

## **Surface Water $p\text{CO}_2$ Measurements from Ships**

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## 1 Abstract

The aim of this project is to quantify the regional sources and sinks of carbon dioxide in the ocean to help understand and predict climate trends, and provide the best available scientific information upon which international policies are based. NOAA investigators are collaborating with academic partners in outfitting 17 research and commercial vessels with automated systems which measure the carbon dioxide (CO<sub>2</sub>) in surface waters and well as the overlying atmosphere in order to determine the direction and magnitude of the flux of CO<sub>2</sub> between the air-water interface. This effort of measuring surface water CO<sub>2</sub> levels and inferring sea-air CO<sub>2</sub> fluxes is the largest coordinated effort in the world. It directly addresses one of the overriding goals of the Climate Observation Division of a measurement-based quantification of the uptake of anthropogenic CO<sub>2</sub> by the ocean. The project is a national partnership between 5 entities: AOML and its TSG group, PMEL, LDEO, RSMAS and BIOS. It has close international interactions with similar efforts undertaken in Norway, Iceland, France, Germany, England, Australia, New Zealand and Japan. The tasks of each investigator are inclusive and range from data collection to data reduction and dissemination. There is currently an international effort (SOCAT) to gather all available surface *p*CO<sub>2</sub> data to which this project is the major contributor. The data has been used in an updated global air-sea CO<sub>2</sub> flux climatology, regional basin fluxes, sea surface CO<sub>2</sub> trend analyses, and new techniques to quantify fluxes such as self-organizing maps/neural networks.

## 2 Project Summary

The oceans are the largest sustained sink of anthropogenic carbon with a flux into the ocean of about  $2 \times 10^{15}$  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<sub>2</sub> levels, and surface oceanic CO<sub>2</sub> concentrations we must constrain the flux of CO<sub>2</sub> across the air water interface. The goal for the mature surface ocean CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> (*p*CO<sub>2</sub>) 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 Carbon Atlas (SOCAT) run under the auspices of the International Ocean Carbon Coordination project (IOCCP). Approximately half of the SOCAT data comes from the participants of the pCO<sub>2</sub> 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<sub>2</sub> 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 bi-monthly sea-air CO<sub>2</sub> 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) that will feed into the IPCC assessments. Ultimately, this work will contribute to policy on greenhouse gas management and assessments of perturbations of the surface ocean (ocean acidification).

### **3 Project participants, data and platforms**

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<sub>2</sub> systems on the ships, auxiliary measurements, data reduction, and data management. The following ships had pCO<sub>2</sub> systems on them during part or all of the performance period: NOAA ships *Ronald H. Brown*, *Gordon Gunter*, *Ka'imimoana* and *Henry B. Bigelow*; Container ships *Schulte*, *Oleander*, *Barcelona Express*, *Reykjafoss* and *Las Cuevas*, research vessels *RVIB Palmer*, *Gould*, *Langseth* and *Healy*, M/V *Turmoil*, 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<sub>2</sub> 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.

## 4 Scientific and Observing System Accomplishments

The main metric for this program is obtaining, reducing, quality controlling and disseminating high quality surface water and marine air  $p\text{CO}_2$  data. The number of cruises with  $p\text{CO}_2$  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-2012.*

<b>SHIP</b>	<b># Cruises</b>	<b># Data Points</b>	<b>% Recovery*</b>
<i>R/V Brown</i>	8	50,000	95.0%
<i>Explorer of the Seas</i>	30	85,500	89.0%
<i>M/V Las Cuevas</i>	15	32,700	30.0%
<i>R/V Gordon Gunter</i>	7	40,000	75.0%
<i>M/V Barcelona Express</i>	8	80,000	56.0%
<i>M/V Reykjavoss</i>	7	70,000	50.0%
<i>R/V Bigelow</i>	7	74,000	98.0%
<i>M/V Schulte</i>	4	23,898	98.0%
<i>R/V Ka'imimoana</i>	4	48,531	44.0%
<i>RVIB Palmer</i>	8	39,705	87.1%
<i>R/V Gould</i>	10	67,610	83.0%
<i>R/V Langseth</i>	7	49,542	93.5%
<i>USCGC Healy</i>	6	69,205	95.5%
<i>M/V Comer Turmoil</i>	7	45,000	N/R
<i>R/V Atlantic Explorer</i>	12	98,664	75%
<i>M/V Oleander</i>	42	95,000	45%
<i>R/V Walton Smith</i>	16	40,000	85%

\* 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: 8**

**Number of  $f\text{CO}_2$  data points: ~50,000\***

**% Data return: 95%\***

*\* estimated*

**Description:** The cruise tracks for each cruise of the *Brown* for FY 2012 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\\_data2012.php](http://www.aoml.noaa.gov/ocd/gcc/rvbrown_data2012.php). During this fiscal 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 4 months in the summer.

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.

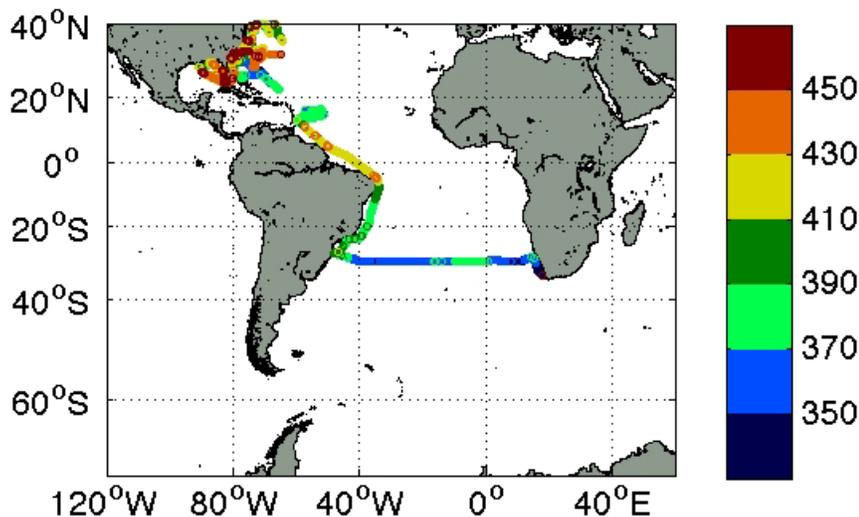


Figure 1. *Ronald H. Brown* cruise tracks and surface  $x\text{CO}_2$  values for FY 2012.

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 technician, which is permanently on board. Most of the data loss is due to common ship's operations failures such as the sea water flow stopped or sensors not being turned on. The system also shows intermittent drops of SCS data. Every once in a while, the ship's data sensors are not logged properly by our system and we are still trying to resolve that issue. We believe that the latest version of the software developed with resources from this program will help greatly.

### **Cruise ship *Explorer of the Seas*-AOML lead**



**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)

**Number of cruises:** 30

**Number of  $fCO_2$  data points:** ~85,500

**% Data return:** 89%.

**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](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 addition to creating substantial air entrainment in the seawater line when the seas are rough, it has also sucked in sargassum algae, which has clogged the pump. The major technical issue besides the pump not working is the loss of acquisition of the GPS signal. We are dealing with the same issue on other ships and we are trying to find a work-around. Lately, the  $CO_2$  analyzer started malfunctioning intermittently and we will replace it in the near future.

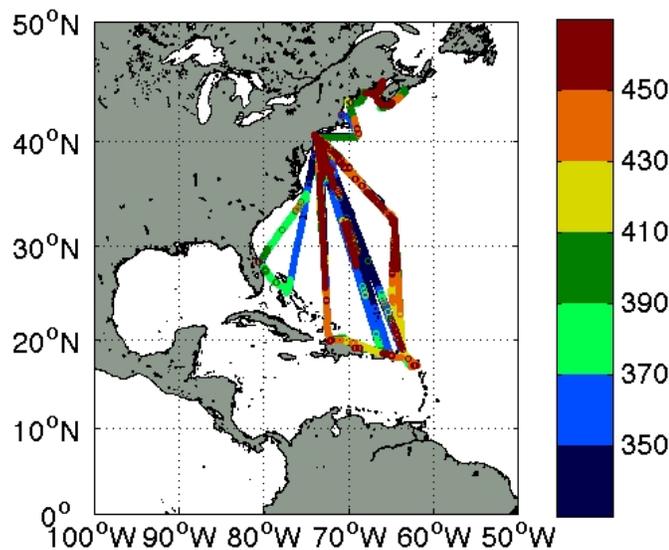


Figure 2. Explorer of the Seas cruise tracks and surface  $xCO_2$  values for FY 2012.

### Methanol Carrier *Las Cuevas*-AOML lead



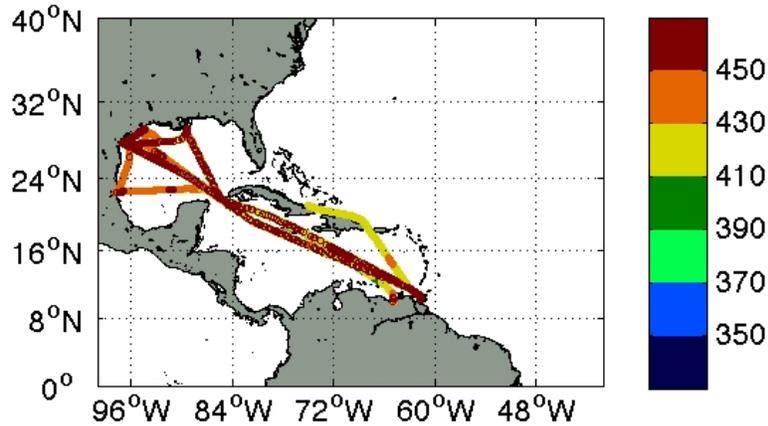
**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)

**Number of voyages:** 15

**Number of  $fCO_2$  data points:** ~32,700

**% Data return:** 30%

**Description:** This system operation used to be partially funded by NASA as part of the NASA ROSES *Ocean Acidification of the Greater Caribbean Region* project and we have taken it over fully since the end of that project a couple years ago. The system has been running since August 2009 and we have put a lot of effort into resolving the many issues that presented themselves. This fiscal year, we put our effort into resolving the iridium transmission issues, which we have. And in the past couple months we have been receiving daily data files very regularly.



*Figure 3.  $xCO_2$  values collected on board the M/V Las Cuevas during FY-2012.*

Unfortunately, we have been plagued with GPS and pump failures and the ship's difficulty of access resulted in substantial data loss and we have not been able to improve on our data return.

**Causes for non-return:** The failures of the system have been mostly minor but caused substantial data loss due to the poor communication with the ship and the difficulty to access it. Examples of failures include the failure of the pump, which evacuates the seawater after it has gone through the system, loss of GPS signal and analyzer malfunction. The access to this ship has been particularly difficult due to several factors: first, the ship has no port of call close to Miami, FL where we are based and we have no collaborator close enough to any of the port of calls that could help. Second, it is a methanol gas carrier, which means that getting on board requires going through tight security. Finally, the owners of the ship could not allow us to ride with our system. These reasons, combined with an aging system more prone to failure, made the maintenance of this operation financially more expensive and we have not improved our data return under the present level-funding conditions.

## NOAA ship *Gordon Gunter* - AOML lead



**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)

**Number of cruises:** 7

**Number of  $f\text{CO}_2$  data points:** ~40,000\*

**% Data return:** 75%\*.

\*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](http://www.aoml.noaa.gov/ocd/gcc/rvgunter_realtime.php)). The only limitation of this installation is the ship's less-than-optimum sea surface temperature probe. We are waiting for an opportunity to replace it with a higher accuracy one.

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

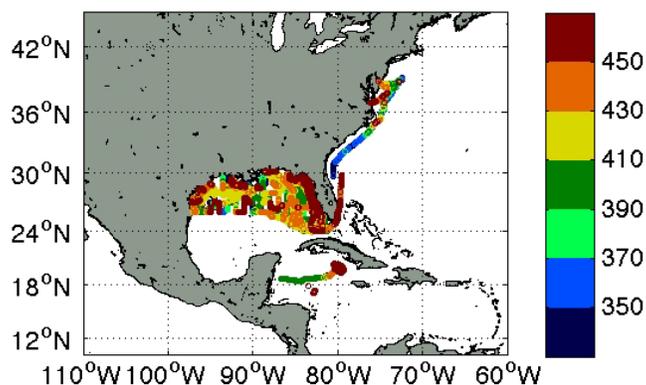


Figure 4.  $x\text{CO}_2$  values along the tracks of the *Gordon Gunter* for fiscal year 2012.

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



**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)

**Number of voyages:** 8

**Number of  $f\text{CO}_2$  data points:** 80,000

**% Data return:** ~56%.

**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  $p\text{CO}_2$  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  $p\text{CO}_2$  and the TSG systems. Here again, the excessive heat experienced by our system 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.

The data is transmitted via Iridium daily and plotted automatically as soon as it is received and can be accessed on our website ([http://www.aoml.noaa.gov/ocd/gcc/barcelona\\_realtime.php](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 seawater delivery system which kept getting clogged and the pump used to evacuate the seawater, which broke down a couple times. Similar to other ships, we've also had issues with losing the GPS signal but we believe that the latest version of our software will solve that issue.

On a couple transits, the seawater temperature was behaving strangely, as if the seawater was being re-circulated even though the ship's engineers assured us it wasn't. The behavior stopped now but we could not use the data while it was happening and that seriously impacted our data return. If this doesn't happen next year, we expect the data return to be much higher.

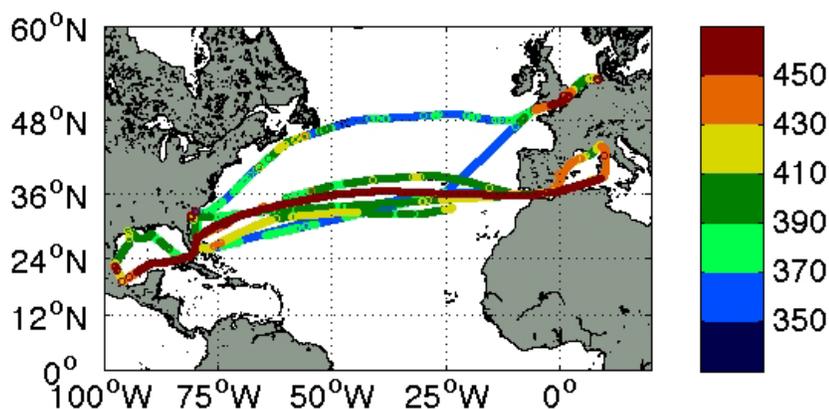


Figure 5.  $x\text{CO}_2$  values along the tracks of the M/V Barcelona Express for fiscal year 2012.

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



**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)

**Number of cruises:** 7

**Number of  $f\text{CO}_2$  data points:** ~70,000\*

**% Data return:** 50%\*.

\*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  $\text{CO}_2$  sink with large seasonal variations. During the early spring,  $p\text{CO}_2$  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  $p\text{CO}_2$  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  $p\text{CO}_2$  system shares resources with the TSG group at AOML where one computer is used to run both the  $p\text{CO}_2$  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.

**Causes for non-return:** We have lost a couple transits due to the fact that the seawater we were analyzing was being re-circulated by the ship, which is done to control the engine's temperature. We did not notice this right away so quite a few days were lost by the time we did notice. We

also had the analytical gas drier fail, which created an accumulation of water in the lines and effectively blocked the gas flow through the system. This repair needs more man power and time resources than we had available so far so we've tried to fix the problem by using other methods of drying the gas and we've had mixed results, which means that we lost a few days of data here as well. Finally, our seawater pump broke down at some point, which did not please the chief engineer, and we lost the data until we could replace the pump.

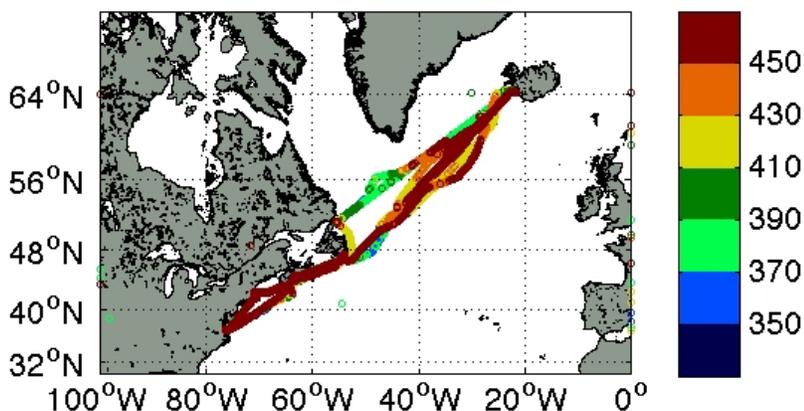


Figure 6.  $x\text{CO}_2$  values along the tracks of the M/V Reykjafoss for fiscal year 2011.

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



**Data Site:** [www.aoml.noaa.gov/ocd/gcc/](http://www.aoml.noaa.gov/ocd/gcc/)  
**Number of cruises:** 7 (16 legs)  
**Number of  $f\text{CO}_2$  data points:** 74,000  
**% Data return:** 98%.

**Description:** The NOAA ship *R/V Henri B. Bigelow* is a newly built 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 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.

**Causes for non-return:** Some data was lost due to seawater flow issues or loss of GPS signal but overall, the system behaved very well.

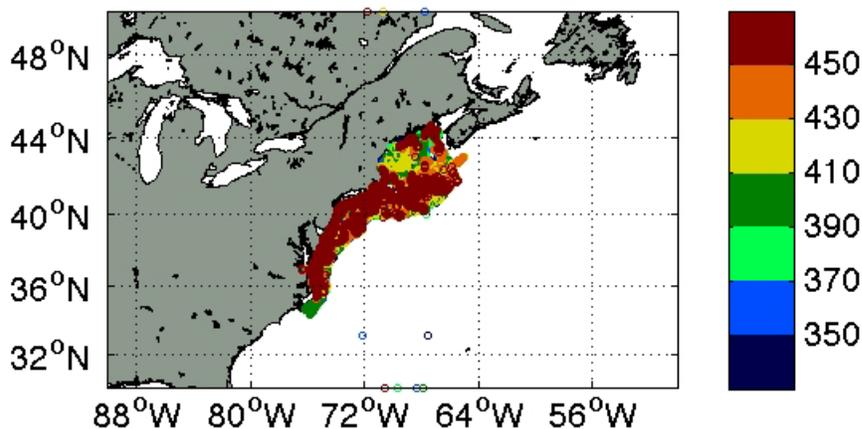


Figure 7.  $x\text{CO}_2$  values along the tracks of the R/V Henri B. Bigelow for fiscal year 2012.

#### Container ships *Natalie Schulte* - PMEL lead



**Data Site:** <http://www.pmel.noaa.gov/co2/>  
**Number of cruises:** 4  
**Number of  $f\text{CO}_2$  data points:** 23,989  
**% Data return:** 98%.

**Causes for non-return:** The underway  $f\text{CO}_2$  systems on the *Natalie Schulte* resulted in a 98% data return during FY2012. A small amount of data was rejected due to stack gas contamination when the ships changed course.

**Description:** In September 2011, PMEL installed an underway  $f\text{CO}_2$  system on the *Natalie Schulte* to continue measurements  $f\text{CO}_2$  across the Pacific from Long Beach to New Zealand. In FY2012, PMEL collected  $f\text{CO}_2$  data on four transits (Figure 8), bringing the total number of cruises along this track to 27 since we began measuring  $f\text{CO}_2$  on container ships in 2004. All data

collected on the *Natalie Schulte* are in final processing and will be submitted to CDIAC for archiving, and posted to the PMEL CO<sub>2</sub> website. An underway *f*CO<sub>2</sub> system will be installed on the container ship *Cap Vilano* in FY2013 to continue our trans-Pacific measurements.

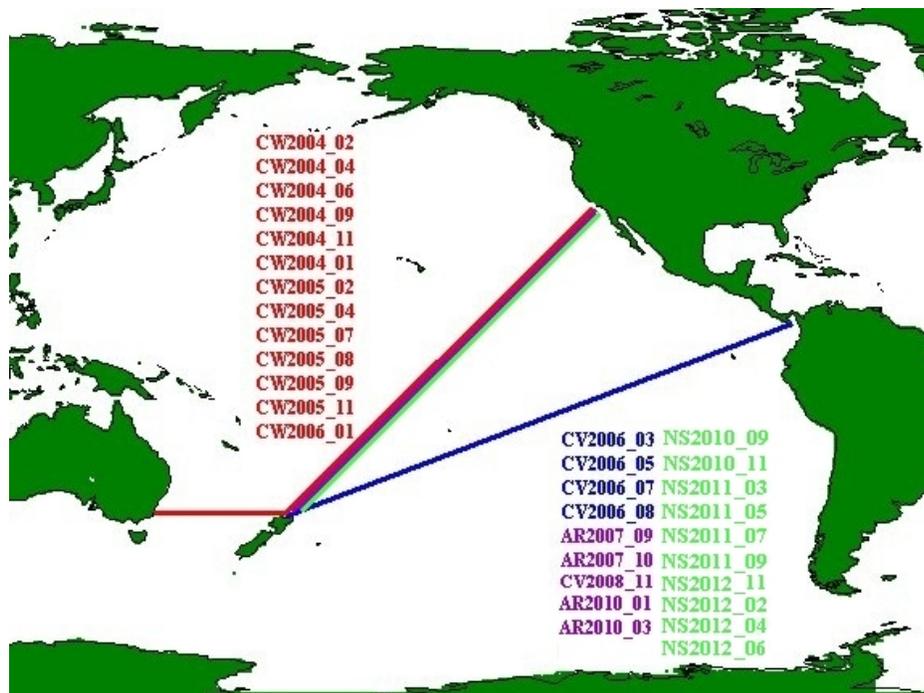


Figure 8. Cruise Tracks of the *Columbus Waikato* (red), *Cap Victor* (blue), *Albert Rickmers* (purple), *Cap Van Diemen* (purple), and *Natalie Schulte* (green) occupied during FY2004-2012. A summary of cruise results from transects across the equatorial Pacific from February 2004 to November 2012 is shown in Figure 9 and Table 2. Transects in red represent data collected from April through September, the warm season in the Northern Hemisphere. Blue transects represent data collected from October through March, the cool season in the Northern Hemisphere. The squares in the graph are 10° averages of  $\Delta f\text{CO}_2$  along the ship's transect line, with the yellow squares representing the averages for the April through September time period, and the cyan squares representing the averages for the October through March time period. There are significant seasonal differences during these two time periods for each of the regions, with the higher *f*CO<sub>2</sub> values occurring in the surface waters in the respective warm seasons – April through September in the North, and October through March in the South. The seasonal differences are significant in both the northern and southern Pacific, but out of phase by 6 months. La Nina conditions persisted in the Pacific Ocean during FY2011 and FY2012, resulting in the highest  $\Delta f\text{CO}_2$  measurements collected to date on PMEL trans-Pacific cruises.

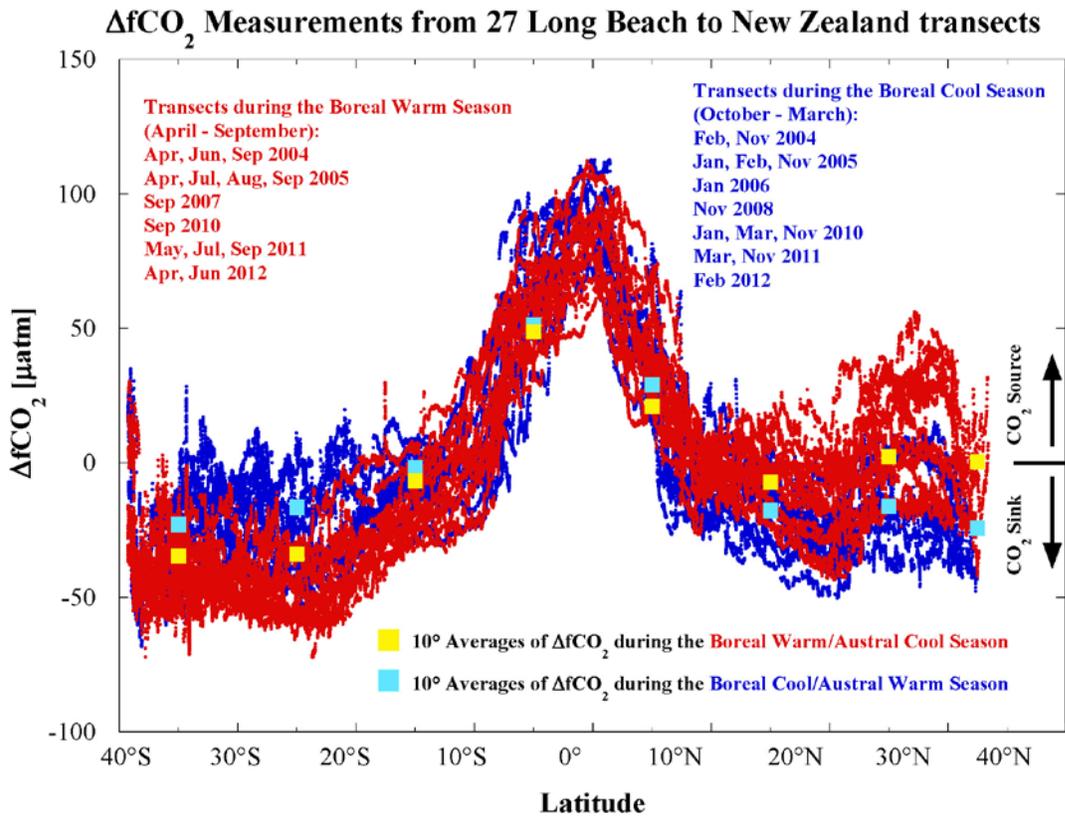


Figure 9. Time-Series of surface water  $fCO_2$  levels in the tropical and subtropical Pacific resulting from Columbus Waikato, Albert Rickmers, Cap Van Diemen and Natalie Schulte repeat observations from 2004 to 2012. Highest  $\Delta fCO_2$  values are measured during La Niña conditions in FY2011 and FY2012.

Table 2. 10 ° averages of  $fCO_2$ ,  $\Delta fCO_2$  and  $CO_2$  flux from trans-Pacific transits 2004-2011.

	Boreal Cool Season (Oct - Mar)				Boreal Warm Season (Apr - Sep)			
	$fCO_{2sw}$ ( $\mu atm$ )	$fCO_{2air}$ ( $\mu atm$ )	$\Delta fCO_2$ ( $\mu atm$ )	$CO_2$ Flux ( $m^3 m^{-2} yr$ )	$fCO_{2sw}$ ( $\mu atm$ )	$fCO_{2air}$ ( $\mu atm$ )	$\Delta fCO_2$ ( $\mu atm$ )	$CO_2$ Flux ( $m^3 m^{-2} yr$ )
40°N - 30°N	352.53 ± 11.33	377.32 ± 1.74	-24.79 ± 10.55	-0.76 ± 0.37	375.15 ± 11.31	374.74 ± 2.45	0.41 ± 12.66	-0.05 ± 0.51
30°N - 20°N	353.69 ± 12.31	373.93 ± 1.98	-20.24 ± 12.63	-0.79 ± 0.49	376.96 ± 14.73	373.39 ± 3.1	3.57 ± 16.31	0.03 ± 0.56
20°N - 10°N	347.23 ± 9.64	368.72 ± 2.56	-21.49 ± 11.41	-1.36 ± 0.69	361.84 ± 7.51	369.66 ± 2.65	-7.82 ± 9.46	-0.45 ± 0.51
10°N - 0°	395.7 ± 35.47	365.55 ± 1.55	30.16 ± 35.52	0.76 ± 1.13	402.14 ± 27.91	367.08 ± 1.5	35.06 ± 28.13	0.83 ± 0.82
	Austral Warm Season (Oct - Mar)				Austral Cool Season (Apr - Sep)			
	$fCO_{2sw}$ ( $\mu atm$ )	$fCO_{2air}$ ( $\mu atm$ )	$\Delta fCO_2$ ( $\mu atm$ )	$CO_2$ Flux ( $m^3 m^{-2} yr$ )	$fCO_{2sw}$ ( $\mu atm$ )	$fCO_{2air}$ ( $\mu atm$ )	$\Delta fCO_2$ ( $\mu atm$ )	$CO_2$ Flux ( $m^3 m^{-2} yr$ )
0° - 10°S	412.96 ± 32.31	363.8 ± 1.37	49.16 ± 31.19	1.18 ± 0.87	418.41 ± 25.17	365.68 ± 1.18	52.74 ± 24.47	1.52 ± 0.83
10°S - 20°S	354.7 ± 8.8	362.5 ± 1.26	-7.81 ± 9.17	-0.19 ± 0.26	350.4 ± 12.12	365.31 ± 1.63	-14.91 ± 13.3	-0.43 ± 0.43
20°S - 30°S	345.81 ± 9.91	366.17 ± 2.32	-20.36 ± 10.79	-0.65 ± 0.42	325.33 ± 8.99	369.52 ± 2.39	-44.19 ± 10.63	-1.57 ± 0.54
30°S - 40°S	343.15 ± 11.35	369.11 ± 1.91	-25.96 ± 11.72	-0.81 ± 0.43	332.22 ± 10.11	372.14 ± 2.15	-39.93 ± 10.07	-1.58 ± 0.6

## NOAA ship *Ka'imimoana*- PMEL lead



**Data Site:** <http://www.pmel.noaa.gov/co2/uwpCO2>  
**Number of cruises:** 4  
**Number of  $f\text{CO}_2$  data points:** 48,531  
**% Data return:** 44% for seawater  $f\text{CO}_2$ , 98% for atmospheric  $f\text{CO}_2$

**Causes for non-return:** The underway  $f\text{CO}_2$  systems on the NOAA Ship *Ka'imimoana* resulted in a 44% return rate for seawater  $f\text{CO}_2$ , and 98% for atmospheric  $f\text{CO}_2$ . The power supply on the computer failed during the FY1202 cruise in April, disabling our ability to stop the program to download and QC data. We removed all equipment from the *Ka'imimoana* in June after the last scheduled cruise for the FY12 field season. Post-processing of the data indicated that additional instrument failure occurred during the last two cruises. The system on the *Ka'imimoana* had been in continuous operation since 2006, and will be completely overhauled at PMEL. A new underway  $p\text{CO}_2$  system will be installed on the University of Hawaii R/V *Ka'imikai-o-Kanaloa* (KoK), which has been identified as the ship to replace the *Ka'imimoana* for the FY2013 field season.

**Description:** From October 2011 through September 2012 the *Ka'imimoana* was involved in studies in the Equatorial Pacific between 110°W and 165°E (Figure 10). Prior to the 2012 field season, the  $f\text{CO}_2$  system was updated with new software, pumps and filters. During the time under review, PMEL collected and processed 48,531  $f\text{CO}_2$  data values from the *Ka'imimoana* on 5 separate cruises in the equatorial Pacific. Though the instrument failed to collect seawater  $f\text{CO}_2$  measurements during the last two cruises, we collected high quality air measurements of  $f\text{CO}_2$  along with salinity, sea surface temperature and barometric pressure. 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'imimoana* during the 2012 fiscal year are in final processing and will be submitted to CDIAC for archiving.

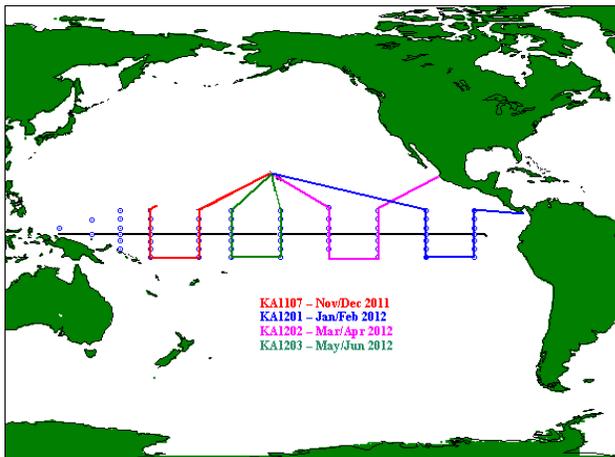


Figure 10. *Ka'imimoana* track lines occupied during FY 2012.

## RVIB Palmer - LDEO lead



**Data Site:** <http://www.ldeo.columbia.edu/CO2>

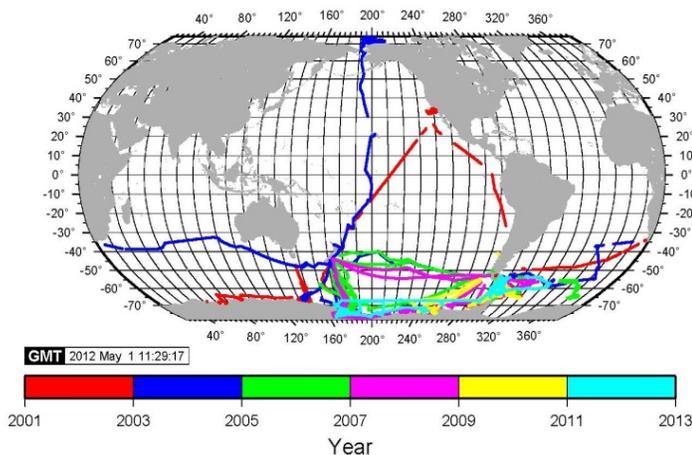
**Number of cruises:** 8

**Number of  $f\text{CO}_2$  data points:** 39,705

**% Data return:** 87.1%.

**Description:** The Lamont group is primarily responsible for the acquisition of the surface water  $p\text{CO}_2$  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  $\text{CO}_2$  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 are shown in *Figure 11*. The total number of surface water  $p\text{CO}_2$  data obtained to date is 930,995, of which about 39,705 measurements were added to the database during the current funding period starting September 1, 2011. 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 87.0%, while that for the current funding period is 87.1%.



*Figure 11. The locations of surface water  $p\text{CO}_2$  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



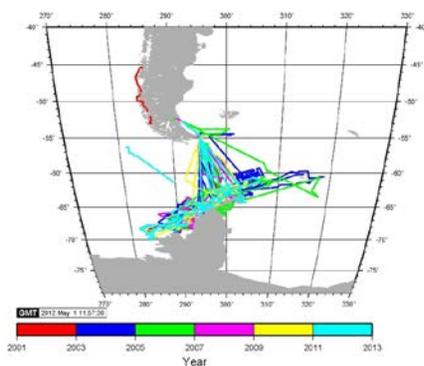
**Data Site:** <http://www.ldeo.columbia.edu/CO2>

**Number of cruises:** 10

**Number of fCO<sub>2</sub> data points:** 67,610

**Data return:** 93.5%.

**Description:** Our underway pCO<sub>2</sub> 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<sub>2</sub> 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 are shown in *Figure 12*. A total of 67,610 pCO<sub>2</sub> measurements were made aboard the R/V *Gould* during the current funding period starting September 1, 2011. The new data make a total of 584,009 pCO<sub>2</sub> measurements for the *Gould* program since its inception in March 2002. The data recovery rate for the current funding period was 93.5% with a mean rate of 86.2% during the ten-year period, 2002-2012. The quality-controlled data have been added to our LDEO database, and submitted to CDIAC for public access.



*Figure 12. The locations of the surface water pCO<sub>2</sub> measurements obtained aboard the R/V L. M. Gould during this project, March 2002 through September 2012. The years of the measurements are color-coded.*

## ***R/V Marcus Langseth – LDEO Lead***



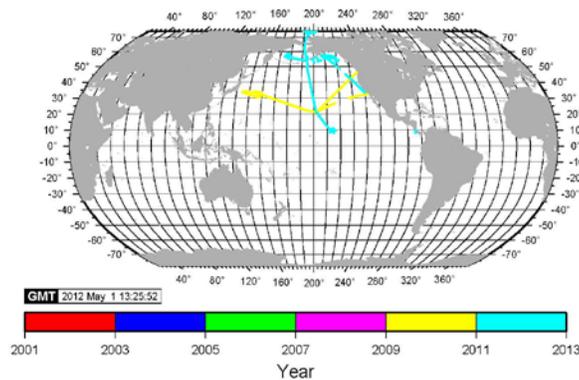
**Data Site:** <http://www.ldeo.columbia.edu/CO2>

**Number of cruises:** 7

**Number of  $f\text{CO}_2$  data points:** 49,542

**Data return:** 95.7%

**Description:** *R/V Marcus Langseth* is a geophysical research vessel operated by LDEO with funds from NSF, and was added to the  $\text{CO}_2$  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  $p\text{CO}_2$  in small ocean areas in details. Our underway  $p\text{CO}_2$  program was commenced on May 8, 2010. Since the inception of the field program in May 2010, 95,017  $p\text{CO}_2$  measurements were obtained with a data recovery rate of 95.1% in the North Pacific Ocean and the Arctic Sea (Figure 13). No measurement was obtained during the four-month period, January-April, 2012 due to system failure (seawater in the IR analyzer caused by computer failure). The ship was laid off during October 2010 through March 2011, and was reactivated in April, 2011.



*Figure 13. The sampling locations for the R/V Langseth in 2010-2012 in the North Pacific and Arctic.*

## USCGC Healy – LDEO Lead



**Data Site:** <http://www.ldeo.columbia.edu/CO2>.

**Number of cruises:** 6

**Number of  $f\text{CO}_2$  data points:** 69,205

**Data return:** 95.5%

**Description:** USCGC Healy is one of the few US ships operating primarily in the Arctic, where seasonal  $\text{CO}_2$  observations are lacking. Since waters flowing out of the Arctic basin should have a significant impact on the North Atlantic  $\text{CO}_2$  budget, our understanding of the time-space variability of  $p\text{CO}_2$  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  $p\text{CO}_2$  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. Since then, about 91,670  $p\text{CO}_2$  measurements (including 69,205 measurements during the current funding period) were obtained (Figure 14). These  $p\text{CO}_2$  and associated temperature, salinity and other data have been added to our database and reported to CDIAC. The surface water  $p\text{CO}_2$  data indicate that the Arctic water is a strong sink for atmospheric  $\text{CO}_2$ .

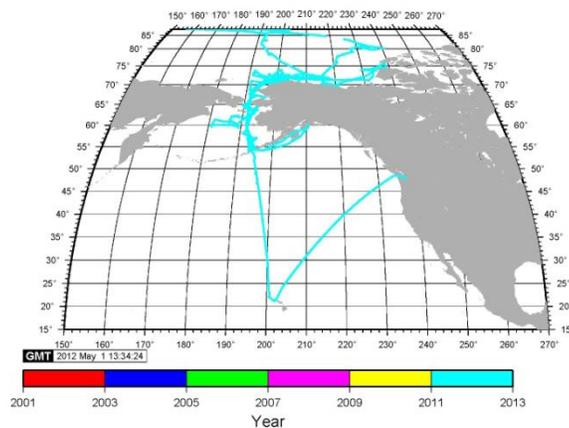


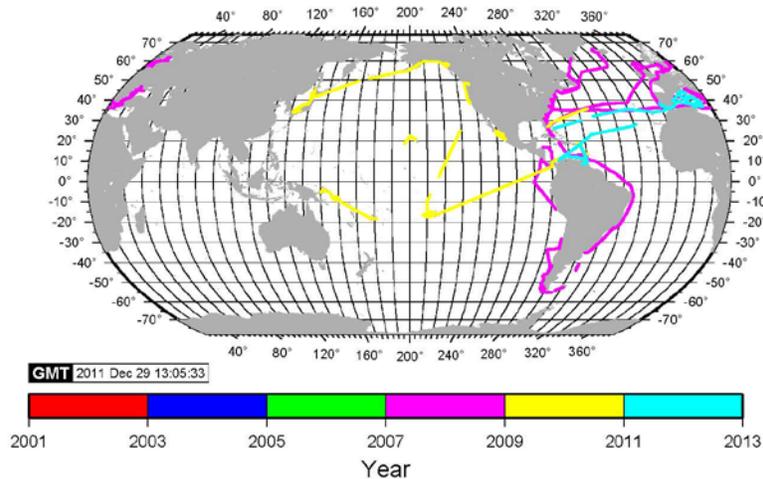
Figure 14. The sampling locations for the USCGC Healy.

### ***M/V Turmoil – LDEO Lead***



***Number of cruises: 7***  
***Number of fCO<sub>2</sub> data points: 45,000***  
***% Data return: N/R***

**Description:** An underway pCO<sub>2</sub> system is operated aboard the Comer family yacht, M/V *Turmoil* with a grant from the Comer Education and Research Foundation for the shipboard operation. *Figure 15* shows the locations of surface water pCO<sub>2</sub> data since 2007. However, this ship is being sold, and the CO<sub>2</sub> program aboard is discontinued as of September 31, 2012. Since the inception of this program, a total of 227,286 pCO<sub>2</sub> measurements have been obtained in the areas where have not been sampled aboard research and merchant ships.



*Figure 15. The locations of the surface water pCO<sub>2</sub> measurements obtained aboard the M/V Comer Turmoil since the inception of the program in 2007. The colors indicate the year of measurements*

## **R/V *Atlantic Explorer* - BIOS lead**



**Data Site:** <http://www.bios.edu/Labs/co2lab/vos.html>

**Number of cruises:** 12

**Number of  $f\text{CO}_2$  data points:** 98,664

**% Data return:** 75%

### **Description:**

The R/V *Atlantic Explorer* operates in the North Atlantic Ocean servicing three oceanographic time-series (e.g., Bermuda Atlantic Time-series Study, BATS, Hydrostation S, and Ocean Flux Program) near the island of Bermuda and other oceanographic research projects. The geographic focus of ship operation is primarily zone NA6 in the North Atlantic Ocean, but also includes 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.

The  $p\text{CO}_2$  system was installed on the R/V *Atlantic Explorer* in April 2006. This data stream provides seawater  $p\text{CO}_2$  datasets primarily for the subtropical gyre of the North Atlantic Ocean. Between 2007 and 2012, the R/V *Atlantic Explorer* has typically had ~135-170 ship days per 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. In 2013, the schedule will include included four transects between Bermuda and Norfolk, and two transects between Bermuda and Puerto Rico. In 2013, the R/V *Atlantic Explorer* will also participate in cruises in the Gulf of Mexico and detailed surveys along the US eastern seaboard (i.e., Maryland, Delaware, New Jersey) as part of US Navy funded work.

### **Data Return:**

In the last fiscal year, approximately 98,600  $p\text{CO}_2$  measurements have been made with a ~45% good data recovery. Maintenance of the seawater  $p\text{CO}_2$  system has become relatively routine during the ship's turnaround at the BIOS dock. This year we have observed more problems with the system primarily due to the increasing age of the  $p\text{CO}_2$  system and requirements for replacement of failed/failing components. We also as well as loss of the underway seawater supply system for the ship during part of the year. The non-return rates typically represent data that were flagged mainly due to problems with low flow rates from the underway system, failure of the LiCor, problems associated with the Valco multi-position valve and distribution of standards through the system, and delays in replacing the  $\text{CO}_2$ -in-air standards. We have a major problem with failure of two motherboard and associated components

of the computer systems (i.e., failure of moving hard disks due to the longterm ship movement/vibration) controlling the pCO<sub>2</sub> system (similar problems with the *Oleander* system as well). As a result, we are in the process of installing a new motherboard with flash drive and USB data access, although this has not been a simple replacement and required rewriting of the software to ensure proper communications between all components of the system. New CO<sub>2</sub>-in-air standards have also arrived and will be installed in November 2012. We have also replaced the LiCOR 7000 for this system. 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.

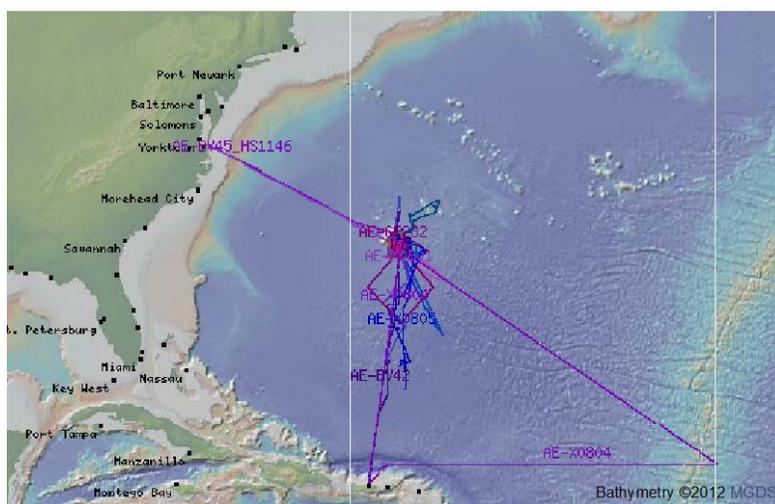


Figure 16. Typical Cruise tracks for the R/V Atlantic Explorer

## Container Ship *MV Oleander*- BIOS lead



**Data Site:** <http://www.bios.edu/Labs/co2lab/vos.html>

**Number of cruises:** 42

**Number of  $f\text{CO}_2$  data points:** 95,000

**% Data return:** 45%

### **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.

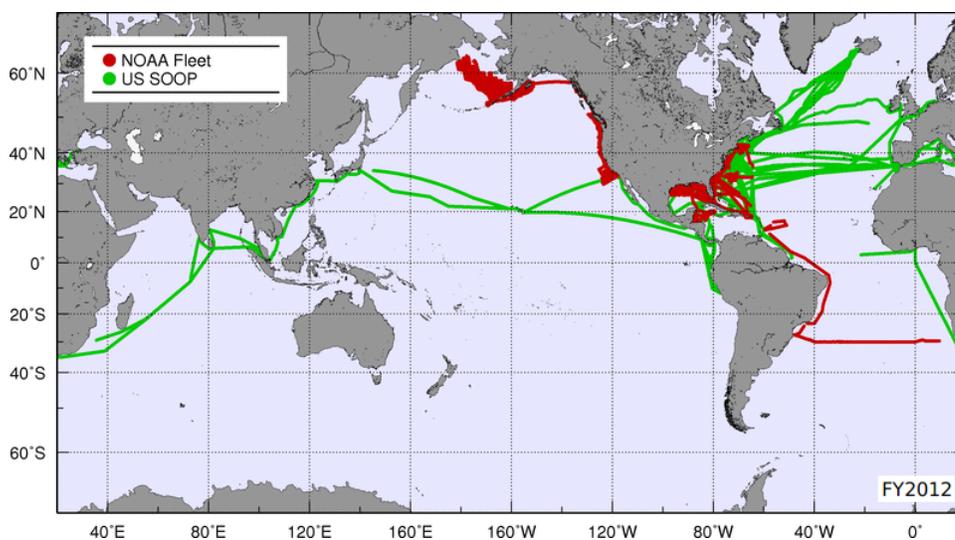
### **Data Return:**

Maintenance of the  $p\text{CO}_2$  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. However, access to the system is not always available due to the quick turnaround of the ship and short time in dock (both in Bermuda and New Jersey). During the last performance period, we have had major problems with the  $p\text{CO}_2$  system. We have observed more problems with the system primarily due to the increasing age of the  $p\text{CO}_2$  system and requirements for replacement of failed/failing components. The  $p\text{CO}_2$  system is installed in the engine room of the *Oleander* and about 2 m below sea level. This necessitates pumping the underway seawater from the  $p\text{CO}_2$  system back into the main supply line so that this subsequently goes over the side. We have unfortunately had multiple failures of the pumps to undertake this with the system being shut down as a result. In the next year, we will be endeavoring to move the system to a better location but this will require cooperation from the ship owners as it requires engineering, entry and exits into the engine room. The LiCOR cell also flooded and has been refurbished with parts replaced to return the instrument to the system onboard. 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. We plan to replace the  $p\text{CO}_2$  system with a solid-state bootable flash drive identical to the *Atlantic Explorer*. The *Oleander* engine room is very warm and with ship vibration, the computer components have failed too frequently to continue with previous movable hard drives, etc. Once the system tests are complete with the new solid-state bootable flash drive (much easier to solve problems), this replacement will be made on the *Oleander*.

## TSG operation – AOML/TSG group Lead

During FY2012 the TSG operations at AOML were carry out in support of the pCO<sub>2</sub> operations with several key developments regarding equipment installation, operation and maintenance, as well as data retrieval, quality control and submission to the GTS and other data centers.

Two new ships were added to AOML's TSG network during FY2012: *MV Las Cuevas* and *Allure of the Seas*. AOML is currently receiving, processing and distributing TSG data from 7 ships of the SOOP (Semester at Sea's *MV Explorer*, *MV Oleander*, *MV Barcelona Express*, *MV Reykjafoss*, *MV Las Cuevas* 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. More than 25 million TSG records were processed at AOML during FY2012 (*Figure 17*).



*Figure 17. Location of more than 25 million TSG observations received and processed by AOML during FY2012 from ships of the SOOP and the NOAA fleet.*

The operation of TSG equipment is performed with the AMVERSEAS software. During FY2012 several modifications were carryout on this software to enhance the control of the TSG when the ship arrives at port or in any other situation in which the position of the ship remains constant. The software also constantly checks the strength of the Iridium signal before attempting data transmissions. Additionally, log files are created with details of the equipment performance and eventual errors messages. These modifications also enable a reduction in the cost of the operation. During FY2012 the new version of the software was installed in *MV Barcelona Express* to test the software before the complete operational release. During FY2013 we plan to install the newest version of AMVERSEAS/TSG in all ships of the SOOP that also have pCO<sub>2</sub> systems installed in order to avoid data loss due to software issues caused by the increase complexity of the data acquisition system in those ships.

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 (Levitus 2005). 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.

Work continued during FY2012 for the installation and operation of a TSG system provided by AOML/TSG group 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 *Dr. Bernardo A. Houssay*. This system is currently installed and several test of data acquisition and transmission are currently being performed. Data from this TSG will be crucial for the calibration of the upcoming NASA Aquarius satellite mission.

Maintenance of the TSG web site at AOML was continued during FY2012, including products displaying data in real time from the *MV Explorer* and the *Explorer of the Seas*. This web site currently contains information regarding data analysis and quality control procedures for the NOAA fleet and the SOOP.

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



***Number of cruises: 16***  
***Number of  $f\text{CO}_2$  data points: 40,000\****  
***% Data return: 85%\****

***\* 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  $p\text{CO}_2$  system has been installed on board the *Walton Smith* since the beginning of July 2008. The  $p\text{CO}_2$  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  $p\text{CO}_2$  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:** The system this year has behaved quite well and the major data losses were due to human error when the system was not turned on or the GPS cable was disconnected by visiting scientists. Other than that, there is the occasional lack of water flow when the science party on board needs more than usual and the ship's system has trouble providing it. We also had to replace the LICOR analyzer early in the fiscal year when it started to malfunction for unknown reasons. We have replaced the unit with a model 840, which is not as accurate but is more reliable.

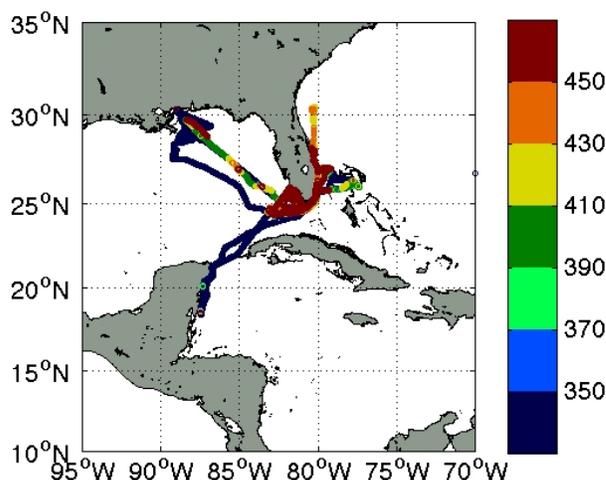


Figure 18.  $x\text{CO}_2$  values along the tracks of the R/V Walton Smith for fiscal year 2012.

#### 4.1 Education and Outreach

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.

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  $p\text{CO}_2$  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.

## 5 Data Management and Usage

The Lamont group is responsible for processing and managing the surface water pCO<sub>2</sub> data acquired by the members of the Volunteer Ocean Survey (VOS) 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. Version 2011 "Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database", which contains 6.4 million pCO<sub>2</sub> data (Takahashi et al., 2012-a), is now on-line at CDIAC. About 1 million new data have been added to the previous Version 2010 .

We have received the data from the following participating members of the VOS program and have added quality-controlled data to our database;

- 1) the NOAA's "Ronald Brown" program, mostly in the Atlantic Ocean (R. Wanninkhof);
- 2) the "Explorer of the Seas" program in and around the Caribbean Sea (R. Wanninkhof);
- 3) the "Ka'imimoana" program in the equatorial Pacific (R. A. Feely);
- 4) the "Gordon Gunter" program, (R. Wanninkhof);
- 5) the "Columbus Waikato" program (R. A. Feely);
- 6) R/V Atlantic Explorer program of BIOS (N. Bates);
- 7) MV *Turmoil* program of LDEO (T. Takahashi);
- 8) R/V Xue Long, Peoples Republic of China (R. Wanninkhof and WJ. Cai);
- 9) R/V Las Cuevas (R. Wanninkhof);

During the current reporting period, 231,832 new pCO<sub>2</sub> data were added to the VOS database.

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 *Ka'imimoana*, and *Natalie Schulte*. This software creates diagnostic plots of *f*CO<sub>2</sub>, 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 *f*CO<sub>2</sub> 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. (2008).

The carbon data are archived at the PMEL ([www.pmel.noaa.gov/co2/](http://www.pmel.noaa.gov/co2/)) website which includes an interactive map allowing quick access to underway *f*CO<sub>2</sub> data collected by PMEL since 1982. To date, *f*CO<sub>2</sub> 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 (see Appendix A).

## 6 Research Highlights

### **The global ocean surface water pCO<sub>2</sub> database.**

A newly updated LDEO Surface Water pCO<sub>2</sub> database Version 2011 “Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database “ has been assembled and made available to the public through the CDIAC (Takahashi et al., 2012a). This is the most extensive database for world ocean surface water pCO<sub>2</sub>, which includes about 6.4 million surface ocean water pCO<sub>2</sub> measurements obtained between 1957 and 2011. We added about 1 million new data to the previous version, v. 2010, that contained 5.3 million pCO<sub>2</sub> measurements covering 1968-2009. According to the CDIAC record, there has been about 132,000 “hits” to the LDEO database during the reporting period, indicating high demands for the updated database.

### ***Climatological Mean Distribution of Sea-air pCO<sub>2</sub> Difference over the Southern Ocean (Takahashi et al., 2012b):***

The difference between the CO<sub>2</sub> partial pressures in surface ocean water and in the overlying atmosphere represents the thermodynamic driving potential for the net sea-air CO<sub>2</sub> gas transfer. When pCO<sub>2</sub> in ocean water is smaller than that in the atmosphere, the ocean absorbs atmospheric CO<sub>2</sub>. Based upon about 2.1 million pCO<sub>2</sub> measurements made in the Southern Ocean surface waters (rightmost top panel, Figure 19), the climatological mean distribution of the monthly sea-air pCO<sub>2</sub> difference is obtained for a reference year 2000 (left two columns, Figure 19). Waters under the seasonal ice field in June through December have pCO<sub>2</sub> exceeding the atmospheric value (yellow-orange), and the seawater CO<sub>2</sub> could escape to the air only through open water areas such as leads and polynyas. On the other hand, the open waters between 30°S and 55°S have pCO<sub>2</sub> lower than the atmosphere and hence a CO<sub>2</sub> sink (green-blue). The mean annual air-to-sea CO<sub>2</sub> flux is estimated using the wind speed product, NCEP-DOE AMIP II Reanalysis (Kanamitsu et al., 2002) and a wind speed squared dependence for the gas transfer rate (rightmost bottom panel). The zone between 30°S and 50°S is found to be a major sink for atmospheric CO<sub>2</sub> with an annual flux of about 1 PgC/yr, accounting for about 50% of the net global ocean uptake of about 2 PgC/yr.

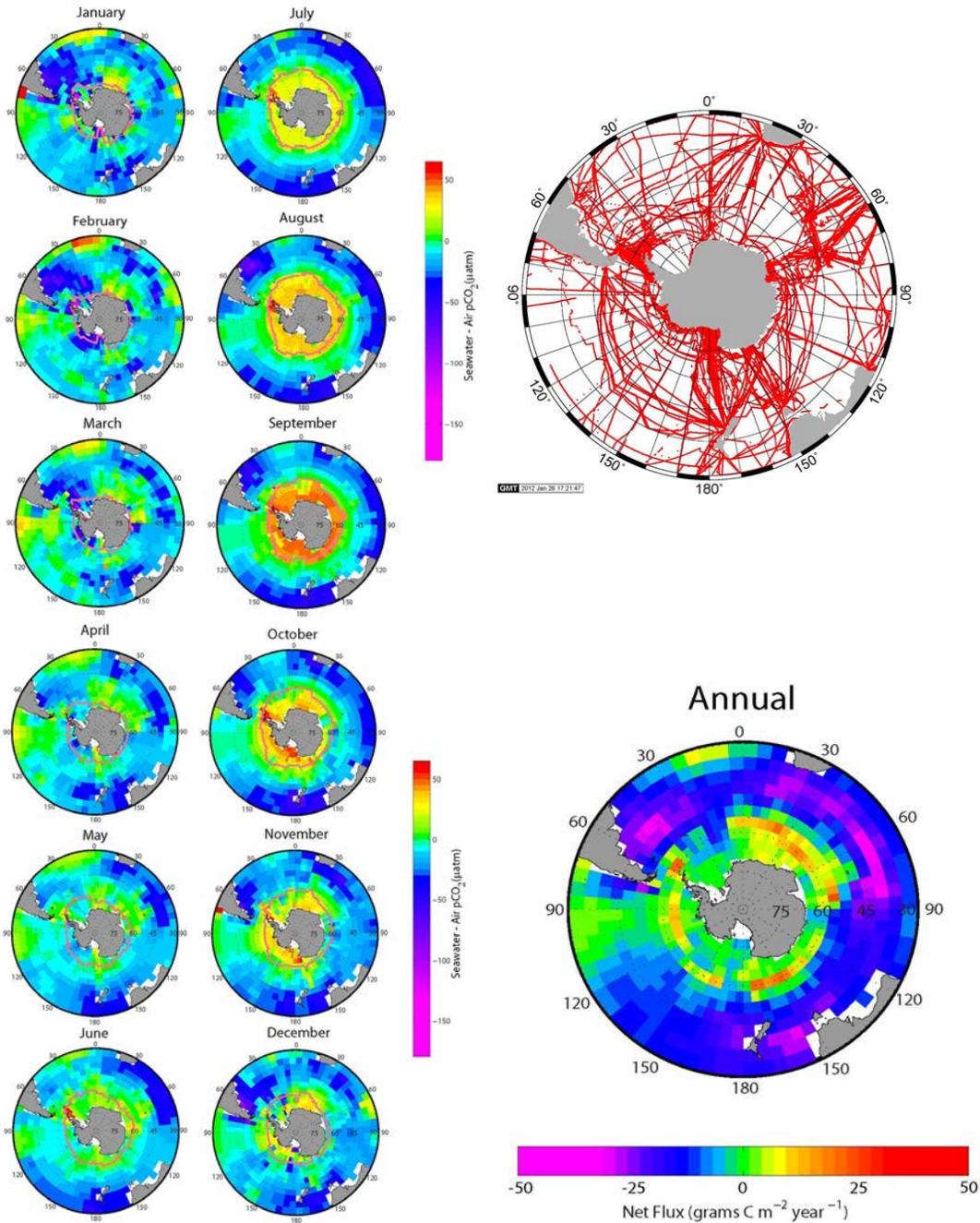


Figure 19. Climatological mean monthly distribution of sea-air  $p\text{CO}_2$  difference (left two columns), the data distribution (top rightmost column) and the mean annual sea-air  $\text{CO}_2$  flux (bottom, rightmost column) in the reference year 2000. In the sea-air  $p\text{CO}_2$  difference maps, the northern edge of ice field is indicated with the pink curve. Although the waters underneath of the ice field have high  $p\text{CO}_2$ ,  $\text{CO}_2$  transfer to the air is blocked by the ice and takes place through polynyas and leads as well as in the ice field margins as indicated by the yellow-orange band in the flux map at bottom right (Takahashi et al., 2009). Spring-summer photosynthesis reduced  $p\text{CO}_2$ , and the waters became a sink for atmospheric  $\text{CO}_2$ . (Takahashi et al., 2012-b)

**New trend of the CO<sub>2</sub> sink in the western tropical North Atlantic.**(Park, Wanninkhof, 2012)

Using the RCCL *Explorer of the Seas* data collected from 2002 to 2009, the study shows a large increase in the CO<sub>2</sub> sink over the period. The result can be largely explained by a lack of increase in the  $f\text{CO}_2(\text{sw})$  over the winter months, thus increasing the air-sea influx of CO<sub>2</sub> in winter. This lack of increase is due to El Nino events in 2002-2003 raising the  $f\text{CO}_2(\text{sw})$  (winter) values. Not enough data is available to explain why the  $f\text{CO}_2(\text{sw})$  values in the summer were also increasing less than the atmosphere. This trend is different than the ones found in other studies in other parts of the Atlantic but agrees with McKinley et al. (2011) in the subtropical gyre

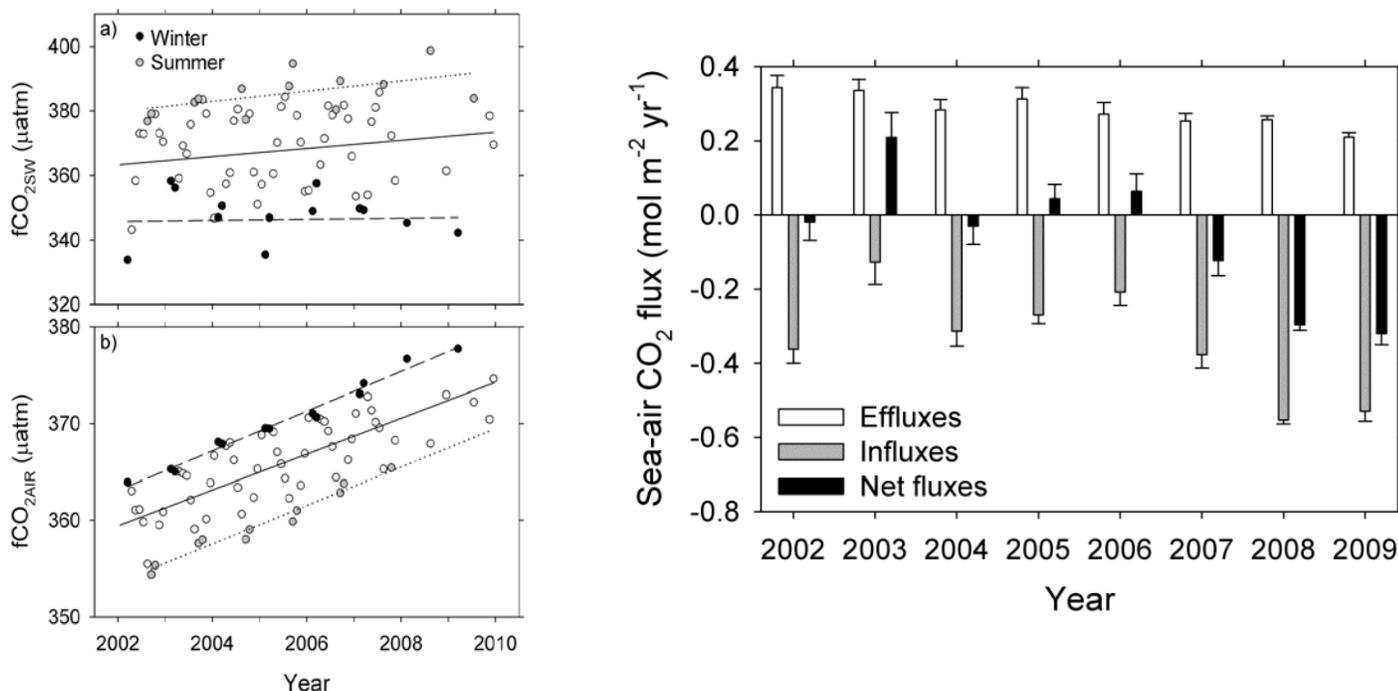


Figure 20.(left) Monthly mean values of (a)  $f\text{CO}_{2\text{SW}}$  and (b)  $f\text{CO}_{2\text{AIR}}$ . Black and gray circles denote the monthly values in winter (February and March) and summer (August and September for  $f\text{CO}_{2\text{SW}}$  and September and October for  $f\text{CO}_{2\text{AIR}}$ ), respectively, while the white circles are the remaining months. The trends in summer and winter for  $f\text{CO}_{2\text{SW}}$  are  $1.57 \pm 0.86$  and  $0.17 \pm 1.23 \mu\text{atm yr}^{-1}$ , and for  $f\text{CO}_{2\text{AIR}}$  are  $2.04 \pm 0.14$  and  $2.05 \pm 0.09 \mu\text{atm yr}^{-1}$ , respectively.

(right) Annual net sea-air CO<sub>2</sub> fluxes (black bars), effluxes (white bars), and influxes (gray bars) for the study period of 2002–2009. Error bars are derived from the standard deviation of monthly mean  $f\text{CO}_{2\text{SW}}$  and  $f\text{CO}_{2\text{AIR}}$  values.

## Assessment of Sea-Air CO<sub>2</sub> fluxes over the past two decades (1990-2009)

The Regional Carbon Cycle Assessment and Processes (RECCAP) is an international activity under the auspices of the Global Carbon Program (GCP) to produce a regional assessment of the sources and sinks of CO<sub>2</sub> (Canadell et al., 2012). The global ocean baseline was re-assessed using the Takahashi et al. (2009) climatology utilizing a consistent global wind field derived from the cross-calibrated multi-platform wind product (CCMP) (Atlas et al., 2011). The  $\Delta p\text{CO}_2$  fields of Takahashi et al. (2009) with the new wind fields and new gas exchange algorithms are used such that consistent regional and global estimates are made over 19-years using the approach of Park et al. (2010). These results are compared with the output of 6 ocean biogeochemistry models, as well as ocean inverse models and atmospheric inverse models as provided in the RECCAP effort for the last two decades in Figure 21. An important result of the work is that the trends in CO<sub>2</sub> uptake by the ocean based on approaches relying on sea-air CO<sub>2</sub> surface fluxes is appreciably smaller than the estimates based on changes in the ocean interior such as the ocean inverse and Green function (Khatiwala et al., 2012).

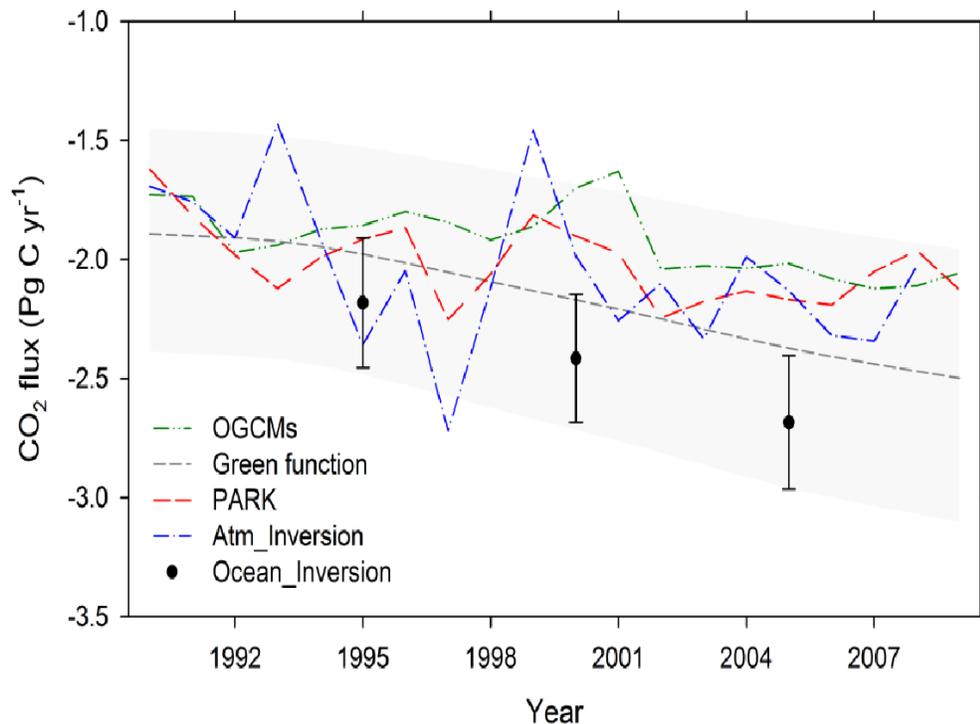


Figure 21. Anthropogenic sea-air CO<sub>2</sub> fluxes based on the empirical approach of Park et al. (2010), and different modeling approaches, from Wanninkhof et al. (2012).

### High-resolution large-scale estimates of the regional fluxes

We have continued to update seasonal and interannual  $f\text{CO}_2$ -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. The data for the updated equations were 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  $f\text{CO}_2$ -SST relationships. A linear fit through the equatorial Pacific data sets yields an inverse correlation between SST and  $f\text{CO}_2$ , with both interannual and seasonal differences in slope. In particular, the results indicate a strong impact of interannual El Niño – Southern Oscillation (ENSO), Pacific Decadal Oscillation (PDO) and weaker seasonal variability. New results indicate a strong interannual (ENSO) and weaker seasonal variability. There is approximately a 20-25% increase in the out-gassing flux of  $\text{CO}_2$  during the 1998.5 – 2010 period relative to the previous decade for the region from  $10^\circ\text{N}$  to  $10^\circ\text{S}$  from  $80^\circ\text{W}$  to  $160^\circ\text{E}$ . A large fraction of this increase is due to increase in wind speeds that began in the summer of 1998 and continued throughout the decade. These increases are coincident with model representations of the recent rebound of the shallow water meridional overturning circulation in the tropical and subtropical Pacific after the PDO shift.

In FY2013, the second version of the Surface Ocean  $\text{CO}_2$  Atlas (SOCAT) will be released to the public, allowing access to all underway  $\text{pCO}_2$  measurements collected globally from 1967 through 2010. PMEL contributed over 150 cruises in the equatorial Pacific from 1982 through 2010, and provided quality assurance for all cruises collected in the Tropical Pacific (Figure 22). Details of the SOCAT project and Atlas can be found in Pfeil et al. (in review) and Sabine et al. (in review).

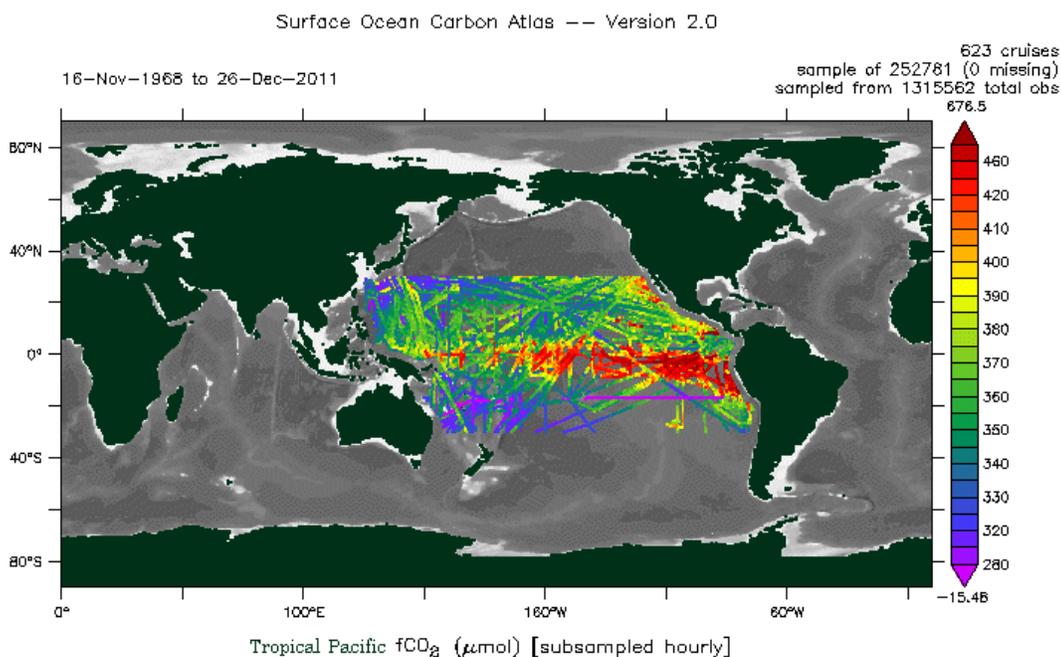


Figure 22. Tropical Pacific Cruises in the Surface Ocean Carbon Atlas (SOCAT) through 2011

## 7 Publications and Reports

### 7.1 Publications by Principal Investigators

Papers supported by the NOAA/COD pCO<sub>2</sub> on ships with funded participants italicized:

#### Published

- Bates, N.R.*, 2012: Multi-decadal uptake of carbon dioxide into subtropical mode waters of the North Atlantic Ocean. *Biogeosciences*, **9**, 2649-2659, doi: 10.105194/bg-9-2649-2012.
- Bates, N.R.*, Best, M.H., *Neely, K.*, *Garley, R.*, *Dickson, A.G.*, and *Johnson, R.J.*, 2012: Indicators of anthropogenic carbon dioxide uptake and ocean acidification in the North Atlantic Ocean. *Biogeosciences*, **9**, 2509-2522, doi: 10.105194/bg-9-2509-2012.
- Feely, R.A.*, *C. L. Sabine*, *R. H. Byrne*, *F. J. Millero*, *A. G. Dickson*, *R. Wanninkhof*, *A. Murata*, *L. Miller* and *Dana Greeley*, 2012: Decadal Changes in the Aragonite and Calcite Saturation State of the Pacific Ocean, *Global Biogeochemical Cycles*, **26**, GB3001, doi:10.1029/2011GB004157.
- Friedrich, T.*, *Timmermann, A.*, *Jungclaus, J.H.*, *Heinemann, M.*, *Chikamoto, M.*, *Abe-Ouch, A.*, *Gonzalez-Davila, M.*, *Santana-Casiano, J.M.*, *Church, M.J.*, *Bates, N.R.*, *Gledhill, D.K.*, *McLead, E.*, and *Mouchet, A.*, 2012: Detecting regional trends in ocean acidification against the background of natural variability. *Nature Climate Change*, **2(3)**, 167-171, doi: 10.1038/NCLIMATE1372.
- Hales, B.*, *Strutton, P.*, *Saraceno, M.*, *Letelier, R.*, *Takahashi, T.*, *Feely, R.*, *Sabine, C.* and *Chavez, F.*, 2012: Satellite-based prediction of pCO<sub>2</sub> in coastal waters of the eastern North Pacific. *Progress in Oceanogr.*, **103**, 1-15. <http://dx.doi.org/10.1016/j.pcean.2012.03.001>
- Lenton, A.*, *N. Metzl*, *T. Takahashi*, *M. Kuchinke*, *R. J. Matear*, *T. Roy*, *S. C. Sutherland*, *C. Sweeney*, and *B. Tilbrook*, 2012: The observed evolution of oceanic pCO<sub>2</sub> and its drivers over the last two decades, *Global Biogeochem. Cycles*, **26**, GB2021, doi:10.1029/2011GB004095.
- Park, G.-H.* and *R. Wanninkhof*, 2012: A large increase of the CO<sub>2</sub> sink in the western tropical North Atlantic from 2002 to 2009, *J. Geophys. Res.*, **117**, C08029, doi:10.1029/2011JC007803.
- Takahashi, T.*, *C. Sweeney* and *S. C. Sutherland.*, 2011: Underway pCO<sub>2</sub> Measurements in Surface Waters and the Atmosphere During the R/V Nathaniel B. Palmer Expeditions. *Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee.*  
[http://cdiac.ornl.gov/ftp/oceans/VOS\\_Palmer\\_Lines/](http://cdiac.ornl.gov/ftp/oceans/VOS_Palmer_Lines/).  
doi:10.3334/CDIAC/otg.VOS\_NB\_Palmer\_Lines
- Takahashi, T.*, *C. Sweeney*, *B. Hales*, *D. W. Chipman*, *T. Newberger*, *J. G. Goddard*, *R. Iannuzzi* and *S. C. Sutherland*, 2012: Changing Carbon Cycle in the Southern Ocean. *Oceanography*, **25(3)**:26–37, <http://dx.doi.org/10.5670/oceanog.2012.71>.
- Takahashi, T.* and *Chipman, D. W.*, 2012: CO<sub>2</sub> transport in deep waters off Wilkes Land. *Oceanography*, **25(3)**:24–25, <http://dx.doi.org/10.5670/oceanog.2012.70>.
- Takahashi, T.*, *Sutherland, S.C.* and *Kozyr, A.*, 2012: Global Ocean Surface Water Partial Pressure of CO<sub>2</sub> Database: Measurements Performed During 1957–2011 (Version 2011).

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### **In review**

Pfeil, B., Olsen, A., Bakker, D.C.E. et al.: A uniform, quality controlled, Surface Ocean CO<sub>2</sub> Atlas (SOCAT). *Earth System Science Data* (In review).

Sabine et al.: Gridding of the Surface Ocean CO<sub>2</sub> Atlas (SOCAT). *Earth System Science Data* (In Review).

### **Abstracts and Proceedings**

Feely, R.A., Sabine, C.L., Byrne, R.H., Millero, F.J., Dickson, A.G., Wanninkhof, R., Murata, A., Miller, L., and Greeley, D., 2011: Decadal Changes in the Aragonite and Calcite Saturation State of the Pacific Ocean, World Climate Research Program (WCRP) Open Science Conference 24-28 October 2011, Denver, Colorado, Abstract.

Sabine, C.L., Feely, R.A., Wanninkhof, R., Hankin, S., Takahashi, T., Millero, F.J., Dickson, A.G., Key, R.M. and Kozyr, A., 2011: Observations for Climate: The NOAA integrated ocean carbon observation network, *World Climate Research Program (WCRP) Open Science Conference* 24-28 October 2011, Denver, Colorado, Abstract.

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