Surface Water pCO_2 Measurements from Ships

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1. PROJECT SUMMARY

The oceans are the largest sustained sink of anthropogenic carbon with a flux into the ocean of about 1.6 10^{15} gram (= 1.6 gigaton) of carbon each year. Changes in this sink are determined by monitoring regional and seasonal patterns of carbon uptake and release. Quantification of regional sources and sinks of carbon dioxide in the ocean are of critical importance to international policy decision making, as well as for forecasting long-term climate trends. In this project NOAA investigators and academic partners have outfitted research and commercial vessels with automated carbon dioxide analyzers as well as thermosalinographs (TSGs) to measure the temperature, salinity and partial pressure of CO_2 (pCO_2) in surface water and air in order to determine the carbon exchange between the ocean and atmosphere. This task is coordinated at national level with the U.S. Carbon Cycle Science Program and its subcommittee on Ocean Carbon and Climate change (OCCC). We work with the International Ocean Carbon Coordination Project (IOCCP) for international coordination. Collaborative efforts are underway to combine datasets in the Atlantic through a Memorandum of Understanding with the European Union project CARBOOCEAN. Pacific collaboration is established through the PICES working group 13. In addition there are one-on-one interactions with investigators in Norway, Iceland, France, the United Kingdom, Australia, New Zealand, and Japan on reciprocal data exchange and logistics support. The overall effort to assemble all surface water pCO_2 data is called the Surface Ocean Carbon Atlas (SOCAT).

Documenting carbon sources and sinks relies critically on other efforts undertaken under sponsorship of the Office of Climate Observation (OCO) including implementation of the ship lines, and moored and drifting buoys. The surface water pCO_2 programs support climate services by providing knowledge and quantification of the radiatively important gas, carbon dioxide. The near-term focus is on completion of the Northern Hemisphere ocean carbon observing system to provide data for quantifying carbon dioxide sources and sinks over the coterminous United States through inverse modeling in collaboration with scientists involved in the atmospheric CO_2 observing system. We are currently expanding our focus on the high-latitude sources and sinks.

The project is a partnership of AOML, AOML/GOOS, PMEL, LDEO of Columbia University, RSMAS of the University of Miami, and the Bermuda Institute of Ocean Sciences (BIOS), formerly known as the Bermuda Biological Station for Research (BBSR). The partners are responsible for operation of the pCO_2 systems on the ships, auxiliary

measurements, data reduction, and data management from all ships. The following ships had pCO_2 systems on them during part or all of the performance period: NOAA ship *Ronald H. Brown*, NOAA ship *Ka'imimoana*, container ship *Albert Rickmers*, RVIB *Palmer*, cruise ship *Explorer of the Seas*, container ship *Oleander*, and UNOLS RV *Atlantic Explorer* (ship owned and operated by BIOS), UNOLS RV *Walton Smith* (owned and operated by RSMAS), and UNOLS RV *Knorr* (owned and operated by Woods Hole Oceanographic Institute). Similar to the previous year, several ships were taken off lines and several new ships were outfitted. The final datasets are combined and sent to CDIAC for dissemination and archival. All work follows established principles of monitoring climate forcing gases and biogeochemical cycles.

2. PROGRESS

2.1. Acquisitions, deployments and data return

The main metric for this program is obtaining, reducing, quality controlling and disseminating high quality surface water and marine air pCO_2 data. The number of cruises with pCO_2 observations from research ships and VOS that have been completed during the performance period are listed in Table 1. Details for each ship are provided below.

Table 1.VOS Data Summary FY-2008.

SHIP	# Cruises	# Data Points	% Recovery*
R/V Brown	9	60,148	85.0%
Explorer of the Seas	11	16,466	85.0%
RVIB Palmer	8	76,112	98.0%
R/V Ka'imimoana	7	189782	97.0%
R/V Atlantic Explorer	TBD	TBD	TBD
OOCL Tianjin	1	4480	94.0%
M/V Albert Rickmers	1	5,945	91.0%
M/V Oleander	TBD	TBD	TBD

*The values are to illustrate overall performance of the program. They should be used with caution when making ship to ship comparisons. The number of data points is a function of frequency of measurements, number of cruises and instrument malfunction that differ for each ship. Percent recovery has been determined in different fashion by each investigator ranging from number of data points that could have been obtained if the units had operated whenever the ship was at sea to number of acquired data points that were discarded during quality control.

Four other critical endeavors in support of determining regional fluxes have been completed during the performance period:
1. To assure uniformity in measurements and to expand the effort within NOAA OCO and beyond, a technology transfer has been done in which General Oceanics Inc. of Miami, FL is building the underway pCO_2 systems to our specifications. Substantial time and effort is involved by participants at AOML and RSMAS to assist in building, troubleshooting, improving instrument design and training customers on the operation of the system. Over 24

units have been produced and sold to customers around the world. So far, about 12 of these units have been purchased by participants of the NOAA program.

2. The GOOS/TSG (thermosalinograph) component lead by Gustavo Goni currently operates and maintains TSGs in four ships of the SOOP: *Albert Rickmers, Explorer of the Seas, M/V Explorer and Oleander*. The *Explorer of the Seas* operations are in transition since December 2007, from a staffed operation to a fully autonomous effort. The pCO_2 and TSG components have been transitioned to a fully automatic mode but water intake and general computer control transition is still underway. AOML receives TSG data in real time. These raw data are submitted to an initial quality control check, where several procedures based on the ten GOSUD (Global Ocean Surface Underway Data Pilot Project) real-time control test are applied. Data are flagged and sub sampled using the median to one sample every 3 minutes. The reduced data are then resubmitted to the full automatic quality check and, if approved, immediately submitted to the Global Telecommunication System (GTS). As part of the TSG project, a web site has been created and maintained at AOML containing several products displaying TSG data location and values (http://www.aoml.noaa.gov/phod/tsg/index.php). This web site currently includes information regarding data analysis and quality control procedures for TSG data corresponding to the ships of the NOAA fleet and the SOOP. In particular, several products display the data obtained from *Oleander* and also from other ships that previously had TSG installations, such as M/V *Explorer of the Seas* and M/V *Skogafoss*. Another product shows the location of TSG real-time data that was inserted into the GTS (see Figure 1).

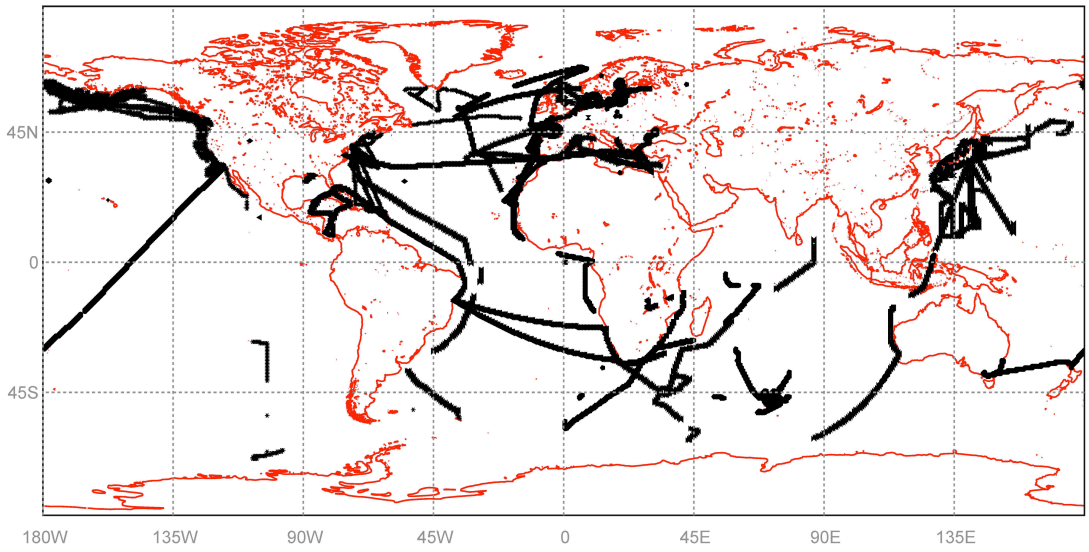

Figure 1. Location of real-time TSG transmissions into the GTS during FY 2008 for ships of the SOOP and the NOAA fleet.

The operations in the *Skogafoss* that transected between Boston and Iceland ended in May 2007, and its data were processed and transmitted until that date. A replacement for this ship, the *Reykjafoss* has been found and we expect to re-install pCO_2 and TSG instruments in a near future pending permission from the owner and operator (Eimskip lines).

AOML supports XBT operations on the M/V *Oleander* (Figure 2) and will do so for the *Reykjafoss* through provision of 1 pallet of XBTs per year, hand launcher, MK21 board, antennas, PC shuttle and transmission costs.

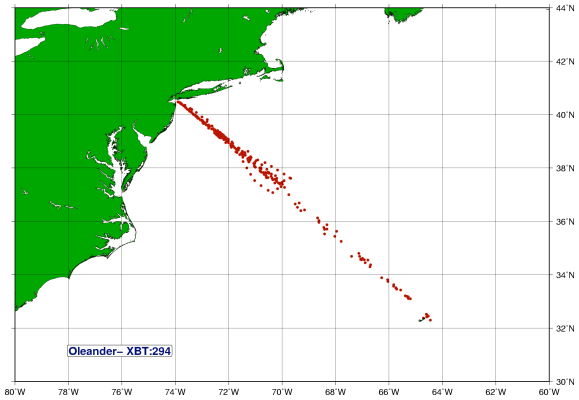

Figure 2. *M/V Oleander XBT drops, October 2007 - September 2008.*

3. In addition to leading the effort on the *Palmer* the LDEO group has provided a global ocean database which includes 4.1 million surface ocean pCO_2 observations made in 1970 - 2007 and which has been assembled in a single uniform format (LDEO Database, version 2007, Takahashi et al., 2008). It is accessible to the public through the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge National Laboratory, TN (http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/LDEO_home.html). This is an updated and improved version of the earlier release (version 1.0), which contained about 3.4 million pCO_2 measurements. For the members of the (VOS) consortium, the participants are able to access the data in a uniform electronic format. For this purpose, an open web site has been established at the following URL: http://www.ldeo.columbia.edu/CO2. The site provides not only the numerical data, but also maps showing the ship's tracks for each data file. The new data will be accessible only to the VOS participants for a period of three years, and will be released to the public after this period. A synthesis of the data set has been accepted for publication in the Surface Ocean CO_2 Variability and Vulnerabilities (SOCOVV) Symposium volume of "Deep-Sea Research".

4. Through two separate efforts, we collected data in the Arctic region where data is sparse. A pCO_2 system was installed on board the R/V *Knorr* to measure the pCO_2 during the International Chemistry Experiment in the Arctic LOwer Troposphere (Icealot) Cruise. The aim of the cruise was to study different aerosols and pollutants over an ice-free region of the Arctic. The system was installed in March and removed in June of this year. The system was operated by the survey technician and scientists on the cruise with oversight from our group on shore.

Last year the AOML group installed a pCO_2 system on the Chinese icebreaker *Snow Dragon (Xue Long)* as part of collaboration with the Third Institute of Oceanography in the People's Republic of China. Although the real-time transmission of the data has been problematic, the system continues to perform well. After completing the work in the Antarctic, the *Xue Long* sailed to the Arctic where she performed several cruises before

going back to Shangai. It will sail again to the Antarctic this winter and we expect to collect data at least until April 2009.

In support of our Northern Gulf of Mexico collaborative project, we also installed a system on the NOAA ship *Gordon Gunter*. The system has been collecting data since March of 2008 and will provide a data set which is needed in the region. While operation on these ships, and several other ships overseen by participants from LDEO and PMEL (see below), are covered by other sources, the data undergoes the same rigorous data reduction and quality control procedures and are included in the (global and coastal) data sets that are currently being assembled.

The responsibilities of the different groups are summarized in the flow diagram below.

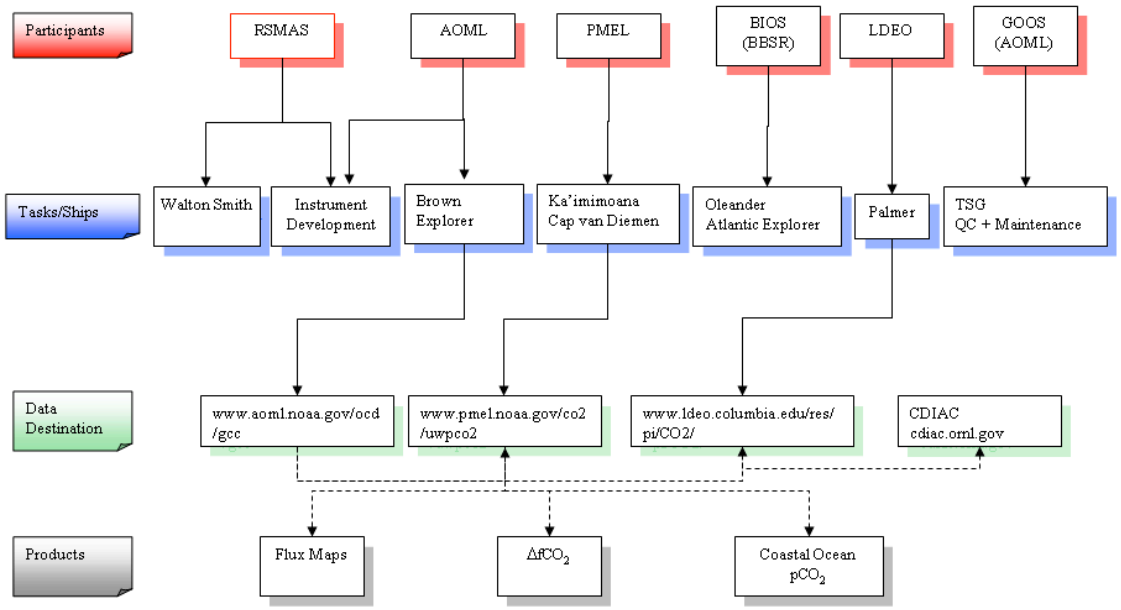

Figure 3. Organizational chart of the VOS project.

A short summary of the efforts on each ship are listed below:

NOAA ship *Ronald H. Brown*- AOML lead

Data Site:
www.aoml.noaa.gov/ocd/gcc/rvbrown_data2007.php
Number of cruises: 9
Number of fCO_2 data points: 60,148
% Data return: 85%.

Causes for non-return: The underway pCO_2 system on the *Brown* performed well with over a 85 % data return. This year, we participated in many of the cruises on the *Brown*, which allowed us to fix any problem that arose immediately. We finally performed the upgrade of the old system to the new ones from General Oceanics, Inc (GO). Both the old and the new system were installed and run during the GOMECC cruise from last year and the GasEx III cruise from this year such that a side-by-side comparison could be performed avoiding possible data biases that sometimes occurs when observing system elements are upgraded. In May of 2008, at the end of the season, both systems were removed and the GO system was re-installed in October, along with a Seabird-45 salinity and temperature sensor. The cruises that used the old system suffered from several problems, due to the age of the system which was first installed in 2000. For example, in two instances, gas flow through the equilibrator failed due to a blockage in the needle valve that controls the flow and the operator did not notice or correct the problem. The thermistor also developed a problem in which it would not record temperatures below ~6 ^{o}C. Finally, during a cruise in 2007, the mass flow meter that measures the flow through the sample cell gave inaccurate readings, causing incomplete flushing of the sample cell for the first half of the cruise. This explains the slightly lower percentage in data return compared to previous years and increased difficulties with data reduction. We expect the new system to yield higher returns.

Description: The cruise tracks for each cruise of the *Brown* for FY 2008 are shown at http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2007.php. The cruises include both legs of the CLIVAR P18 line as well as the Southern Ocean Gas Exchange Experiment which took place from February to April of 2008 (http://www.ldeo.columbia.edu/~david/duck-rabbit/so_gasex). Figure 4 shows the pCO_2 along the P18 cruise track.

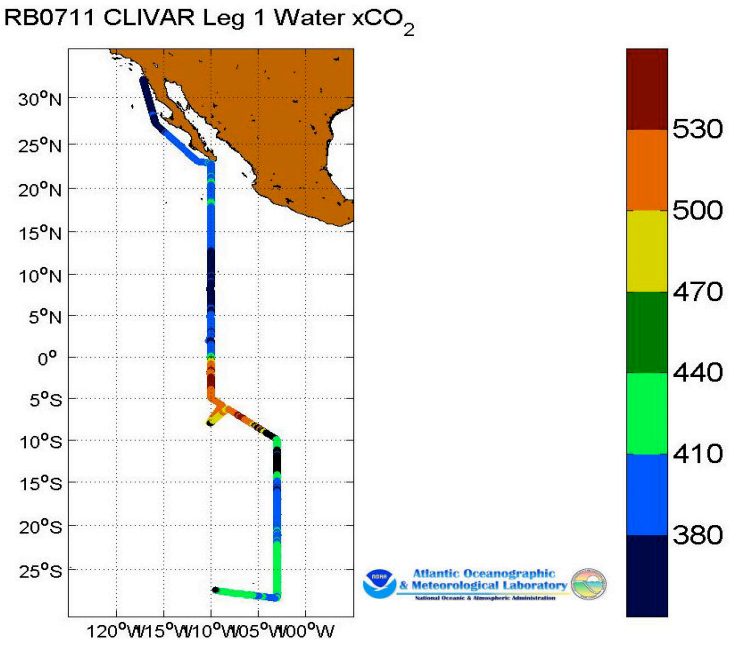

Figure 4. P18 Leg 1 cruise track and surface pCO_2 values.

NOAA ship *Ka'imimoana*- PMEL lead

Data Site:
http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: *7*
Number of fCO_2 data points: 189,782
% Data return: 97%.

Causes for non-return: The underway fCO_2 system on the *Ka'imimoana* yielded a 97% data return during FY 2008. A small amount of data was rejected due to stack gas contamination when the ship was on station to service and deploy buoys.

Description: From October 2007 through September 2008 the *Ka'imimoana* was involved in studies in the Equatorial Pacific between 95°W and 165°E. Prior to the 2007-2008 field season, the fCO_2 system was updated with new software, pumps and filters. During the time under review, PMEL collected and processed 189,782 fCO_2 data values from the *Ka'imimoana* on 7 separate cruises in the equatorial Pacific. The cruise data can be obtained from our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2. A summary of the cruise results from November 1997 through July 2008 is shown in Figure 5. The results show weak seasonal and strong interannual variability of CO_2 fluxes from the oceans to the atmosphere. A ten-year record of observations is shown in Figure 6. Comparison with the ENSO index (Figure 7) shows a strong correlation between negative/positive indices and

strong/weak CO_2 sources in the region. All data collected from the *Ka'imimoana* during the 2007-2008 fiscal year are in final processing and will be submitted to CDIAC for archiving.

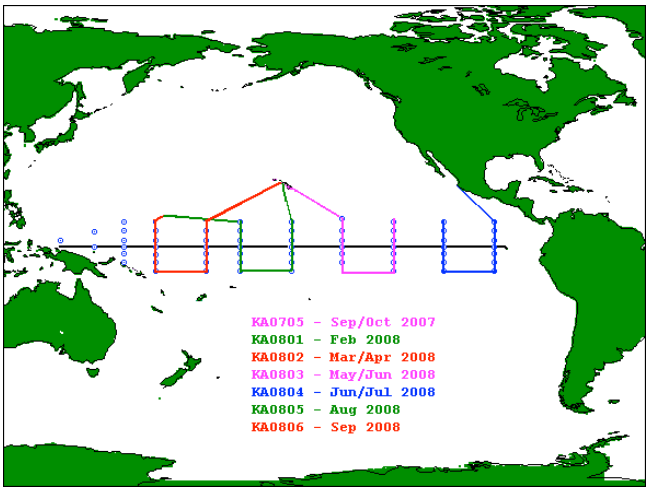

Figure 5. Ka'imimoana track lines occupied during FY 2008.

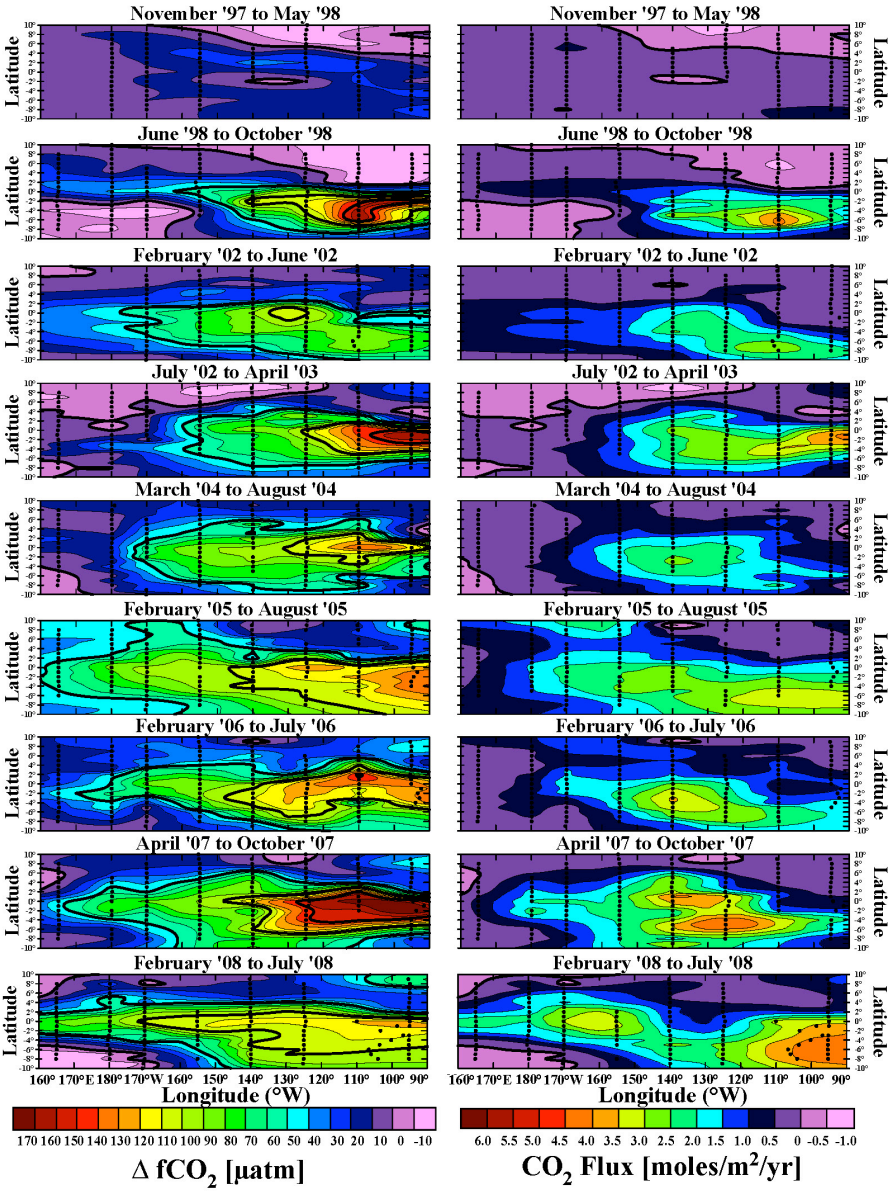

Figure 6. Time-Series of surface water fCO_2 levels in the tropical Pacific resulting from Ka'imimoana repeat observations from 1997 thru 2008.

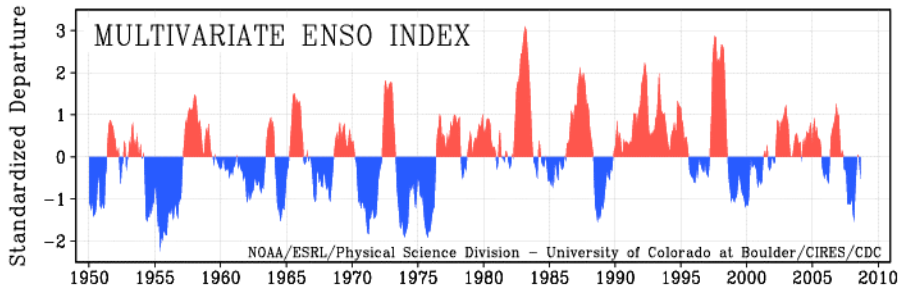

Figure 7. ENSO events through October 2008. Positive values (red) relate to El Niño events and negative values (blue) relate to La Niña events.

Container ship *Albert Rickmers* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO_2
Number of cruises: 1
Number of fCO_2 data points: 5945
% Data return: 91%.

Causes for non-return: The underway fCO_2 system on the *Albert Rickmers* resulted in a 91% data return during 2007. There were problems associated with inadequate flushing time prior to equilibrator measurements, resulting in rejection of a small fraction of the seawater fCO_2 values.

Description: During October 2007, an fCO_2 system was deployed on the container ship *Albert Rickmers*. The *Albert Rickmers* is involved in studies in the tropical and subtropical Pacific (Figure 8). All data collected on the *Albert Rickmers* has been submitted to CDIAC for archiving, and can also be obtained from our website: http://www.pmel.noaa.gov/co2/uwpco2.

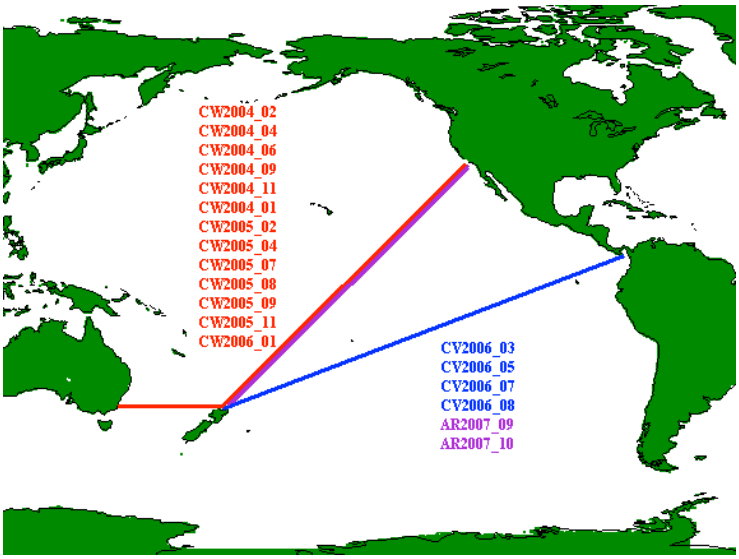

Figure 8. Cruise Tracks of the Columbus Waikato (red), Cap Victor (blue) and Albert Rickmers (purple) occupied during FY2004-2008.

A summary of the cruise results from Fall 2005 to November 2007 is shown in Figure 9. The results show strong seasonal variability of CO_2 fluxes in the southern and northern subtropical Pacific Ocean, that are out of phase by 6 months. The most recent data shows high seawater fCO_2 values due to La Niña conditions in the equatorial Pacific.

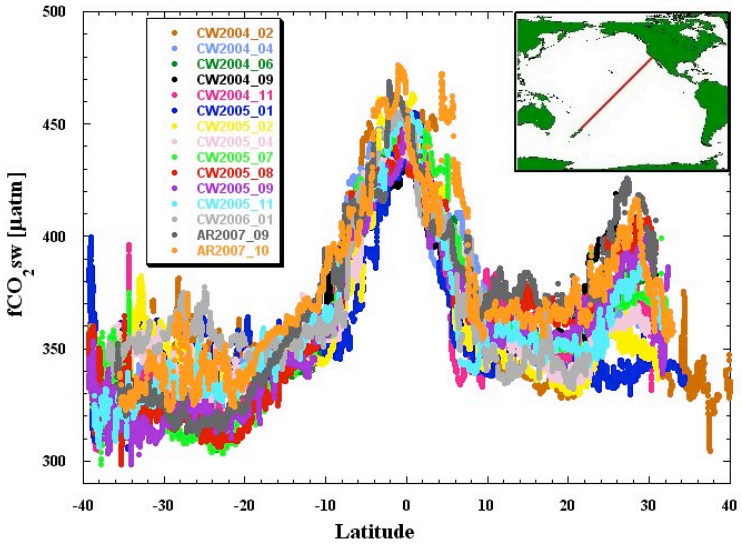

Figure 9. Time-Series of surface water fCO_2 levels in the tropical and subtropical Pacific resulting from Columbus Waikato and Albert Rickmers repeat observations from 2004 to 2007.

In December 2007, the fCO_2 system was removed from the *Albert Rickmer* when the ship changed routes. The Alpha Ship *Cap Van Diemen* was identified as a replacement for the *Albert Rickmers*, and installation of an underway fCO_2 system on the *Cap Van Diemen* began in the summer of 2008.

Container ship *OOCL Tianjin* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 1
Number of fCO_2 data points: 4480
% Data return: 94%.

Causes for non-return: The underway fCO_2 system on the *OOCL Tianjin* resulted in a 94% data return during FY 2008. There were problems associated with inadequate water flow to equilibrator measurements, resulting in rejection of a small fraction of the seawater fCO_2 values.

Description: During the summer of 2008, an fCO_2 system was deployed on the container ship *OOCL Tianjin*. The *OOCL Tianjin* is involved in studies in the North Pacific, an important sink region for atmospheric CO_2. Data will be analyzed to determine how ocean circulation and biological photosynthesis interact to control the rate of exchange of carbon dioxide gas between the atmosphere and North Pacific Ocean. This research is done in collaboration with Dr. Paul Quay of the University of Washington, and Dr. Kitack Lee of the Pohang University of Science and Technology. In addition to supporting our underway

fCO_2 measurements, they are also collecting samples for carbon isotope measurements (Quay) and DIC and nutrients (Lee). For this reason, we have combined resources to place ship riders on each of the cruises. Underway fCO_2 and temperature data from the first cruise on board *OOCL Tianjin* is shown in Figure 10. The cruise data can be obtained from our website**:** http://www.pmel.noaa.gov/co2/uwpco2, and will be submitted to CDIAC for final archival.

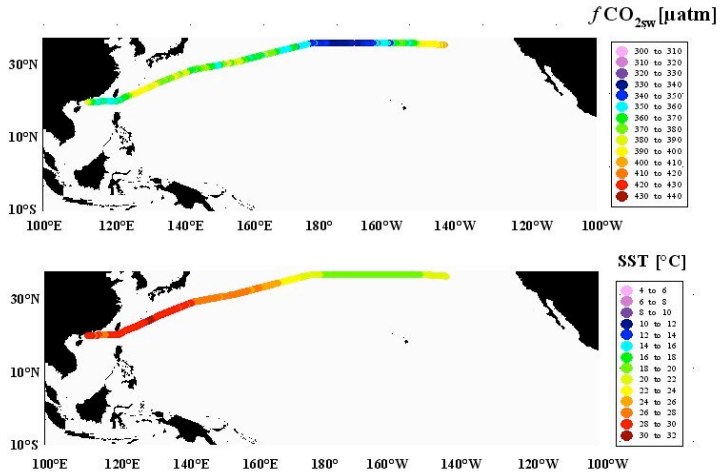

Figure 10. fCO_2sw and SST from the first cruise of the OOCL Tianjin.

RVIB *Palmer* - LDEO lead

Data Site: http://www.ldeo.columbia.edu/CO2
Number of cruises: 8
Number of fCO_2 data points: 76,112
% Data return: 98%.

Description: We have operated successfully a semi-automated surface water pCO_2 system aboard the RVIB *Nathaniel Palmer* with vital operational assistance from the Raytheon Polar Support group. Since RVIB *Palmer*, an ice-breaking research vessel is one of the few research ships which are operated in high latitude areas of the Southern Ocean even during winter months, our CO_2 program aboard this vessel allows us to make observations in hostile environments of the high latitude oceans, where deep and intermediate water masses are formed in winter. The ship was not at sea during the period May 10 through August 27, 2007, for refit in a dry dock and test cruises, and no data were obtained. On September 1, 2007, our measurement program was resumed. During the expeditions, we obtained the following information: pCO_2 in surface ocean water, SST, salinity, wind speeds, barometric pressure and atmospheric CO_2 concentration. The data were obtained successfully for better than 98% of time during the at-sea periods.

The locations of our data obtained since the beginning of this project in 2001 are shown in Figure 11. The total number of surface water pCO_2 data obtained to date is 668,537, of which 76,112 measurements were added to the database during this project year, September, 2007 through August, 2008.

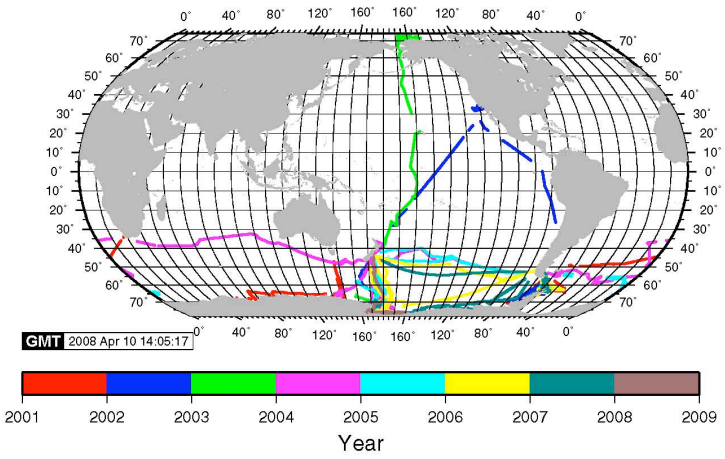

Figure 11. The locations of surface water pCO_2 measurements made aboard the RVIB Palmer since 2001. During the current project year August, 2007-August, 2008 (dark green and brown lines), about 76,112 pCO_2 measurements were obtained.

Cruise ship *Explorer of the Seas*-AOML lead

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of cruises: 11
Number of fCO_2 data points: 16,466
% Data return: 85%.

Causes for non-return: On the few cruises where we could run the system, it performed quite well with only minimal data loss. We now upgraded the system to the one produced by General Oceanics, Inc. The whole system has been moved to the bow engineering space and upgraded, as explained in the following section, and we are working out the unique operational challenges of the new installation. So far, it performed very well in the new configuration.

Description: Due to lack of funding, the program on board the *Explorer of the Seas* with a dedicated marine technician which was led by the University of Miami's Rosenstiel School of Marine and Atmospheric Science ended abruptly in March of last year, depriving us of the necessary support to run our instrument. After negotiations with Royal Caribbean Cruise Lines, the program has been resurrected on a smaller scale in a fully automated mode, which allowed us to keep a pCO_2 instrument on board but required us to upgrade our system and

relocate it. This was achieved at the end of August of this year. As part of the upgrade an airline to the bow of the ship was installed such that we can now obtain air and surface water fCO_2 measurements. The system can presently only be run by an observer because the automated seawater valve and safety shutoff operations are not in place yet. An upgrade of the support system is underway to make the whole operation completely integrated and autonomous, at which point our instrument will run permanently unattended. In the meantime, we plan to send an observer every three months to run the system and take discrete samples for DIC and TA.
During the last performance period a near-real time data display was instituted where daily pictorial updates of concentrations along the cruise track. This will no longer an option but rather the data will be downloaded automatically every week to 10 days when the ship is in its home port in Bayonne, NJ by wireless communication to an on-shore network which will then relay the data to our host computer for display and reduction.

***RV F.G. Walton Smith*- RSMAS lead**

Description: The RV *Walton Smith* is a shallow draft catamaran which is based at the University of Miami. As a University-National Oceanographic Laboratory System (UNOLS) vessel, its destinations vary but range from the Florida Keys, Florida bay to the Caribbean, the Gulf of Mexico and occasionally the east coast. In a typical year, the ship spends about 200 days at sea. It has the capability of routinely measuring sea surface temperature and salinity, as well as chlorophyll.A pCO_2 system has been installed on board the *Walton* Smith in the beginning of July 2008. So far, it has been on 4 cruises.

Causes for non-return: The main problem on the Walton Smith is the seawater supply which is not sufficient when the demand for it is too great. We are working with the crew to fix that problem. Most of the issues that were encountered did not so much cause a loss of data as it caused a loss of quality. One of these issues was the wrong calibration of a standard gas, which prevented the system to be calibrated over the oceanic CO_2 range encountered. One of the standard tanks which was used for the calibration of the analyzer was not opened. Not only the data will have to be re-calculated but the analyzer will not be as well calibrated over that time.

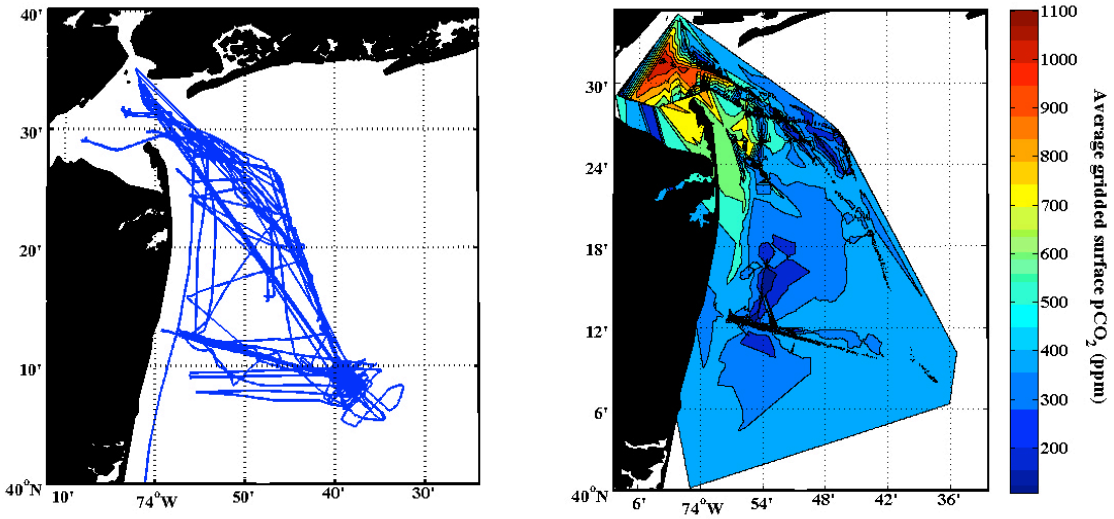

Figure 12. Northern section of the coastal track (left) and average gridded surface pCO_2 values of the R/V F.G. Walton Smith during underway surface sampling along the coast of New Jersey and New York.

Container Ship *Oleander* - BIOS lead

Description: The MV *Oleander* crosses weekly between New Jersey and Hamilton, Bermuda. Given the ~100 crossings a year, this gives excellent temporal and spatial coverage of the North Atlantic subtropical gyre, Gulf Stream, middle Atlantic Bight and coastal zone. The MV *Oleander* transits the region of Subtropical Mode Water (STMW) formation during the winter southeast of the Gulf Stream, and the highly productive coastal zone of the Eastern Seaboard.

R/V *Atlantic Explorer* - BIOS lead

Description: The R/V *Atlantic Explorer* operates in the North Atlantic Ocean (zone NA6), servicing four oceanographic time-series (e.g., Bermuda Atlantic Time-series Study, Hydrostation S, Bermuda Testbed Mooring, Ocean Flux Program) and other research projects. This data stream provides groundtruthing pCO_2 datasets for the subtropical gyre of the North Atlantic Ocean.

2.2. Adherence to monitoring principles

The efforts of the NOAA VOS pCO_2 group have met the important monitoring principle of uniform instrumentation with a quantifiable accuracy. All systems are calibrated with compressed standards that are traceable to the WMO scale. We are actively involved in assuring uniform instrumentation, through close interactions including organizing training session for customers with the manufacturer General Oceanics who is building instruments to our specifications, uniform operating protocol, and uniform data reduction procedures.We are in the process of creating a discussion forum which would be accessible to pCO_2 systems owners where common problems and issues would be discussed and the solutions would be accessible to others. To assure uniform data reduction procedures, we now have two programs, in Excel ® and Matlab ® which automate some of the steps involved. These are outlined in a manuscript by Pierrot et al. 2009. We have started to use them to reduce data and we will make them available to other users soon.
An inter-comparison exercise similar to the one held in 2003 is being organized by the National Institute for Environmental Studies (NIES) in Japan in March 2009 with active involvement of our group. This exercise will involve many international participants, different kind of onboard systems as well as buoys and will improve on the last exercise by reducing the effect of error sources such as the accuracy of temperature sensors. The results will be reported to CDIAC who will make them publicly available along with the 2003 results. This will give good insights into the performance of the systems used in this program.

2.3. Data management and dissemination

An important part of the VOS effort is to disseminate quality controlled data to the community at large in an expedient fashion.

Thermosalinograph (TSG) data from ships of the Ship of Opportunity Program (SOOP) and NOAA fleet are now automatically placed into the GTS by the AOML/GOOS group.

During FY2008 a total of 301,243 TSG quality controlled data from the ships of the SOOP and the NOAA fleet were placed into the GTS. TSG data are being test coded in BUFR (both BUFR Edition 3 and Edition 4 specifications) format, using templates that have been specifically designed to serve operational needs. This effort seeks to improve the future migration from the Traditional Alphanumeric Codes (TACs) to Table-Driven Code Forms (TDCFs), as required by WMO, and has a deadline set to 2010. The current testing will provide the feedback necessary to detect, identify and correct problems that can arise in the migration process, providing a robust framework for near-real-time collection, quality control and distribution of TSG data. The new transmission of TSG data into the GTS in BUFR format constitutes an important improvement because the BUFR message can include metadata and quality control flag information.

During the 2008 fiscal year, the PMEL group wrote new diagnostic software to automatically process daily underway data files when data files arrive via iridium satellite from the *Ka'imimoana*, *OOCL Tianjin*, *Albert Rickmers* and *Cap Van Diemen*. This software creates diagnostic plots of fCO_2, temperature, salinity, barometric pressure, pumps, water flow and gas flow. The plots are posted on an internal website and are used as a diagnostic tool for data processing and quality control of the underway fCO_2 data. During the time in review, data from 7 VOS cruises have been processed and submitted to CDIAC, and data from 2 VOS cruises are in final data processing. All current and previous VOS data files are quality controlled using the data protocol outlined in Pierrot et al. (2009).

The LDEO group, in close interaction with the data acquisition groups, oversees shipboard quality control so that the quality of data and consistency is monitored for the whole group. The participants of the VOS program are able to access the data which are listed in a uniform format. For this purpose, the LDEO group established an open web site at the following URL: http://www.ldeo.columbia.edu/CO2. The site provides not only the numerical data, but also maps showing the ship's tracks for each data file. The new data will be accessible only to the VOS participants for a period of three years, and will be sent to the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge, TN, for the permanent archiving and distribution to the public after this period. This close coupling of the data acquisition with data processing/evaluation and interpretation will guarantee high quality field observation data.

As a part of the VOS program, the LDEO group processed and added to its database the measurements from the 2 other field operations; 1) the R/V *Laurence M. Gould*, which is supported by NSF as a part of the Long-Term Research in Environmental Biology (LTRE) program in the Drake Passage area, Southern Ocean; 2) Yacht *Turmoil* in coastal waters.
A total of approximately 68,403 pCO_2 measurements that were made aboard the R/V *Gould* and 101,053 that were made aboard the Yacht *Turmoil* during the calendar year 2008 have been added to the database. This makes a total of 356,557 pCO_2 measurements for the VOS participants from August, 2007 through August, 2008.

Table 2. Summary of the new data contributed to the database by the VOS participants during this funding period, August, 2007 – August, 2008.

Programs	**PI / Institutions**	**No. of pCO_2 Observations**	**Primary Locations**
RVIB Palmer	Takahashi/LDEO	76,112	Southern Ocean
R/V Gould	Sweeney/ESRL/NOAA Takahashi/LDEO	68,403	Drake Passage, Southern Ocean
Explorer of Seas	Wanninkhof/AOML/NOAA	53,268	Caribbean
R/V Kaimimoana	Feely/PMEL/NOAA	57,721	Tropical Pacific
M/V Oleander	Bates/BIOS	Not reported	N. Atlantic
R/V Atlantic Explorer	Bates/BIOS	Not reported	Bermuda
M/V Turmoil	Takahashi/LDEO	101,053	Coastal
TOTAL FOR AUG. 07-AUG. 08		**356,557**	

2.4. Research highlights

1. We have developed seasonal and interannual fCO_2-SST relationships from shipboard data that were applied to high-resolution temperature fields deduced from satellite data to obtain high-resolution large-scale estimates of the regional fluxes in the Equatorial Pacific (Figure 6). The data were gathered onboard research ships from November 1981 through September 2008. Data were collected during the warm boreal winter-spring season (January through June) and during the cooler boreal summer-fall season (July through December) of each year making it possible to examine the interannual and seasonal variability of the fCO_2-SST relationships. A linear fit through the equatorial Pacific data sets yields an inverse correlation between SST and fCO_2, with both interannual and seasonal differences in slope. In particular, the results indicate a strong interannual El Niño – Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and weaker seasonal variability. There is also a slight increase in the out-gassing flux of CO_2 after the 1997–1998 PDO mode shift. Most of this increase is due to increase in wind speeds after the spring of 1998 (Figure 6). These increases are consistent with the recent rebound of the shallow water meridional overturning circulation in the tropical and subtropical Pacific after the PDO 1997-98 shift. In the summer of 2007, equatorial CO_2 flux values were extremely high, resulting from the development of La Niña conditions in the late summer of 2007 which persisted into the summer of 2008 (Figure 7).

2. A unique and novel application of our 4-year time series of data in the Caribbean Sea from the *Explorer of the Seas* has been the assessment of ocean acidification in the region. Utilizing the in situ fCO_2, salinity, and SST data along with high resolution remotely sensed and assimilated SST, wind and salinity data a ten-year record of ocean acidification was produced (Figure 13) (Gledhill et al., 2008). This product is now being served through NESDIS Coastwatch. This analysis was covered under other grants but it illustrates the wide reach of collaboration and application of the datasets.

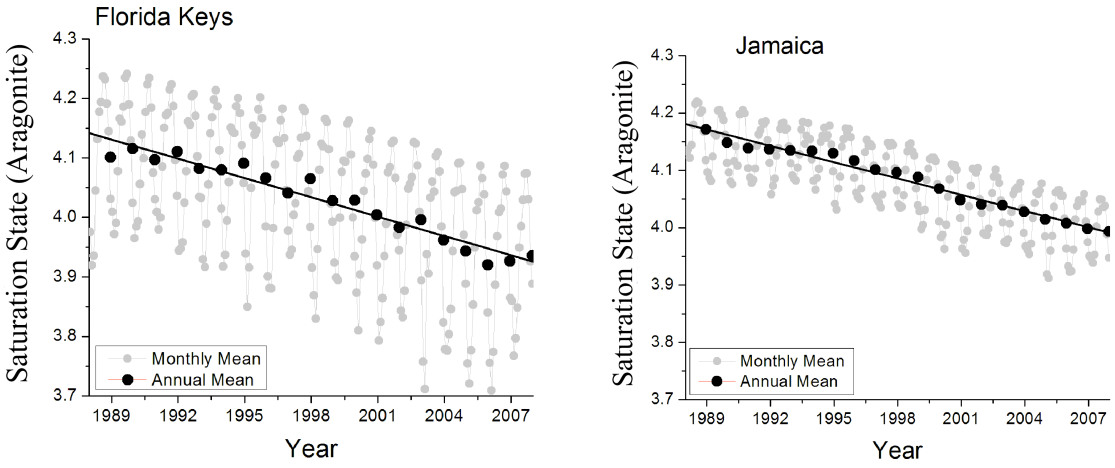

Figure 13. Increases in surface water fCO_2 lead to decreases in saturation state that is unfavorable for coral growth in the Caribbean. Data from the Explorer of the Seas along with high resolution remotely sensed and assimilated data were used to obtain the estimates of declining saturation states in different parts of the Caribbean Sea. Note the large seasonal excursions primarily due to seasonal changes in surface water fCO_2 (from Gledhill et al., 2008).

3. The publication of the updated climatology of Takahashi et al. (2009) has been delayed because of issues with the release of the special volume. Important updates have been made in the interim including addition of 0.8 M data points (many obtained under auspices of this effort). New findings include a breakdown of the estimate's uncertainty into the uncertainty in the ΔfCO_2, the uncertainty in the gas transfer velocity, and the uncertainty introduced by mapping the data onto a single year and the assumptions about the trend of surface seawater fCO_2 over the 3 decades that span the climatology (Table 3). In addition, the updates show an increase in surface water fCO_2 in the Southern Ocean that is greater than the atmospheric increase pointing towards a decreasing sink (Figure 14).

Table 3. Breakdown of error in air-sea CO_2 flux estimate[1] (from Takahashi et al. 2009).

Error	% Error	Source
± 0.18 Pg-C yr^{-1}	± 13%	ΔpCO_2 measurements
± 0.42 Pg-C yr^{-1}	± 30%	scaling factor for the gas transfer velocity parameterization,
± 0.28 Pg-C yr^{-1}	± 20%	wind speeds
± 0.5 Pg-C yr^{-1}	± 35%	mean rate of change in ocean water

[1]the total flux is estimated at 1.6 Pg-C yr^{-1} and the anthropogenic CO_2 flux at 2 Pg-C yr^{-1}.

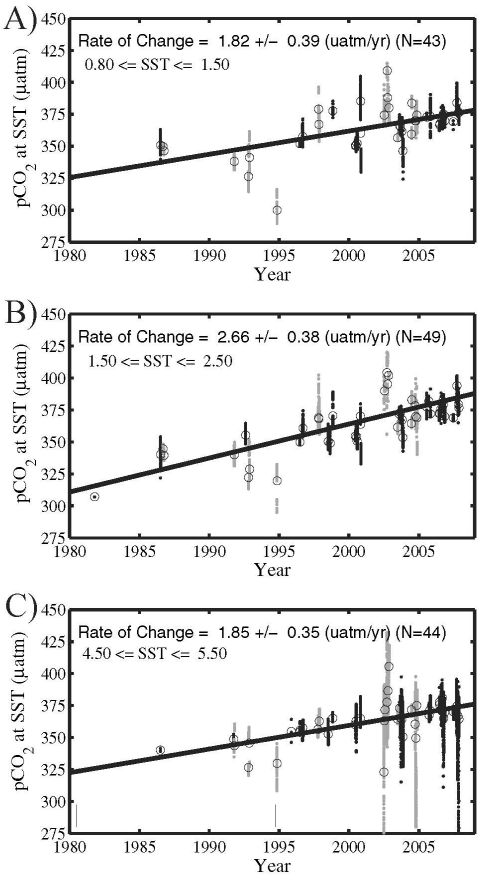

Figure 14. Rates of increase in surface water pCO_2 in the subpolar region (south of 50˚S) of the Southern Ocean in the winter months (Julian dates from 172 to 326) during the period from 1986 to 2006. The top panel is for SST between 0.8 to 1.5˚C; the middle panel for SST between 1.5 and 2.5˚C; and the bottom panel for SST between 4.5 and 5.5˚C. (From Takahashi et al. (2009).

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