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 2 10^{15} grams (= 2 gigaton) of carbon each year thereby partially mitigating the rapid increase of this climate forcing gas in the atmosphere. To provide meaningful projections of future atmospheric CO_2 levels, and surface oceanic CO_2 concentrations we must constrain the flux of CO_2 across the air water interface. The goal for the mature surface ocean CO_2 observing system is to accomplish this to within 20 % on regional and seasonal scales. This will be accomplished through creation of seasonal sea-air CO_2 flux maps that will feed directly into national and international assessments. Of particular interest is quantification and attribution of variability and trends. In this project four NOAA investigators and three academic principal investigators have outfitted 17 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 the subcommittee of the Ocean Carbon and Biogeochemistry (OCB) program, the Ocean Carbon and Climate Change (OCCC) effort. Collaborative efforts are underway to combine datasets, and create and update global climatologies that are lead by our academic collaborator Dr. T. Takahashi of LDEO/Columbia. Furthermore, we assemble, document and serve global datasets through the Surface Ocean CO_2 Atlas (SOCAT version 2) (Bakker et al. 2013) run under the auspices of the International Ocean Carbon Coordination project (IOCCP). Approximately half of the SOCAT version 2 data release comes from the participants of the pCO_2 from ships effort.

Documenting carbon sources and sinks relies critically on other efforts undertaken under sponsorship of the Climate Observation Division (COD) 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 data are used along with robust interpolation methods utilizing remotely sensed products to produce monthly sea-air CO_2 flux fields that are served on the web with a one to three month lag. Products and data are used in the international Regional Carbon Cycle Assessment Project (RECCAP) of the Global Carbon Program (GCP) and the information has been utilized in the latest IPCC assessment report (AR5). This work provides critical information for policies on greenhouse gas management and mitigation, and assessments of perturbations of the surface ocean (ocean acidification).

2 Scientific and Observing System Accomplishments

The project is a partnership of the Atlantic Oceanographic and Meteorological Laboratory (AOML) and its TSG group, the Pacific Marine Environmental Laboratory (PMEL), the Lamont-Doherty Earth Observatory (LDEO) of Columbia University, the Rosenstiel School of Marine and Atmospheric Science (RSMAS) of the University of Miami, and the Bermuda Institute of Ocean Sciences (BIOS). The partners are responsible for operation of the pCO_2 systems on the ships, auxiliary measurements, data reduction, and data management. The following ships had pCO_2 systems on them during part or all of the performance period: NOAA ships *Ronald H. Brown, Gordon Gunter, Ka'imikai-o-Kanaloa, Bell Shimada, Oscar Dyson* and *Henry B. Bigelow;* Container ships *Cap Vilano, Oleander, Barcelona Express, and Reykjafoss,* research vessels *RVIB Palmer, Gould, Langseth* and *Healy*, RCCL cruise ship *Explorer of the Seas*, and UNOLS research vessels *Atlantic Explorer* (ship owned and operated by BIOS), and *Walton Smith* (owned and operated by RSMAS). This effort is the largest single coordinated entity of obtaining surface water CO_2 data in the world. Approximately 500 K new data points are acquired each year. As outlined below, outfitting of some of the ships was funded from other sources but all the data was reduced and collated in a uniform manner and provided to CDIAC as part of this effort. Similar to the previous years, several ships were taken off lines and several new ships were outfitted. The final data sets are combined and sent to CDIAC for dissemination and archival, and to the SOCAT effort. All work follows established principles of monitoring climate forcing gases and biogeochemical cycles.

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 ships of opportunity (SOOP) that have been completed during the performance period are listed in *Table 1*. Details for each ship are provided below.

Table 1:SOOP Data Summary FY-2013.

SHIP	# Cruises	# Data Points	% Recovery*
R/V Brown	5	50,000	95.0%
Explorer of the Seas	14	24,500	80.0%
R/V Gordon Gunter	8	43,000	93.0%
M/V Barcelona Express	13	110,000	83.0%
M/V Reykjafoss	12	42,000	42.0%
R/V Bigelow	5	56,000	88.0%
M/V Cap Vilano	3	16,040	99.0%
R/V Ka`imikai-o-Kanaloa	1	16,454	85.0%
R/V Bell Shimada	*7*	*23,966*	*95.0%*
R/V Oscar Dyson	*8*	*33,633*	*87.0%*
RVIB Palmer	7	66,118	83.4%
R/V Gould	11	44,551	87.8%
R/V Langseth	7	60,978	86.0%
USCGC Healy	2	29,099	97.0%
R/V Atlantic Explorer	25	65,000	75.0%
M/V Oleander	48	110,000	55.0%
R/V Walton Smith	13	32,000	59.0%

* 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 deemed acceptable during quality control.

NOAA ship *Ronald H. Brown*- AOML lead

Data Site:
http://www.aoml.noaa.gov/ocd/gcc/
***Number of cruises:* 5**
Number of fCO_2 data points: ~50,000*
% Data return: 95%*.
** estimated*

Description: The cruise tracks for each cruise of the *Brown* for FY 2013 are shown in Figure 1. Each individual track with links to the data can be found on our website at http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2013.php. Every year, the ship spent an extended period of time in dry dock for repairs. Including the sea trials following the dry dock period, the ship was out of commission for about 3 months.

The system is connected to the Scientific Computer System (SCS), which is on board most NOAA ships. It takes advantage of the array of sensors logged by the system and gets GPS and TSG data from the ship. The data is automatically transmitted daily via email and plotted on AOML's website. Additional plots of the different sensor data are automatically generated and are internally accessible for quality control purposes. This allows the near real time detection of potential problems.

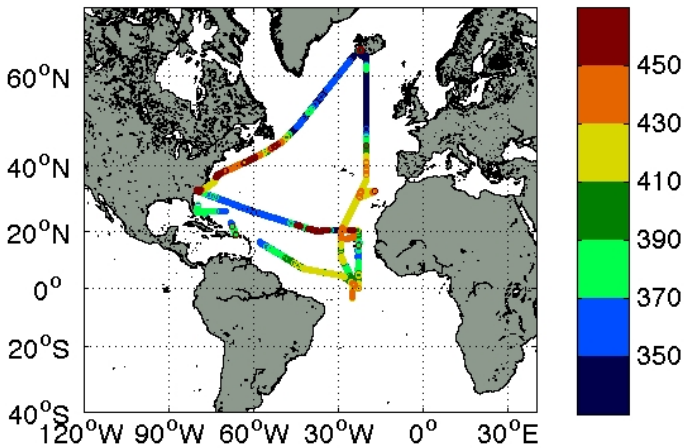


Figure 1. R/V Ronald H. Brown cruise tracks and surface xCO_2 values for FY 2013.

The system was upgraded with a water-jacketed equilibrator in 2010 and it has been working reliably since then. The high data return is directly related to the great support we get from the crew, and the science technician in particular.

Causes for non-return: The system is maintained by a survey technician, who is permanently on board. Most of the data loss is due to common ship's operations failures such as the seawater flow stopped or sensors not being turned on. The system also shows intermittent drops of SCS data. We have upgraded the software to the latest version, which improved the reliability of the sensors logging.

Cruise ship *Explorer of the Seas*-AOML lead

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of cruises: 14
Number of fCO_2 data points: ~24,500
% Data return: 80%.

***Description*:** The program is led by the University of Miami's Rosenstiel School of Marine and Atmospheric Science. The manifold controlling and distributing the seawater to several instruments is fully automated and remotely controlled via a Virtual Private Network (VPN) interface. Our system is a fully integrated part of the manifold. Through the VPN, we even have remote access to the system's computer to optimize the operations of the instrument.
The data is automatically downloaded daily via FTP to a server at the University of Miami. It is then plotted on our website in near real time (http://www.aoml.noaa.gov/ocd/gcc/explorer_realtime.php).

Causes for non-return: The whole installation still suffers from the fact that the seawater intake has been located too close to the surface when the ship was built. In this fiscal year, the seawater pump has been nonoperational for a substantial period of time due to a leak that remained undetected for a while and has only been repaired late in the year. It is working now and the system has been collecting data reliably again. This ship usually shows great data return and we expect it to continue collecting high quality data for the next fiscal year. This ship is scheduled to be re-routed to Asia in January 2015 and will be replaced by the *Allure of the Seas*. We are currently looking into moving our system to this new vessel.

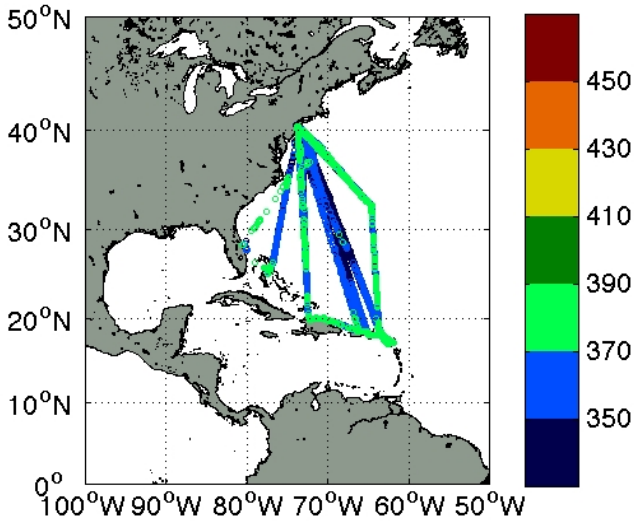


Figure 2. Explorer of the Seas cruise tracks and surface xCO_2 values for FY 2013.

***NOAA* ship *Gordon Gunter* - AOML lead**

Data Site: www.aoml.noaa.gov/ocd/gcc/
***Number of cruises:* 8**
Number of fCO_2 data points: ~43,000*
% Data return: 93%*.

***estimated**

Description: This system has been installed on the *Gordon Gunter* for our Northern Gulf of Mexico collaborative project and has been collecting data since March of 2008. This project ended two years ago and we are continuing to maintain the operation under the auspices of this program. The system is performing well, being attended continuously by a field operation officer on board. It is interfaced with the ship's computer system (SCS) and takes advantage of the array of sensors being recorded by the ship. The data is automatically being transmitted daily via email, reproducing the setup that was done for the NOAA ship *Ronald Brown* (see above). The data is plotted daily on the near real-time display of our website (http://www.aoml.noaa.gov/ocd/gcc/rvgunter_realtime.php). This year, we manage to install a high-accuracy sea surface temperature probe close to the seawater intake, which will greatly improve the accuracy of our fCO_2 measurements reported at sea surface temperature. As shown on *Figure 3*, the ship has spent a substantial amount of time out of the Gulf of Mexico where it usually sails and along the eastern seaboard.

***Causes for non-return*:** The system is maintained by a field operation officer who has been trained on the instrument. Overall, the system performed very well with some data loss occurring due to some minor issues like seawater lines getting clogged or GPS data momentarily lost.

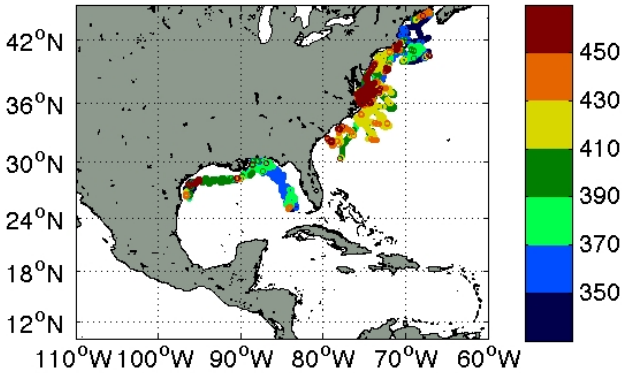


Figure 3. xCO_2 values along the tracks of the R/V Gordon Gunter for fiscal year 2013.

***M/V Barcelona Express* - AOML lead**

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of voyages: 13
Number of fCO_2 data points: 11,000
% Data return: ~83%*.

****estimated***

Description: The *M/V Barcelona* Express is operated by Hapag-Lloyd and transits between the Mediterranean Sea and the Gulf of Mexico in about a month and a half. The route corresponds to the AX7 line, which has been occupied about 4 times a year since 1994 for high-density XBT measurements by the TSG group at AOML. The pCO_2 system has been installed since February 2010. We have collaborated with the TSG group to share resources and provide them with a platform to do TSG measurements while using their Iridium communication software to transmit the data. We used this installation as a test bed to share resources and improve the reliability of both the pCO_2 and the TSG systems. The excessive heat experienced by our system in the engine room has caused multiple failures and the long transit and short turnaround time of the ship has seriously hampered our efforts to collect data. In October of 2010, we upgraded the system with a custom built computer and it has been running more reliably since then. This year, we manage to obtain a very good data return of 83%. Unfortunately, we just got word that the ship would not return to the United States and we were asked to remove the instrument. The whole system has been removed on October 8th, 2013 and we will search for a new ship to re-install it.
The data was transmitted via Iridium on a daily basis and plotted automatically as soon as it was received and can be accessed on our website (http://www.aoml.noaa.gov/ocd/gcc/barcelona_realtime.php).

***Causes for non-return*:** The major reasons for data loss have been due to issues with the pump used to evacuate the seawater. Despite the filters placed in line, the pump gets clogged by silt and can't push the seawater fast enough. The tank then overflows and the crew has to close the intake valve. The GPS signal had been very reliable lately so it was not an issue anymore. What developed, however, is the heat exchanger of the Peltier cooling device used to dry the analytical gas getting covered with dust and not functioning properly. The moist gas stream then condensed in the lines and clogged the filters and nafion tubings. The heat exchanger is very hard of access and almost impossible to clean without taking it out. Instead, we reduced the moisture with an extra nafion tubing which we replaced regularly.

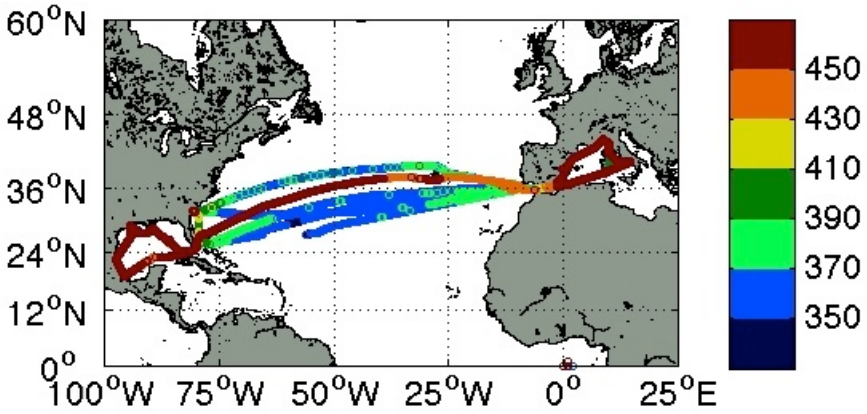


Figure 4. xCO_2 values along the tracks of the M/V Barcelona Express for fiscal year 2013.

***M/V Reykjafoss*- AOML lead**

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of cruises: 12
Number of fCO_2 data points: ~42,000*
% Data return: 42%*.

****estimated***

Description: The *Reykjafoss* belongs to the Icelandic shipping company EIMSKIP and sails between Iceland and Boston. It covers a critical high latitude region that has been shown to be a large CO_2 sink with large seasonal variations. During the early spring, pCO_2 values well above atmospheric levels are measured over most of the ocean transect due to entrainment of deep water to the surface. In late spring, values decrease significantly as a result of high biological productivity during this time. This ship is a replacement for the M/V *Skogafoss* which sailed the same route and had a pCO_2 system for about 3 years, before it was sold to another company in 2007. This installation was completed in February of 2011. Similar to the M/V Barcelona Express, this pCO_2 system shares resources with the TSG group at AOML where one computer is used to run both the pCO_2 and the TSG attached to it and both data sets use the same Iridium hardware and software to transmit the data daily back to land. The data is sent via FTP to AOML where it is displayed in near-realtime on our website. We work closely with the NOAA National Marine Fisheries Laboratory in Narragansett who send people to meet the ship in Boston and perform the maintenance and most of the repairs, when necessary. Earlier this year, the ship changed route and now only stops in Portland, Maine before turning back toward Iceland. Just recently, we were told that the ship would not sail to the U.S. anymore and would be replaced by a new ship called *Westerkade*. We are in the process of scoping out the new ship and seeing if it would be possible to move our instrument to the new ship. In the meantime, we are trying to

keep our instrument running on the *Reykjafoss* which is now sailing between Iceland and the Netherlands. Should something malfunction in our system, we would be forced to shut it down and assess if sending someone to fix it would be worthwhile.

Causes for non-return: This year has been plagues with issues beyond our control. Besides time spend in dry dock for repairs, the ship had a substantial leak in the engine room close enough to our system that it flooded our instrument and created substantial damage to its electronics. After having sent someone to do the repairs, the leak happened a second time with similar damages to the system. After the second repairs, we installed a tarp to isolate our system from potential subsequent leaks. Besides minor GPS losses and sensor failures, the system has been operating well.

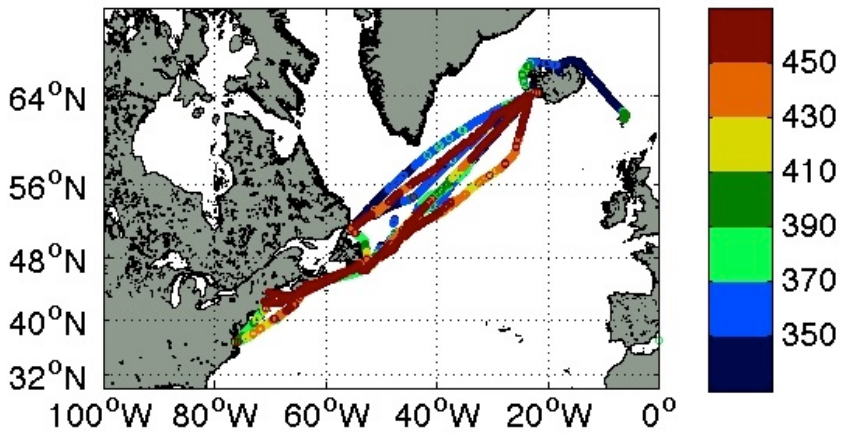


Figure 5. xCO_2 values along the tracks of the M/V Reykjafoss for fiscal year 2013.

***R/V Henry B. Bigelow* - AOML lead**

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of cruises: 5 (9 legs)
Number of fCO_2 data points: 56,000
% Data return: 88%.

Description: The NOAA ship *R/V Henri B. Bigelow* is a new generation Fisheries survey vessel based in Newport, RI and operating primarily in coastal U.S. waters from Maine to North Carolina. The region includes Georges Bank, one of the world's best known and most productive marine areas. The installation was completed in February of 2011 and the system has been operating very well, due in part to the great collaboration of the crew and the scientific technician on board. We are also collaborating with the NOAA fisheries in Narragansett, RI with

funding from the NOAA Ocean acidification program to have the ship visited regularly to perform maintenance if necessary. The system is connected to the Ship's Computer System (SCS) and collects co-located data from the sensors installed on board. The data is automatically emailed on a daily routine and displayed on our website for troubleshooting purposes. This year, we have augmented our system with two new sensors: a membrane-based dissolved oxygen sensor from SeaBird Electronics, Inc. and a Submersible Ultraviolet Nitrate Analyzer (SUNA) from Satlantic. We are working on the procedures to reduce these data.

***Causes for non-return*:** The system behaved very well with some losses due computer issues and the inexperience of a new survey technician onboard. This was corrected with time and the instrument has been working reliably since.

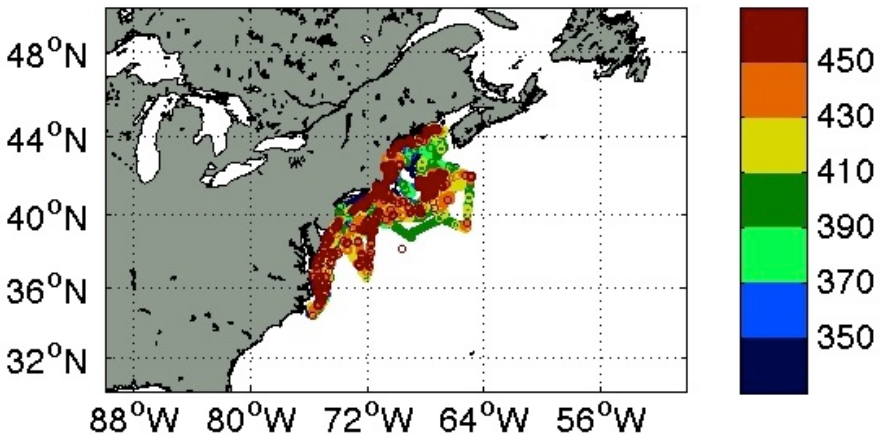


Figure 6. xCO_2 values along the tracks of the NOAA ship Henry B. Bigelow for fiscal year 2013.

Container ships *Cap Vilano* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 3
Number of fCO_2 data points: 16,040
% Data return: 99%.

Description: In January 2013, PMEL installed an underway fCO_2 system on the *Cap Vilano* to continue a decade long time-series of fCO_2 measurements across the Pacific from Long Beach to New Zealand. In FY2013, PMEL collected fCO_2 data on three transits (*Figure 7*), bringing the

total number of cruises along this track to 30 since we began measuring fCO_2 on container ships in 2004. All data collected on the *Cap Vilano* are in final processing and will be submitted to CDIAC for archiving, and posted to the PMEL CO_2 website. An underway fCO_2 system will be installed on the container ship *Cap Blanche* in FY2014 to continue our trans-Pacific measurements.

Causes for non-return: The underway fCO_2 systems on the *Cap Vilano* resulted in a 99% data return during FY2013. A small amount of data were rejected due to stack gas contamination when the ship changed course.

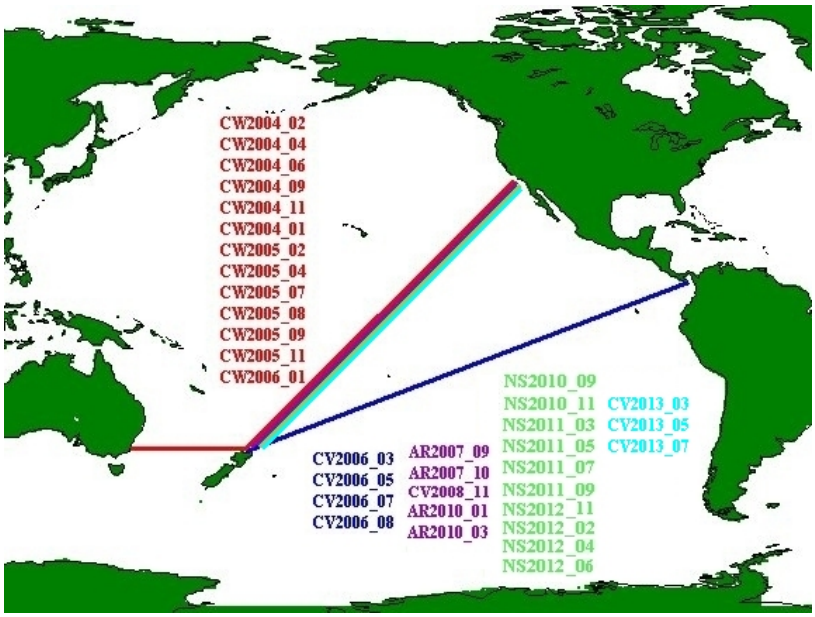


Figure 7. Cruise Tracks of the Columbus Waikato (red), Cap Victor (blue), Albert Rickmers (purple) and Cap Van Diemen (purple), and Natalie Schulte (green) and Cap Vilano (Cyan) occupied during FY2004-2013.

Trans-pacific fCO_2 measurements taken from 2004 through 2013 during normal ENSO conditions (3 month running mean of SST between -5°C and 5° in the Nino 3.4 region) are shown in *Figure 8*. The transects represent data collected from April through September, the warm season in the Northern Hemisphere, and show an trend of increasing fCO_2sw values in the equatorial Pacific over the past decade. A similar trend is apparent in data collected during the Northern Hemisphere Cool season.

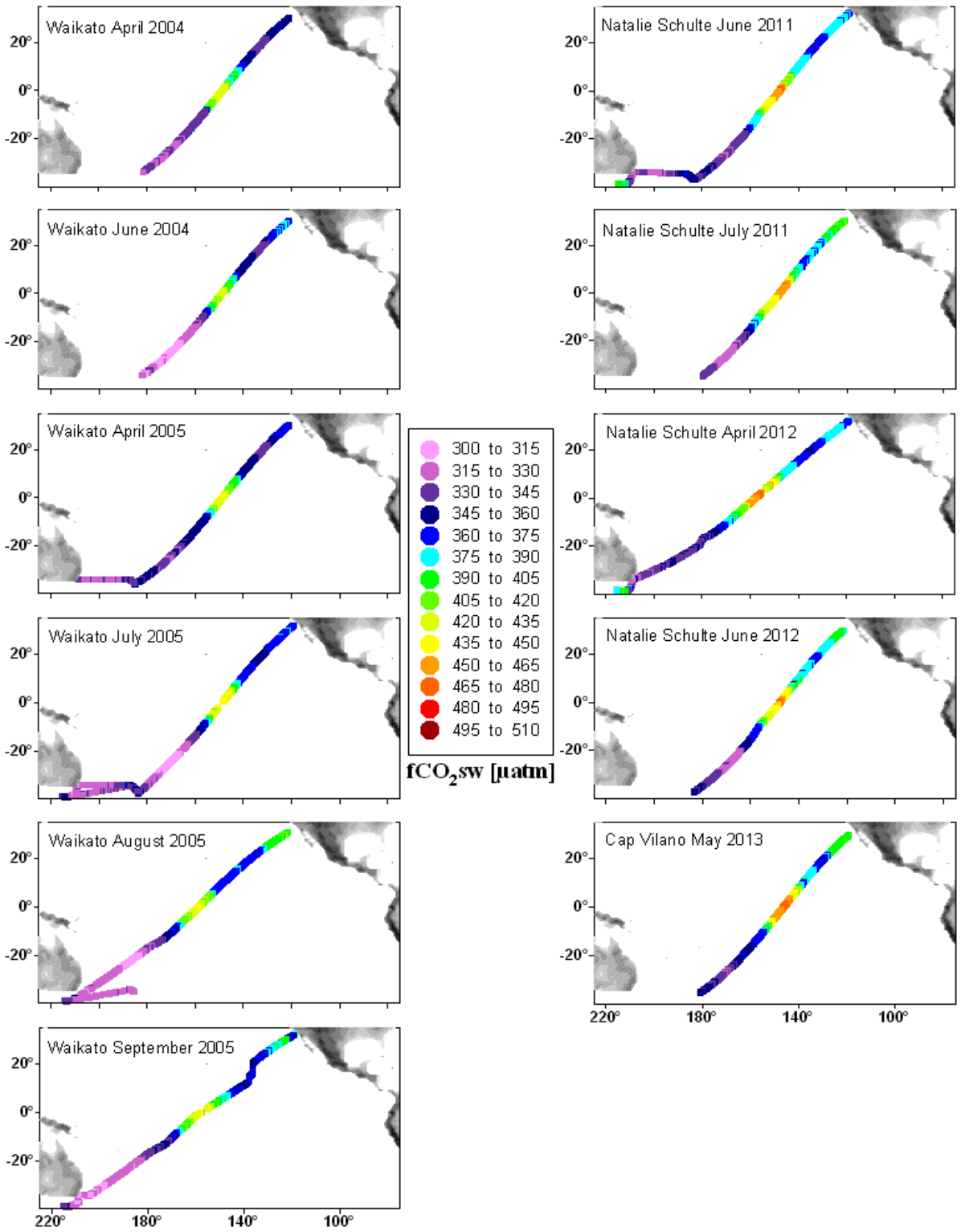


Figure 8. Decade long time-series of surface water fCO_2 levels in the tropical and subtropical Pacific collected during the Northern Hemisphere warm season, and during normal ENSO conditions.

R/V *Ka`imikai-o-Kanaloa* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 1
Number of fCO_2 data points: 16,454
% Data return: *85% for seawater* ***fCO_2***
98% for atmospheric fCO_2

Description: In January 2013, PMEL installed an underway pCO_2 system on the University of Hawaii's R/V R/V *Ka`imikai-o-Kanaloa*. The ship was schedule as a replacement for the NOAA ship *Ka'imimoana* tp conduct buoy recovery and deployment in the equatorial Pacific between 110°W and 165°E. The *Ka`imikai-o-Kanaloa* was only able to complete one cruise (*Figure 9*) before returning to port due to mechanical issues. The final cruise data will be posted to our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2. All data collected from the *Ka`imikai-o-Kanaloa* during the 2013 fiscal year are in final processing and will be submitted to CDIAC for archiving.

Causes for non-return: The underway fCO_2 systems on the R/V *Ka`imikai-o-Kanaloa* resulted in a 85% return rate for seawater fCO_2, and 98% for atmospheric fCO_2. A new equilibrator pump was supplied by General Oceanics, but was susceptible to salt buildup until a new in-line filter was put in place. The ship experienced many technical problems, resulting in an abbreviated field season. The pCO_2 system installed on the R/V Ka`imikai-o-Kanaloa (KoK) will remain on for the FY2014 field season since the ship is scheduled to be repaired.

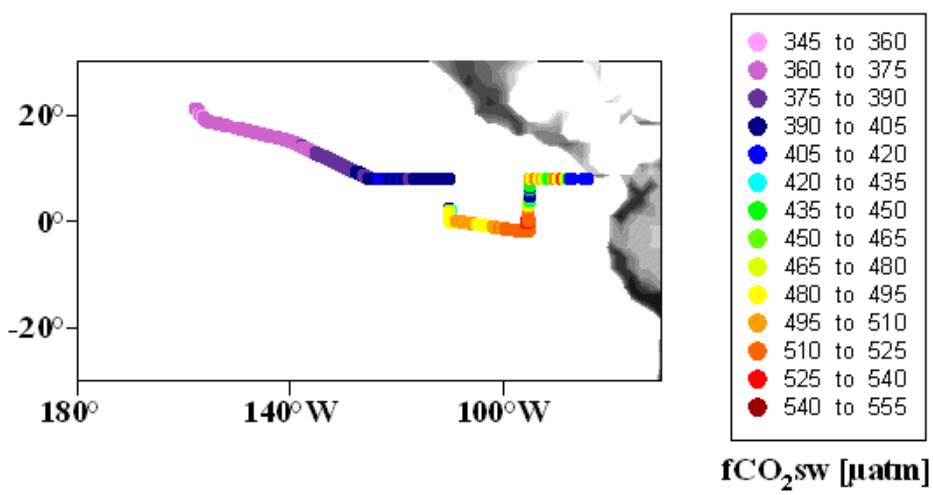


Figure 9. Ka`imikai-o-Kanaloa *track line occupied during FY 2013.*

NOAA Ship *Bell Shimada* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 7
Number of fCO_2 data points: 23,966
% Data return: *95% for seawater* ***fCO_2***
98% for atmospheric fCO_2

Description: From January 2013 through September 2013 the *Bell Shimada* was involved in studies along the North American West Coast (*Figure 10*). Prior to the 2013 field season, the fCO_2 system was updated with new software, pumps and filters. During the time under review, PMEL collected and processed 23,996 fCO_2 data values from the *Bell Shimada* on 7 separate cruises. Data collected during the summer along the North American West Coast exhibits strong coastal upwelling in the near-shore waters throughout the year, particularly during summer months, with biological uptake of carbon becoming the dominant feature away from the coast. The final cruise data will be posted to our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2. All data collected from the *Bell Shimada* during the 2013 fiscal year are in final processing and will be submitted to CDIAC for archiving.

Causes for non-return: The underway fCO_2 systems on the NOAA Ship *Bell Shimada* resulted in a 95% return rate for seawater fCO_2, and 98% for atmospheric fCO_2. Occasional problems with the condenser resulted in a small amount of data being rejected.

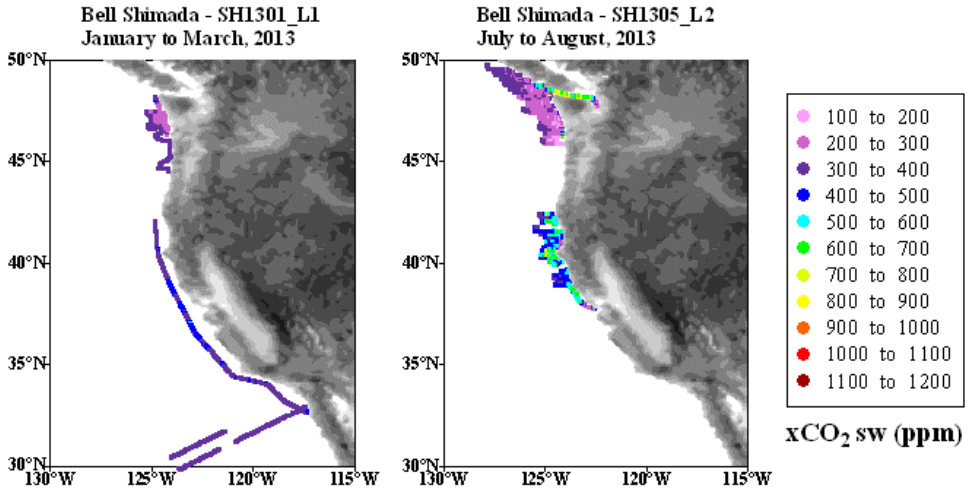


Figure 10. Bell Shimada *track lines occupied during FY 2013.*

NOAA Ship *Oscar Dyson* - PMEL lead

Data Site: http://www.pmel.noaa.gov/co2/uwpCO2
Number of cruises: 8
Number of fCO_2 data points: 33,633
% Data return: *87% for seawater fCO_2*
98% for atmospheric fCO_2

Description: From February 2013 through September 2013 the *Oscar Dyson* was involved in studies in coastal Alaskan waters (*Figure 11*). Prior to the 2013 field season, the fCO_2 system was updated with new software, pumps and filters. During the time under review, PMEL collected and processed 33,633 fCO_2 data values from the *Oscar Dyson* on 8 separate cruises. Data collected in Alaskan waters exhibits a pattern of upwelling around the Aleutian Islands, and biological drawdown of CO_2 away from the coast. The Alaskan waters show a strong seasonal pattern as warming becomes a dominant feature in the summer, increasing fCO_2 levels. The final cruise data will be posted to our website located at**:** http://www.pmel.noaa.gov/co2/uwpco2. All data collected from the *Oscar Dyson* during the 2013 fiscal year are in final processing and will be submitted to CDIAC for archiving.

Causes for non-return: The underway fCO_2 systems on the NOAA Ship *Oscar Dyson* resulted in a 87% return rate for seawater fCO_2, and 98% for atmospheric fCO_2. A new equilibrator pump was supplied by General Oceanics, but was susceptible to salt buildup until a new in-line filter was put in place.

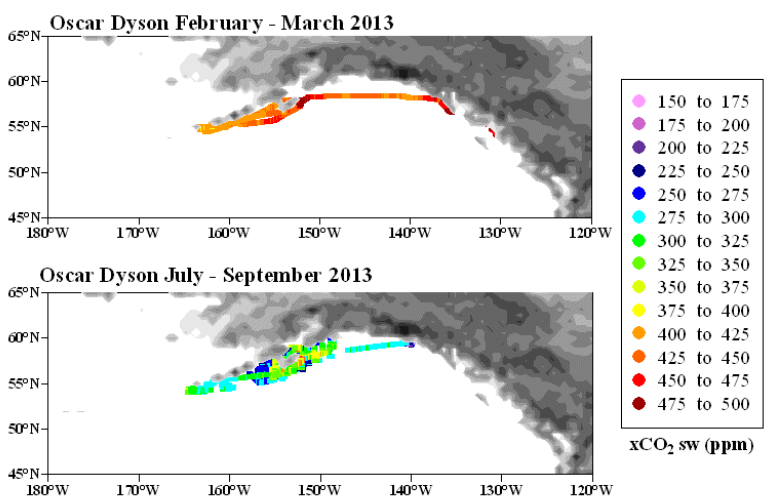


Figure 11. Oscar Dyson *track lines occupied during FY 2013.*

***RVIB Palmer* - LDEO lead**

Data Site: http://www.ldeo.columbia.edu/CO2
Number of cruises: 7
Number of fCO_2 data points: 68,118
% Data return: 83.4%.

Description: The Lamont group is primarily responsible for the acquisition of the surface water pCO_2 data aboard the RVIB *Palmer*. The data are processed and coordinated into a single uniform format along with vital supplemental information including the time, date, SST, salinity, wind speeds, barometric pressure and atmospheric CO_2 concentration. These quality-controlled data are made available to the participants within three months, and are submitted to CDIAC within a year for the public access.

The locations of our data obtained since the beginning of this project in 2001 through September 2013, are shown in *Figure 12*. The total number of surface water pCO_2 data obtained to-date is 1,004,445, of which about 68,118 measurements were added to the database during the current funding period starting September 1, 2012. The data recovery % is computed as the ratio of the time period for successful observations to the total at-sea time. The mean data recovery rate since 2001 is 91.7%, while that for the current funding period is 83.4%. A low recovery rate of 40.7% observed for May-June 2013, is attributed to the failure of the system-control laptop computer.

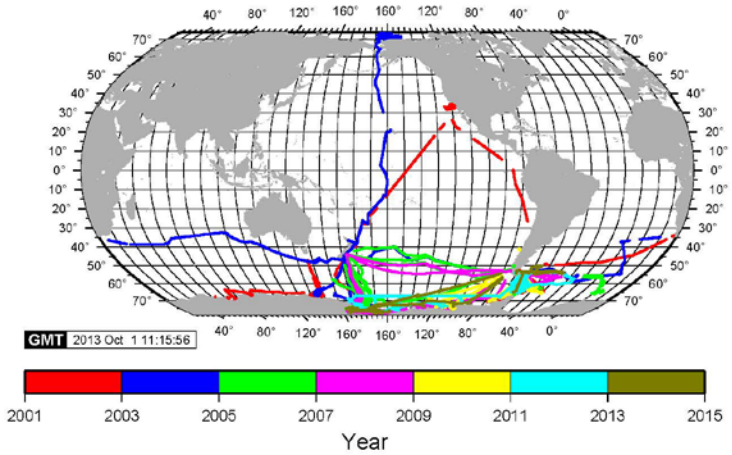


Figure 12. The locations of surface water pCO_2 measurements made aboard the RVIB Palmer since 2001. The years when the observations were made are color-coded.

***R/V L. M. Gould* – LDEO Lead**

Data Site: http://www.ldeo.columbia.edu/CO2
Number of cruises: 11
Number of fCO_2 data points: 44,551
Data return: 87.8%.

Description: Our underway pCO_2 system has been operated aboard R/V *Laurence M. Gould*, which is run by NSF as a part of the Long-Term Research in Environmental Biology (LTRE) program in the Drake Passage area, Southern Ocean. The surface water pCO_2 program aboard the R/V L. M. *Gould* is maintained and the data are processed and managed with support of this grant. The sampling locations of the surface water pCO_2 measurements are shown in *Figure 13*. A total of 44,551 pCO_2 measurements were made aboard the R/V *Gould* during the current funding period starting September 1, 2012. The new data make a total of 666,718 pCO_2 measurements for the Gould program since its inception in March 2002. The data recovery rate for the current funding period was 87.8%. The quality-controlled data have been added to our LDEO database, and submitted to CDIAC for public access.

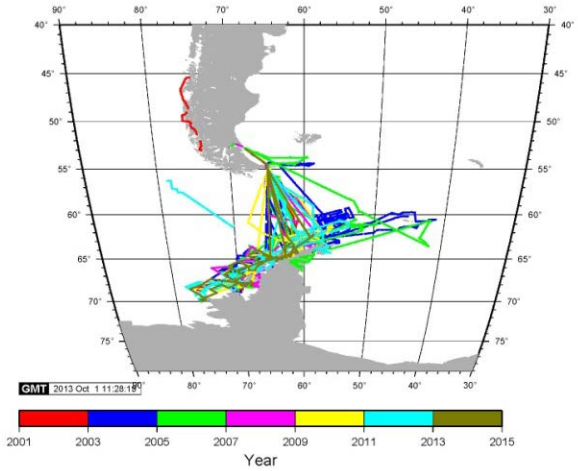


Figure 13. The locations of the surface water pCO_2 measurements obtained aboard the RVIB Gould during this project, March 2002 through September 2013. The years of the measurements are color-coded.

***R/V Marcus Langseth* – LDEO Lead**

Data Site: http://www.ldeo.columbia.edu/CO2
Number of cruises: 7
Number of fCO_2 data points: 60,978
Data return: 86.0%

Description: R/V *Marcus Langseth* is a geophysical research vessel operated by LDEO with funds from NSF, and was added to the CO_2 program in May 2010. Since the ship is used for geophysical studies in small areas for month at a time, it is suited for investigating variability of pCO_2 in small ocean areas in details. Our underway pCO_2 program was commenced on May 8, 2010. However, the ship was laid off during October 2010 through March 2011, and was reactivated in April 2011. Since the inception of the field program in May 2010, 136,214 pCO_2 measurements were obtained with a mean data recovery rate of 70.5% in the North Pacific Ocean and the Arctic Sea (*Figure 14*). During the current funding period, May 2012 - June 2013, 60,978 pCO_2 data were obtained with a recovery rate of 86.0%.

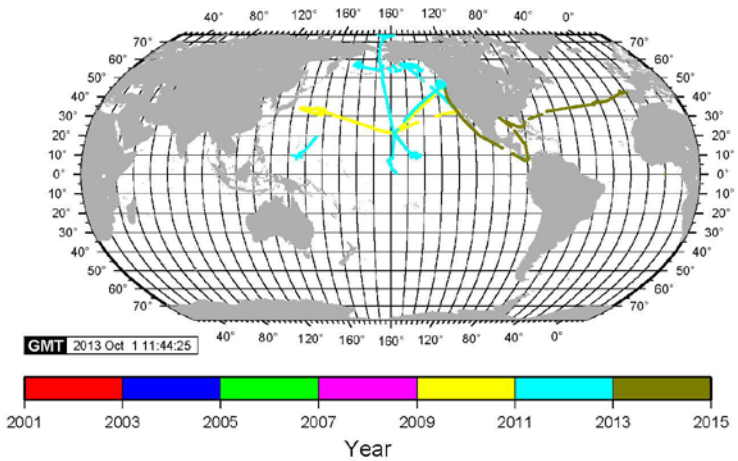


Figure 14. The sampling locations for the R/V Langseth in 2010-2013 in the North Pacific and Arctic.

***USCGC Healy* – LDEO Lead**

Data Site: http://www.ldeo.columbia.edu/CO2.
Number of cruises: 2
Number of fCO_2 data points: 29,099
Data return: 97.0%

Description: USCGC *Healy* is one of the few US ships operating primarily in the Arctic, where seasonal CO_2 observations are lacking. Since waters flowing out of the Arctic basin should have a significant impact on the North Atlantic CO_2 budget, our understanding of the time-space variability of pCO_2 in surface waters in this basin is important. In April 2011, we were given permission by the US Coast Guard for the installation of our underway pCO_2 system, which was constructed during the previous funding period of this grant. Our measurements were commenced on May 27, 2011 from Seattle, WA, to the North Pacific and then to the Arctic basin. 100,450 pCO_2 measurements (including 29,099 measurements during the current funding period) were obtained with a mean data recovery rate of 97.0% (*Figure 15*). During the first half of 2013, a new underway scientific pumping system was installed, and the system became operational in August. For this reason, we were not able to make measurements in the spring of 2013. These pCO_2 and associated temperature, salinity and other data have been added to our database and reported to CDIAC. The surface water pCO_2 data indicate that an extensive area of the Arctic waters is a strong sink for atmospheric CO_2 (Robbins et al. 2013).

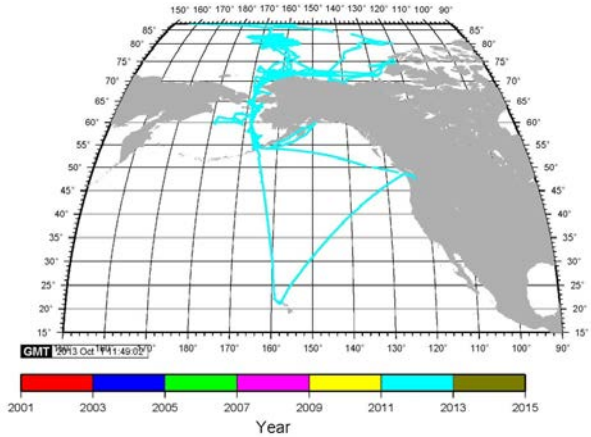


Figure 15. The sampling locations for the USCGC Healy.

R/V *Atlantic Explorer* - BIOS lead

Data Site: **http://www.bios.edu/Labs/co2lab/vos.html**
Number of cruises: 25
Number of fCO_2 data points: 65,000
% Data return: 75%

***Description*:** The R/V Atlantic Explorer operates in the North Atlantic Ocean servicing four oceanographic time-series (e.g., Bermuda Atlantic Time-series Study, Hydrostation S, Bermuda Testbed Mooring, Ocean Flux Program) and other research projects. The geographic focus of data collection is primarily zone NA6, but included several transects between Bermuda and Puerto Rico (across an infrequently sampled part of the permanently stratified oligotrophic gyre of the North Atlantic) and Bermuda and Norfolk, Virginia (*Figure 16*).

The pCO_2 system was installed on the RV Atlantic Explorer in April 2006. This data stream provides groundtruthing pCO_2 datasets for the subtropical gyre of the North Atlantic Ocean. The R/V Atlantic Explorer has typically had ~135-170 ship days per year with most work undertaken in the North Atlantic Ocean in zone NA06. However, this also includes transects between Bermuda and Puerto Rico, and repositioning/shipyard visits that results in transects between Bermuda and Norfolk.

***Causes for non-return*:** In the last fiscal year, a total of 65,000 pCO_2 measurements have been made with a ~75% good data recovery. The non-return rates typically represent data that were flagged mainly due to problems with low flow rates from the underway system, due to problems associated with the Valco multi-position valve and distribution of standards through the system, and delays in replacing the standards. However, it should be noted that maintenance of the seawater pCO_2 system has become relatively routine during the ship's turnaround at the BIOS dock. All the SeaBIRD sensors from the underway and CTD systems are maintained by BIOS Marine Technicians, and calibrated every six months. We are in the process of preparing the metadata information and data QC/QA for submission of data to CDIAC in yearly reports.

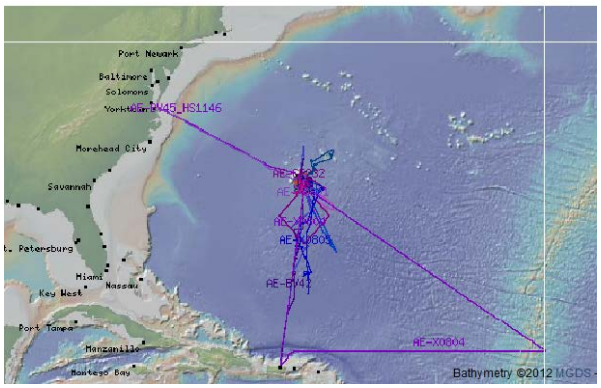


Figure 16. Cruise tracks for the R/V Atlantic Explorer

Container Ship *MV Oleander*- BIOS lead

Data Site: **http://www.bios.edu/Labs/co2lab/vos.html**
Number of cruises: 48
Number of fCO_2 data points: 110,000
% Data return: 55%

***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 US Eastern Seaboard.

***Causes for non-return*:** During the last performance period we have had major problems with the pCO_2 system. The average temperature of the engine room has been ~47°C with the CPU failing in 2006 due to temperatures over 60°C. We have modified the dry box, adding new fans, and replaced the CPU with one that has a higher temperature threshold (80°C) with no problems since. The engine room air is quite dirty requiring cleaning of all filters each week. As stated earlier, we have routinely replaced the system hard-drive with a solid-state bootable hard-drive to run the pCO_2 system software as high engine room temperatures and ship motion continues to exact a heavy toll on the pCO_2 system components. Maintenance of the pCO_2 system occurs with weekly visits to the ship during the ship's turnaround (giving our team a couple of hours on Monday morning to work on the system) in Hamilton, Bermuda. Our group has developed a good rapport with the ship officers, engineers and crew, and their good will has contributed greatly to the success of the system installation on the ship.

R/V F.G. Walton Smith- RSMAS lead

Data Site: www.aoml.noaa.gov/ocd/gcc/
Number of cruises: 13
Number of fCO_2 data points: 31,000*
% Data return: 59%*

****estimated***

Description: The R/V *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. A pCO_2 system has been installed on board the *Walton* Smith since the beginning of July 2008. The pCO_2 system is an older version of the ones now produced by General Oceanics, Inc. in Miami and still needs to be upgraded, as the computer controlling it is not commercially available anymore. In the meantime, we are using one of AOML's systems and collaborating closely with them for data retrieval, reduction and archiving. The data collected by the pCO_2 system is transmitted from the ship via FTP using the program developed by AOML's TSG group and the ship's permanent internet connection. The data is not available in real time due to processing requirements. The delayed mode data will be made publicly available on the CDIAC Global Coastal Ocean Database. The data will be archived annually

Causes for non-return: Most of the data losses were due to human error when either the whole system or simply the equilibrator temperature sensor were not turned on. We also had some issues with the LICOR analyzer and the water flow system, which is not optimal and becomes potentially problematic when the demand by the scientific party is too great.

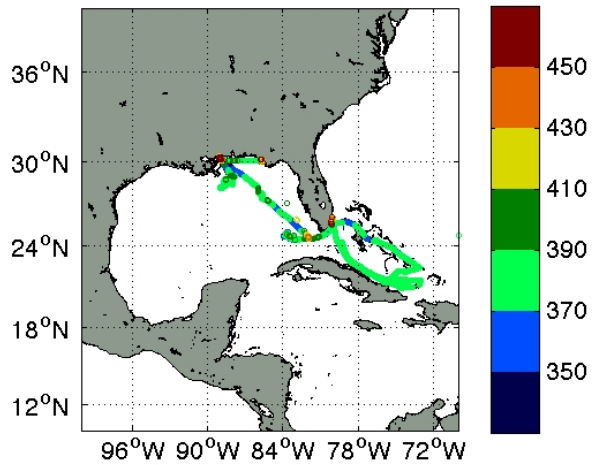


Figure 17. xCO_2 values along the tracks of the R/V Walton Smith for fiscal year 2013.

TSG Operation – AOML/SOOP Lead

During FY2013 AOML continued the TSG operation as a component of the Ship Of Opportunity Program (SOOP) in support of the pCO_2 operations. During this period AOML received, processed and distributed TSG data from 7 ships of the SOOP (Semester at Sea's *MV Explorer*, *MV Oleander*, *MV Barcelona Express*, *MV Reykjafoss*, *MV Bernardo Houssay* in collaboration with the Argentinean Coast Guard, and Royal Caribbean's *Explorer of the Seas* and *Allure of the Seas* in collaboration with University of Miami/RSMAS) and 10 ships of the NOAA fleet (*Okeanos Explorer*, *Pisces*, *Oregon II*, *Ronald H Brown*, *Bell M Shimada*, *Oscar Elton Sette*, *Gordon Gunter*, *Oscar Dyson*, *Nancy Foster*, *Hi'ialakai*). More than 100 million TSG records were processed at AOML during FY2013 (*Figure 17*).

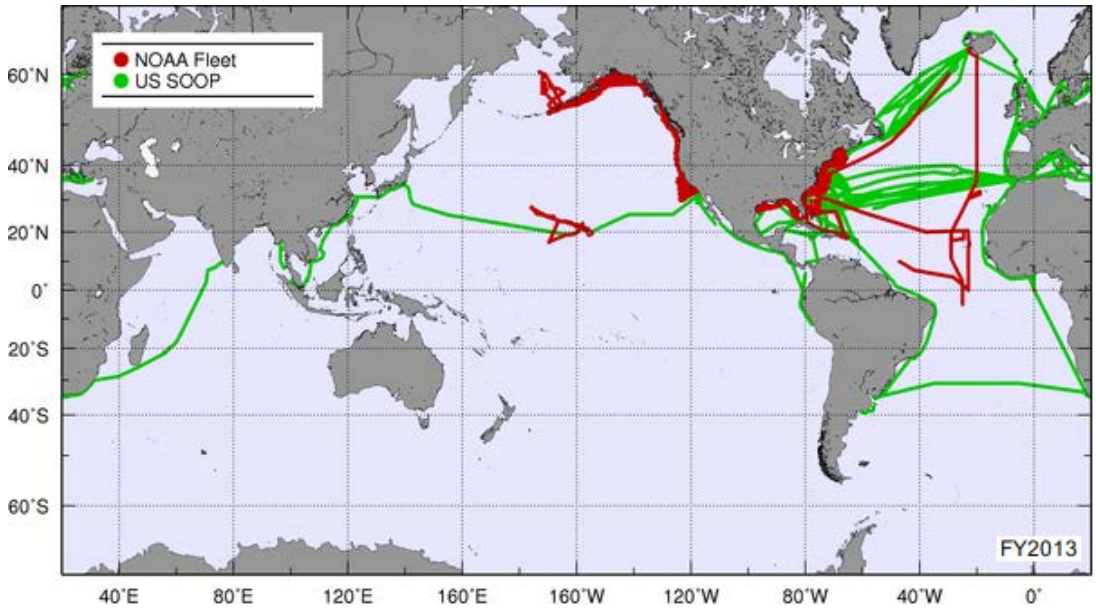
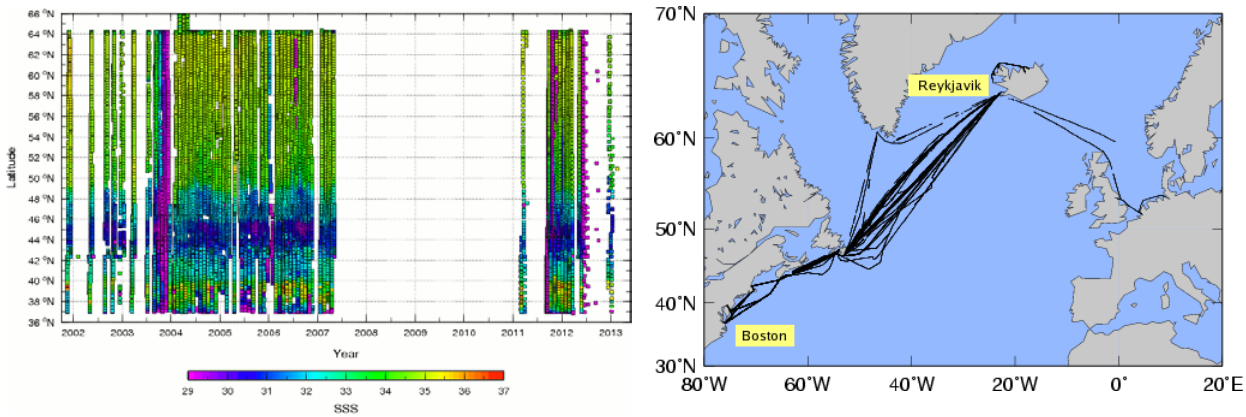


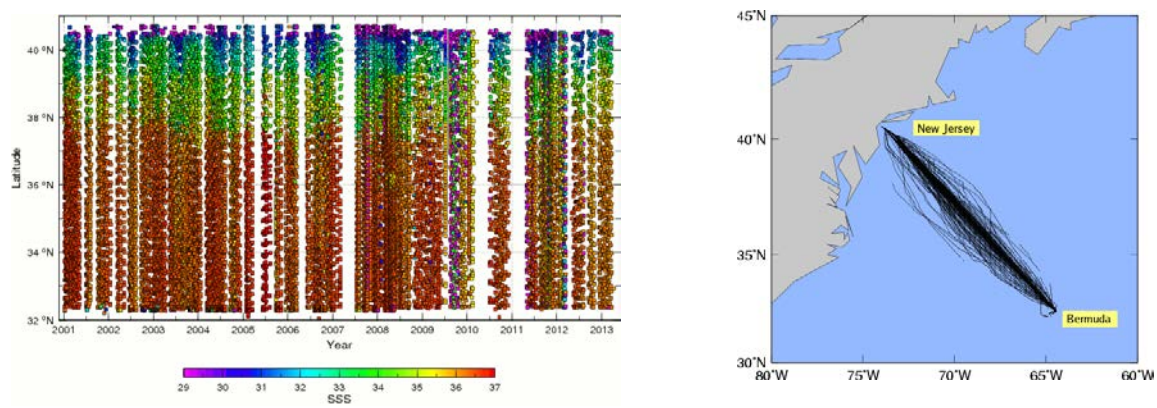
Figure 18. Location of more than 100 million TSG observations received and processed by AOML during FY2013 from ships of the SOOP and the NOAA fleet.

TSG instruments are operated with the AMVERSEAS software. During FY2013 the newest version of this software was tested and installed in several ships of the SOOP. This new version, compatible with Windows 7, contain several improvements that enhance the collection and transmission of TSG data as well as the control of the TSG equipment when the ship arrives at port or in any other situation in which the position of the ship remains constant. The new software has also implemented a new transmission method using FTP vs. SMTP protocol that has dramatically reduced the Iridium transmission costs. Additionally, log files are created with details of the equipment performance, including eventual error messages. One important feature of the new software is the capability of doing a remote computer reboot when data is not received as expected. This new feature avoids losing data and allows for a more efficient operation.

All the TSG data received at AOML is quality controlled through several steps based on the GOSUD (Global Ocean Surface Underway Data Pilot Project) real-time control tests. Among other parameters, the quality control procedures check the data for errors in date, location, platform identification, ship speed, global and regional temperature and salinity ranges compatibility, gradient and the presence of spikes. The TSG data is also compared with a monthly climatology (Antonov et. al., 2006, Locarnini et. al. 2006). The data approved in the quality control tests is then reduced to one point every three minutes. The whole data set is distributed by the National Oceanographic Data Center (NODC) and Coriolis. This system is currently fully functional in real-time, providing important tools to automatically detect problems in data transmission, equipment calibration and marine operations of ships with TSG data transmission in real-time in general.



MV Reykjafoss



MV Oleander

Figure 19. Space-time diagrams of salinity observations (left) and location of these observations (right) obtained from MV Reykjafoss (top) and MV Oleander (bottom).

During FY2013 the installation and operation of a TSG system provided by AOML/PHOD on the former WHOI's *Atlantis*, now commissioned as an oceanographic research vessel in Argentina and operated by the Prefectura Naval Argentina (Coast Guard) as the *MV Bernardo Houssay* was completed. This system is currently operational and data acquisition and transmission were performed during FY2013 in real-time. Data from this TSG will be crucial for the calibration of the NASA Aquarius satellite mission. *MV Bernardo Houssay* and *MV Explorer*, are currently the only two ships providing TSG data regularly from the South Atlantic Ocean, a region severely under-sampled.

During FY2013, we also continued the TSG operation on two Royal Caribbean cruise ships: *Explorer of the Seas* and *Allure of the Seas*. This operation is a collaboration between AOML and the University of Miami's Rosenstiel School of Marine and Atmospheric Science (RSMAS), in which AOML provides the TSG instruments, equipment calibration, as well as data processing

and distribution while RSMAS scientist conduct the installation and operation of the system.

In addition, TSG data was received from 10 ships of the NOAA fleet. Data from ships of the NOAA fleet are mostly located in coastal regions of the U.S. with a large number of observations located at high latitudes. These data are very important for coastal studies, front variability analysis, pCO_2 ocean inventory, as well as the calibration of satellite observations.

Maintenance of the TSG web site at AOML was continued during FY2013, including products displaying data in real time from the *MV Explorer* and the *Explorer of the Seas* on our website (http://www.aoml.noaa.gov/phod/tsg). This web site also contains information regarding data analysis and quality control procedures for the NOAA fleet and the SOOP.

Data Management and Usage

The Lamont group is responsible for processing and managing the surface water pCO_2 data acquired by the members of the pCO_2 on ships consortium, so that the participants of the program are able to access of the data in a uniform electronic format. For this purpose, we have 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. In each year, the new quality-controlled data are added to our database and submitted the Carbon Dioxide Information and Analysis Center (CDIAC), Oak Ridge, TN, for dissemination to the public. A newly updated LDEO Surface Water pCO_2 database Version 2012 "Global Ocean Surface Water Partial Pressure of CO_2 Database " has been assembled and made available to the public through the CDIAC (Takahashi et al. 2013).

During the 2012 fiscal year, diagnostic software was automated by PMEL to quality control and process daily underway data files when data files arrive via e-mail from the ships. 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 PMEL website and are used as a diagnostic tool for data processing and quality control of the underway fCO_2 data. Data from the VOS cruises in FY12 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 carbon data are archived at the PMEL (www.pmel.noaa.gov/co2/) website which includes an interactive map allowing quick access to underway fCO_2 data collected by PMEL since 1982. To date, fCO_2 data from over 160 cruises have been posted on the interactive map. The carbon data are also submitted to CDIAC and NODC data centers. The carbon data management plan is accessible at the PMEL website.

AOML provides data to the LDEO pCO_2 climatology effort and submits its data to CDIAC that in turn goes to the SOCAT database. The in house serving of data www.aoml.noaa.gov/ocd/gcc provides an important venue to provide more information and data than is submitted to the data centers and provides the user easy access to the holding of the quality data. This resource is also helpful for investigators who have done projects on the ships and require access to the co-located pCO_2, temperature, and salinity data.

As soon as the data is reduced, posted on our websites and submitted to CDIAC, it is also submitted to SOCAT. It undergoes a secondary QA/QC procedure by other scientists organized in regional groups who flag the data on a per cruise basis and incorporate the data into the next SOCAT release scheduled for 2014 (see Research Highlights below).

Research Highlights

The Takahashi 2005 surface water pCO_2 climatology

A newly updated LDEO Surface Water pCO_2 database Version 2012 "Global Ocean Surface Water Partial Pressure of CO_2 Database " has been assembled and made available to the public through the Carbon Dioxide Information and Analysis Center CDIAC (Takahashi et al. 2013**).** This is an extensive database for world ocean surface water pCO_2, which includes over 9 million surface ocean water pCO_2 measurements obtained between 1957 and 2012. About 3 million new data were added to the previous version, v. 2011, that contained 6.4 million pCO_2 measurements covering 1968-2010. According to the CDIAC record, there has been over 10^5 "hits" to the LDEO database during the reporting period, indicating high demands for the updated database.

The 2012 version (v.2012) of the dataset has been used to create an updated version the surface water pCO_2 climatology following the procedures outlined in Takahashi et al. (2009). The climatology is centered on 2005. The year 2005 is approximately the median of all data in the LDEO database v.2012. As in the previous versions, it is provided on a 4˚ by 5˚ grid on monthly scales. The data is adjusted to virtual year 2005 by assuming the pCO_2 of Surface Ocean follows the atmospheric CO_2 growth rate that was obtained from Globalview-CO_2 (2012). The development of the flux climatology from the surface water pCO_2 climatology is detailed in the data management and synthesis report. The climatological maps of partial pressure difference between surface water pCO_2 and air (ΔpCO_2) for February and August are shown in *Figure 20* (left plots). Also shown in *Figure 20* (right plots) are the differences between the 2005 and 2000 ΔpCO_2 climatologies. If the climatologies were invariant the difference plots in the figure would be colorless. Regions in yellow and reds indicate an increasing CO_2 source to the atmosphere and blues and purples indicate an increasing sink. Most of the differences are attributed to improved data coverage. In particular inclusion of a single cruise in the SE Pacific in a region where no data was available previously shows a large change for the entire year indicating the importance of filling in regional data gaps. While most of the large differences between the 2005 and 2000 climatologies are due to improved data coverage, the increased sink in the North Atlantic is in accord with temporal analysis of Schuster et al. (2013) that shows the increasing uptake of the North Atlantic since 2000.

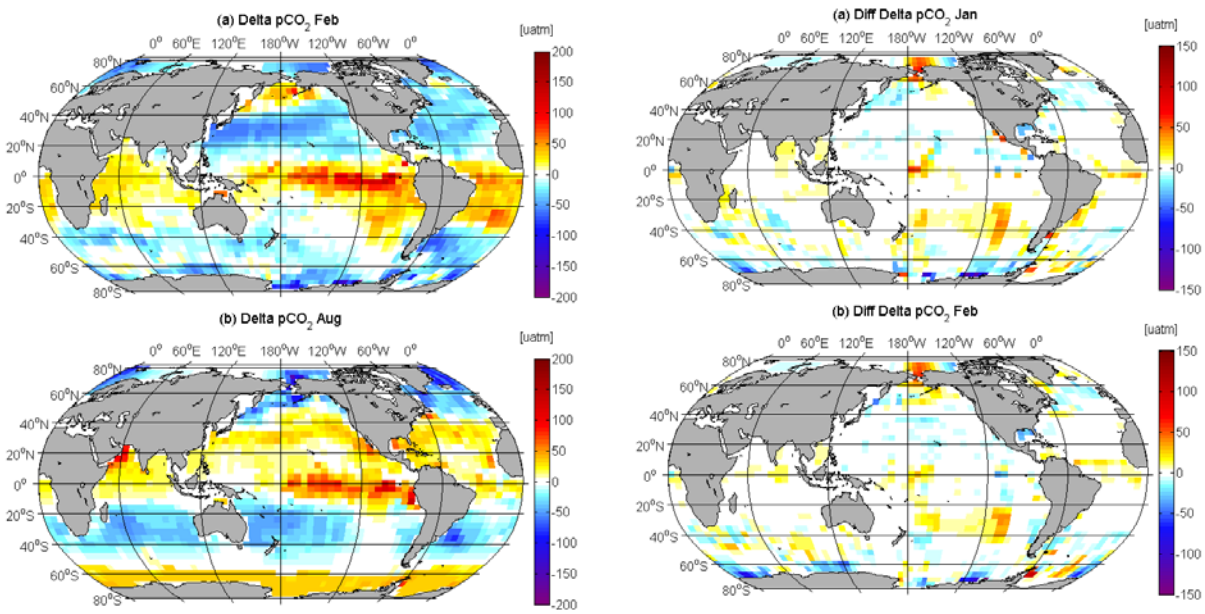


Figure 20. Climatological mean monthly distribution of sea-air pCO_2 difference: Left Plots: for the reference year 2005 in February (top) and August (bottom). Right Plots: difference between the 2005 and 2000 climatologies in January (top) and February (bottom) (Takahashi et al. 2013).

Incorporating data from alternative sensors into the SOCAT database

The Surface Ocean CO_2 Atlas (SOCAT) is a global surface ocean CO_2 data collection that incorporates fugacity or partial pressure of CO_2 (fCO_2, pCO_2)[1] data for the open oceans and coastal seas into a uniform dataset. The first release, version 1.5, occurred in 2011 and was comprised of 6.3 million observations. The second release happened in June of 2013 (Bakker et al. 2013) and includes more than 10 million observations and significant input from participants in the pCO_2 from ships efforts (see *Figure 21*). These datasets are iterations upon which the international marine carbon research community continues to build using agreed data and metadata formats, and standard quality-control procedures. The effort is endorsed and partially supported by several international ocean science programs.

[1] The chemical potential of CO_2 gas in water is either expressed as a partial pressure (pCO_2) or, when accounting for the non-ideality of CO_2, fugacity (fCO_2) with a conversion utilizing virial coefficients as described in Weiss (1974). The $fCO_2 \approx 0.993\ pCO_2$. Here we generally use the term fCO_2 as this is the reported quantity in the SOCAT dataset.

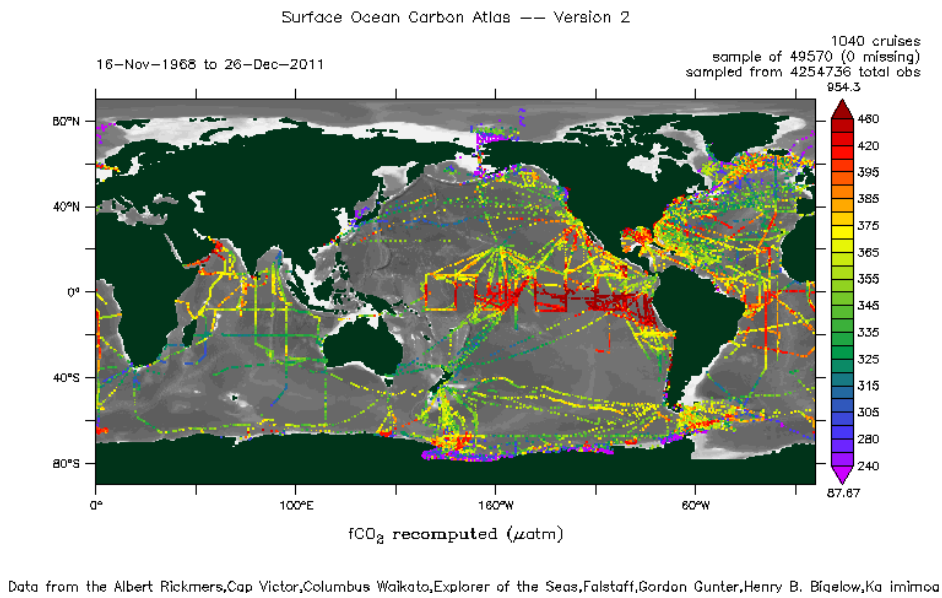


Figure 21. Contribution of this program to the Surface Ocean CO_2 *Atlas (SOCAT version 2) database through 2011*

The version 1.5 and 2 releases mostly contained data acquired from automated underway pCO_2 systems based on infrared analysis (IR) of CO_2 in the headspace of equilibrators operated on research and commercial vessels. Over half of the data originates from the NOAA/CPO/COD pCO_2 from ships effort. The data was acquired largely following the standard operating procedures (SOP) as outlined in SOP 5 of Dickson et al. (2007). Some older data (prior to ~1995) were measured by gas chromatographic (GC) analysis of the CO_2 content in the headspace. During the assembly and quality control of the SOCAT version 2 release, observations were submitted from alternative platforms and alternative sensors whose data did not fit well in the current quality assessment scheme. It is anticipated that in the future there will be significantly more data arising from alternate approaches. This requires a reassessment of dataset quality control flags, as used for version 1.5 (Table 6 from Pfeil et al. 2013).

A group led by Wanninkhof provided recommendations regarding fCO_{2w} measurements made from platforms other than ships, and instruments that differ from conventional IR headspace analysis from flowing equilibrators. This will greatly facilitate maintaining a climate quality dataset with appropriate metadata. The assessment included:

- Whether the data should be included in version 3 of SOCAT,
- What metadata is necessary to perform the secondary quality control, and,
- What added information should be provided in the SOCAT output files such that queries can easily distinguish the data obtained from different approaches.

The resulting white paper (Wanninkhof et al. 2013) described the alternative sensors and platforms and provided a new and consistent set of criteria to be used in dataset quality control (See *Table 2*).

Table 2. Updated criteria for dataset quality control flags of the SOCAT database version 3.0

Flag (Value)	*Criteria*[a]
A (11)	(1) Accuracy of calculated fCO_{2w} (at SST) is better than 2 µatm (2) A high-quality cross-over with another dataset is available (3) Followed approved methods/SOP[b] criteria (4) Metadata documentation complete (5) Dataset QC was deemed acceptable
B (12)	(1) Accuracy of calculated fCO_{2w} (at SST) is better than 2 µatm (2) Followed approved methods/SOP criteria (3) Metadata documentation complete (4) Dataset QC was deemed acceptable
C (13)	(1) Accuracy of calculated fCO_{2w} (at SST) is better than 5 µatm (2) Followed approved methods/SOP criteria (3) Metadata documentation complete (4) Dataset QC was deemed acceptable
D (14)	(1) Accuracy of calculated fCO_{2w} (at SST) is better than 5 µatm (2) Did or did not follow approved methods/SOP criteria (3) Metadata documentation incomplete (4) Dataset QC was deemed acceptable
E (17)	(Primarily for alternative sensors) (1) Accuracy of calculated fCO_{2w} (at SST) is better than 10 µatm (2) Did not follow approved methods/SOP criteria (3) Metadata documentation complete (4) Dataset QC was deemed acceptable
F (15)	(1) Does not meet A through E criteria listed above
S (Suspend) (15)	(1) More information is needed for dataset before flag can be assigned (2) Dataset QC revealed non-acceptable data and (3) Data are being updated (part or the entire cruise)
X (15)	(Exclude) The cruise (dataset) duplicates another cruise (dataset) in SOCAT
NA…NF	Submitted data to SOCAT that has not undergone independent dataset quality control as indicated by the "N". The NA though NF are the flags provided by the submitting group

[a] the accuracy takes precedent over the criteria that follow
[b] SOP or Standard Operating Procedure following Dickson et al. 2007

The Arctic Ocean is a strong sink for atmospheric CO_2

The surface water pCO_2 data obtained aboard the USGCC *Healy* during the summer months of 2011 indicate that the surface waters of the entire Canada Basin (including the Beaufort Sea) are a strong sink for atmospheric CO_2. The observed pCO_2 values range between 220 µatm and 380 µatm, which are considerably below the present atmospheric pCO_2 of about 390 µatm. The higher values are found on and near the shallow shelf areas, whereas the lower values are found in the open ocean areas in association with melting ice. The ocean sink appears to be formed by the intense photosynthetic utilization of CO_2 in the highly stratified low-salinity layer, as well as by the dilution of water by melting ice and river waters. The large portion of the Canada Basin surface waters is also found to be undersaturated with respect to mineral aragonite ($CaCO_3$) (Robbins et al. 2013). This supports the initial findings of Cai et al. (2010) on the Chinese icebreaker *Xue Long* whose pCO_2 operations were lead by the "pCO_2 from ships" group and supported by the NOAA/CPO/Polar programs.

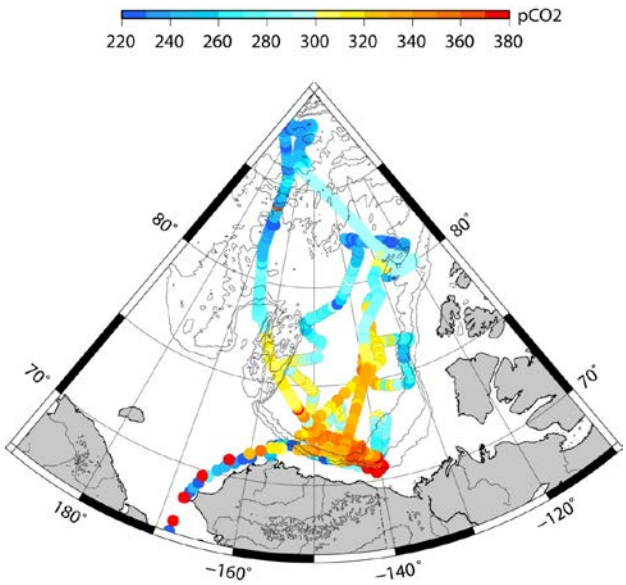


Figure 22. – Surface water pCO_2 distribution obtained aboard USCGC Healy during the summer months of 2011(Takahashi et al. 2013). All the observed values are below the current atmospheric pCO_2 level of about 390 uatm indicating that the sea is a strong sink for atmospheric CO_2 . The blue areas are especially strong sink areas and coincide with the melting ice field (Robbins et al. 2013).

Updated seasonal and interannual fCO_2-SST relationships

We have continued to update seasonal and interannual fCO_2-SST relationships from shipboard data gathered onboard research ships from November 1981 through October 2012. 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. The equations were applied to monthly sea surface temperatures from the NOAA Optimum Interpolation (*OI*)

Sea Surface Temperature V2 for the region 6°N to 10°S, 160°E to 90°W. The relationships were used to estimate the mean fCO_2 for the region for both *El Niño* (red) and *non- El Niño* (blue) conditions (*Figure 23*). Note the large increase in fCO_2 after the PDO phase shift in 1998-1999, particularly during the *El Niño* periods. This is primarily due to the increase in winds after the PDO shift that caused enhanced upwelling of CO_2-rich waters from the Equatorial Undercurrent. Our preliminary calculations suggest a 30% increase in the outgassing CO_2 flux from this region during the decade following this phase shift. This is an example of one of the largest documented observation of a decadal change of CO_2 outgassing in the global oceans.

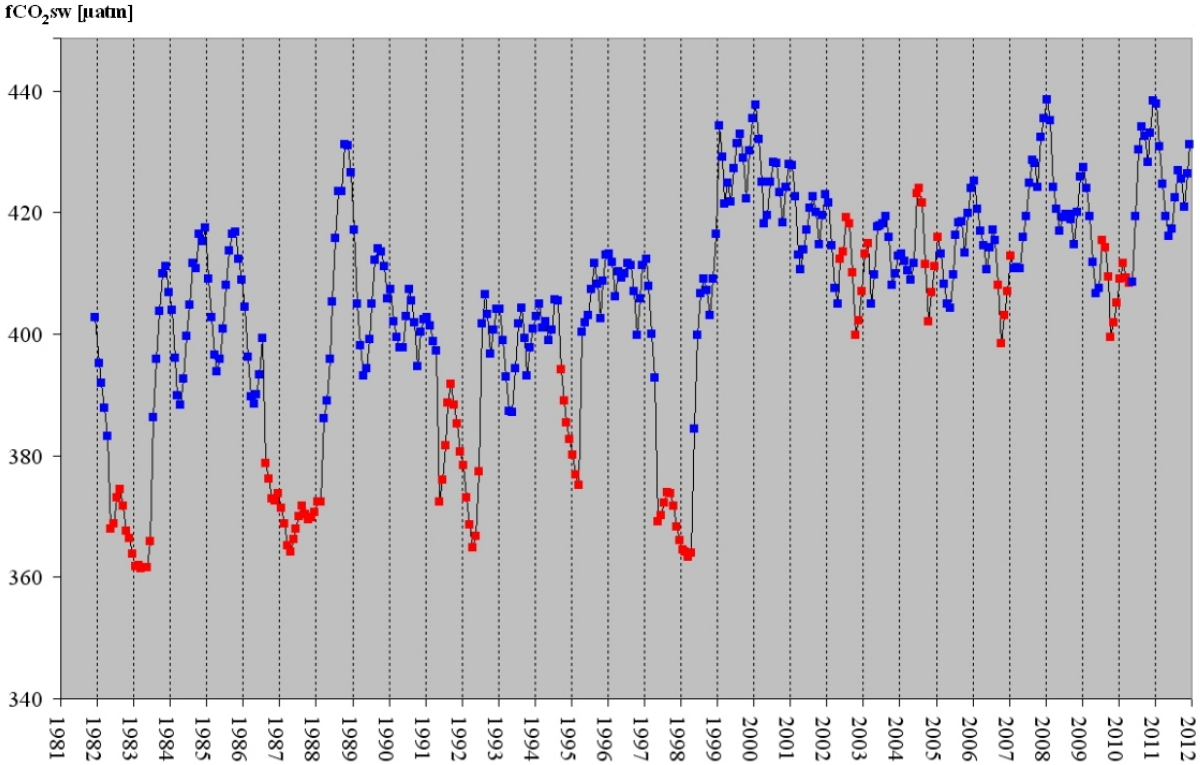


Figure 23. fCO_2 sw calculated from SST-fCO_2 relationships in the equatorial Pacific region 6°N to 10°S, 160°E to 95°W. Red squares represent El Niño conditions; Blue squares represent non-El Niño conditions.

3 Outreach and Education

Investigators in this project have been active in several outreach efforts. They presented public lectures; given guest lectures at schools and universities and are members of national and international steering committees. Bates is a member of the Scientific Steering Group for the US Carbon Cycle Interagency Working Group. Takahashi has served the following committees as a full member.

Fellows Committee, American Geophysical Union, Washington, D. C., 2007-present.

Science Steering Committee, Ocean Carbon Biogeochemistry Program, (multi-agency supported) Woods Hole Oceanographic Institution, Woods Hole, MA, 2009-present.

Pierrot, Wanninkhof, and Cosca are active members of the SOCAT group that includes an active effort to entrain developing nations in global CO_2 measurements. The R/V *Walton Smith* is used by the University of Miami's Department of Marine Science to provide undergraduate students with at sea experience in marine chemistry. The pCO_2 data collected during these cruises are used by the students in exercises designed to introduce them to the collection and analysis of oceanographic data, and the preparation of a cruise data report.

4 Publications and Reports

4.1 Publications by Principal Investigators

Papers supported by the NOAA/COD pCO_2 on ships with funded participants italicized:

Published

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