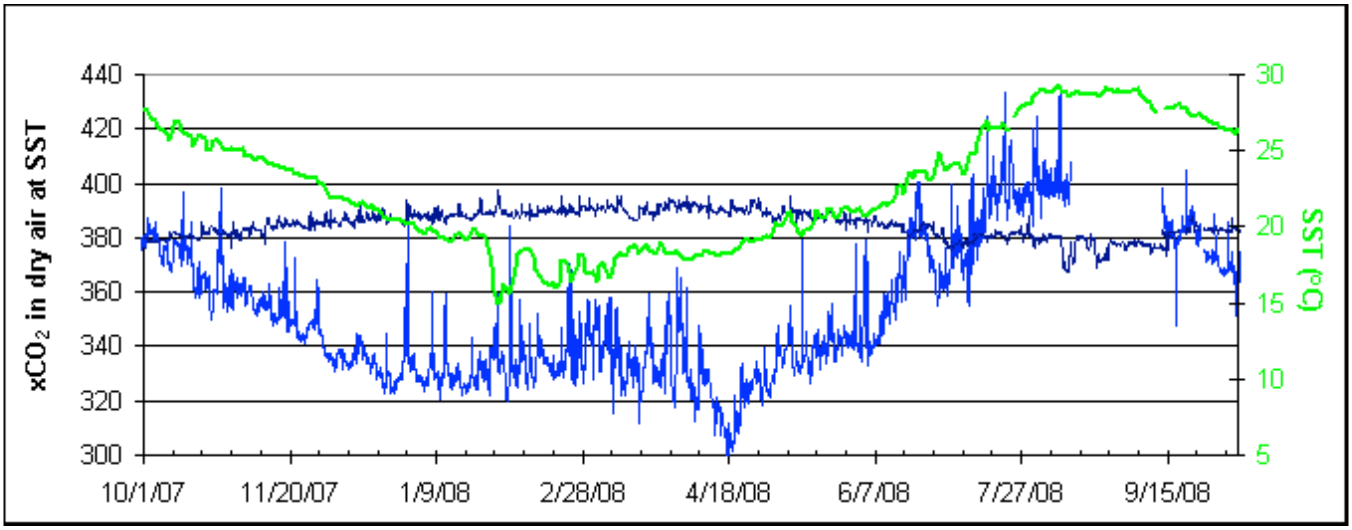


Figure 2. Time series plot of surface water CO_2 mole fraction (light blue), atmospheric CO_2 mole fraction (dark blue), and sea surface temperature (green) for FY08 (146.5°E, 38°N) on the northwestern edge of the North Pacific subtropical gyre.

In contrast to the northwestern North Pacific, the seasonal range at the Hawaii Ocean Time series site in the southeastern North Pacific is only 50-60 ppm and is a much smaller net sink for atmospheric CO_2 (Figure 3). The smaller seasonal cycle partially results from a smaller temperature range, but Hawaii also does not have a strong spring phytoplankton bloom to maintain the low seawater CO_2 concentrations. The minimum CO_2 values off Hawaii occur in January to February while at KEO the minimum occurs about three months later.

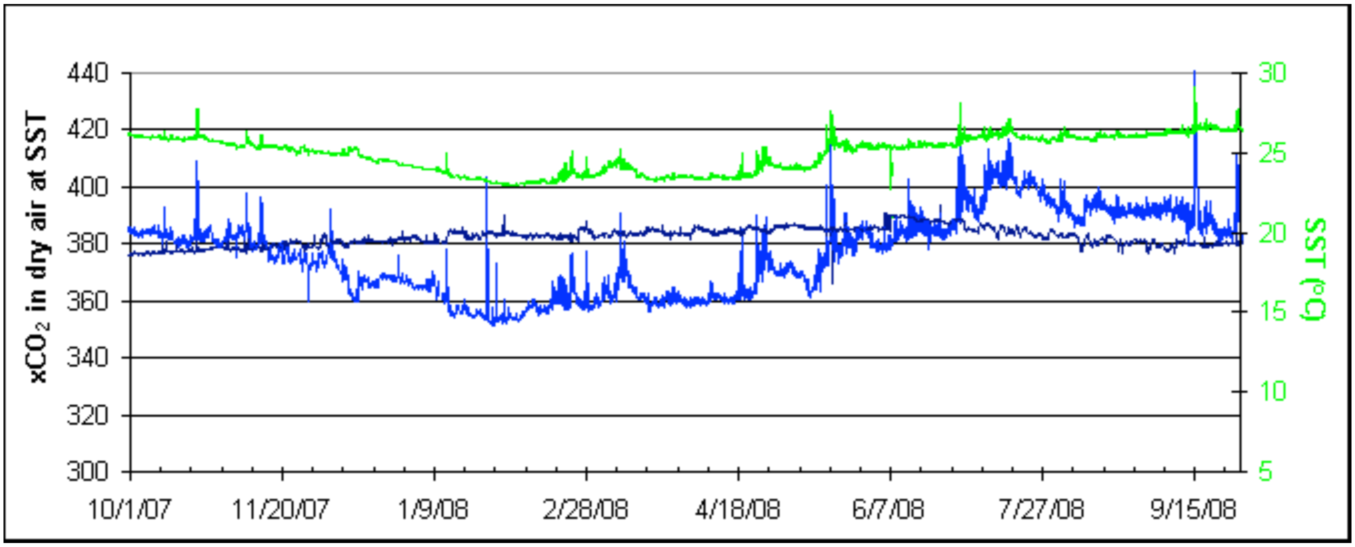


Figure 3. Time series plot of surface water CO_2 mole fraction (light blue), atmospheric CO_2 mole fraction (dark blue), and sea surface temperature (green) for FY08 at the Hawaii Ocean Time-series site (157°W, 22°N) in the south eastern edge of the subtropical North Pacific gyre.

Of course the value of time series observations grows as the data sets become longer. The moored time-series program in the equatorial Pacific is among the longest in the world. These data have been able to directly document the increase in surface water CO_2 over time (see figure 4).

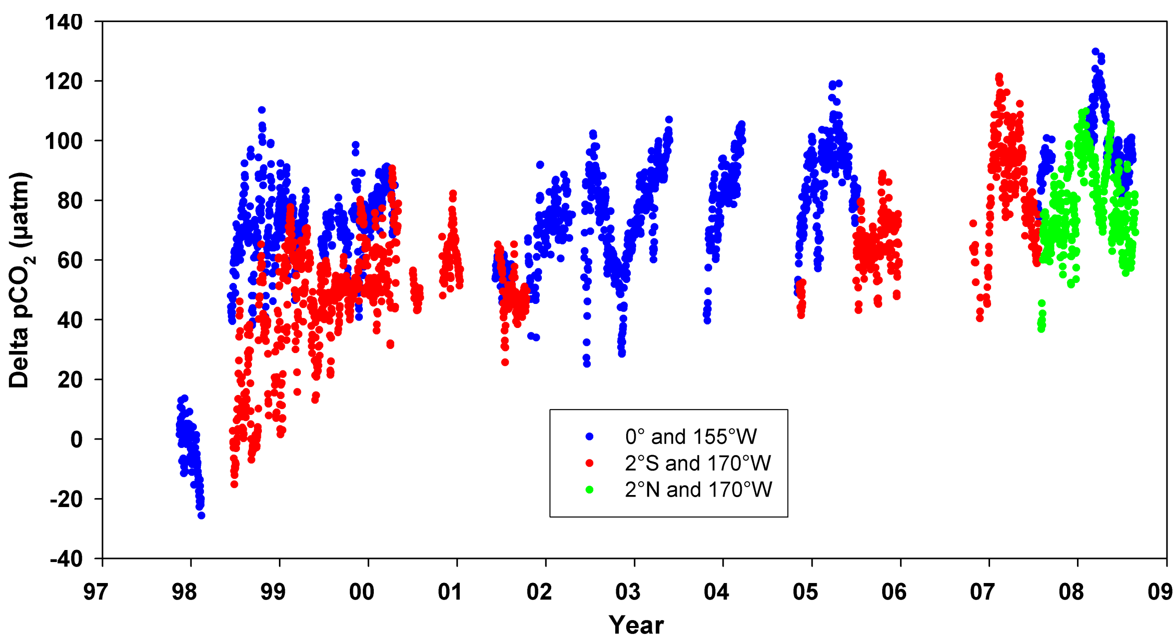


Figure 4. Daily average sea-air pCO_2 observations on the equator at 155°W, 2°S, 170°W and 2°N, 170°W from 1997 to present. An increase in pCO_2 cover the course of the record can be seen.

The time series of mooring based pCO_2 measurements in the equatorial Pacific have also been enhanced by the collection and analysis of discrete chlorophyll and nutrient samples in the upper 200 meters. About 500 samples per year have been processed from these cruises since 1997. Time series of the averaged nitrate and chlorophyll data along 155°W are shown in Figure 5. Although these data do not show the secular increases that are observed in CO_2, they do show inter-annual variations that correlate well with CO_2 variability. These changes are primarily associated with changes in upwelling strength.

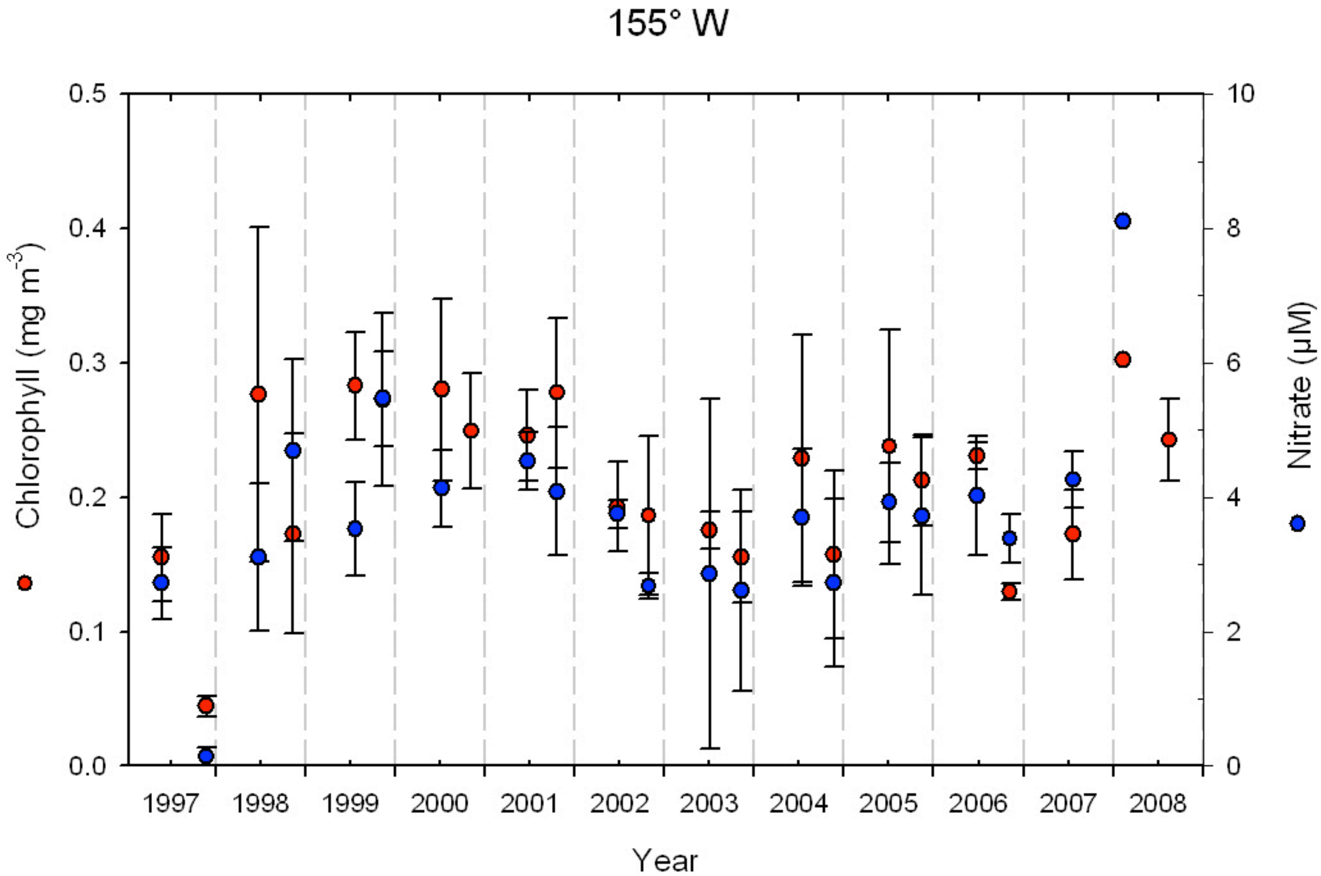


Figure 5. Average sea surface chlorophyll and nitrate levels along 155°W during the spring and autumn cruises from 1997 until 2008. The close correlation between chlorophyll and nitrate is evident.

2.6. Relevant FY08 Publications Resulting From This Project

Chavez, F.P., T. Takahashi, W.-J. Cai, G. Friederich, B. Hales, R. Wanninkhof, and R.A. Feely, 2007: Coastal Oceans. In: *The First State of the Carbon Cycle Report (SOCCR): The North American Carbon Budget and Implications for the Global Carbon Cycle*. A Report by the U.S. Climate Change Science Program and the Subcommittee on Global Change Research[King, A.W., L. Dilling, G.P. Zimmerman, D.M. Fairman, R.A. Houghton, G. Marland, A.Z. Rose, and T.J. Wilbanks (eds.)]. National Oceanic and Atmospheric Administration, National Climatic Data Center, Asheville, NC, USA, pp. 157-166.

Cronin, M.F., C. Meinig, C.L. Sabine, H. Ichikawa, and H. Tomita, 2008: Surface mooring network in the Kuroshio Extension. IEEE Systems Special Issue on GEOSS, 2(3), 424–430.

Friederich, G.E., J. Ledesma, O. Ulloa and F.P. Chavez, 2008: Air-Sea carbon dioxide fluxes in the coastal southeastern tropical Pacific. *Progress in Oceanography*, in press.

Kamphaus, R., M. Cronin, C. Sabine, S. Emerson, C. Meinig, and M. Robert, 2008: New surface mooring at Station Papa monitors climate. PICES Press, 16(2), 26–27.

Pennington, J.T., Castro, C.G., Collins, C.A., Evans, W.W. IV, Friederich, G.E., Michisaki, R.P., Chavez, F.P., 2008: A carbon budget for the northern and central California coastal upwelling system. Continental Margins Task Team, The Synthesis Book. Chapter 2.2, California Current System, in press.

Sabine, C.L., R.A. Feely, and R. Wanninkhof, 2008: The global ocean carbon cycle. In *State of the Climate in 2007*, D. H. Levinson and J. H. Lawrimore (eds.). *Bull. Am. Meteorol. Soc.*, 89(7), S52–S56.

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Vandemark, D., R. K. Varner, P. Beckman, J. Salisbury, R. Talbot, V. R. Sawyer, W. R. McGillis, and C. L. Sabine, 2008: Atmospheric CO_2 in the coastal marine boundary layer: observations and implications. *Mar. Chem.*, submitted.