

# Global Carbon Data Management and Synthesis Project

Christopher L. Sabine<sup>1</sup>, Richard A. Feely<sup>1</sup>, Steve Hankin<sup>1</sup>, Rik Wanninkhof<sup>2</sup>, Robert Key<sup>3</sup>, Alex Kozyr<sup>4</sup>, Frank Millero<sup>5</sup> and Andrew Dickson<sup>6</sup>

<sup>1</sup>NOAA Pacific Marine Environmental Laboratory, Seattle WA

<sup>2</sup>NOAA Atlantic Oceanographic and Meteorological Laboratory, Miami FL

<sup>3</sup>Princeton University, AOS Program, Princeton, NJ

<sup>4</sup>Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge TN

<sup>5</sup>University of Miami, RSMAS, Miami FL

<sup>6</sup>University of California San Diego, Scripps Institution of Oceanography, La Jolla CA

## Table of Contents

1. Project Summary.....	1
2. Scientific Accomplishments .....	2
2.1. Surface Ocean CO <sub>2</sub> .....	3
2.2. Ocean Interior Carbon.....	6
2.3. Ocean Acidification.....	10
2.4. References .....	11
3. Education and Outreach.....	12
4. Publications and Reports.....	12
4.1. Publications with Principal Investigators as First Author.....	12
4.2. Publications with PI as co-author .....	13

## 1. Project Summary

Over the past two and a half centuries, the surface oceans have absorbed approximately 30% of the total anthropogenic carbon dioxide emissions from the atmosphere, equaling >550 billion tons of carbon dioxide (Canadell et al., 2007). This absorption of CO<sub>2</sub> from the atmosphere has reduced the accumulation of greenhouse gases in the atmosphere, thus slowing the rate of climate change (IPCC, 2007; Sabine and Feely, 2007). The details of this uptake and storage as well as the mechanisms controlling them are still not fully understood. Continued monitoring and scientific analysis of the ocean carbon cycle is critical for understanding how this important sink for anthropogenic CO<sub>2</sub> is functioning and how ocean carbon storage might change in the future.

Recognizing the need to constrain the oceanic uptake, transport, and storage of anthropogenic CO<sub>2</sub> for the anthropocene and to provide a baseline for future estimates of oceanic CO<sub>2</sub> uptake, two international ocean research programs, the World Ocean Circulation Experiment (WOCE) and the Joint Global Ocean Flux Study (JGOFS), jointly conducted a comprehensive survey of inorganic carbon distributions in the global ocean in the 1990s (Wallace, 2001). After completion of the US field program in 1998, a five year effort called the Global Ocean Data Analysis Project (GLODAP) was begun to compile and rigorously quality control the US and international data sets including a few pre-WOCE data sets in regions that were data limited (Key et al., 2004). These data have greatly improved our understanding of the spatial distributions of natural and anthropogenic carbon in the ocean and are being used to examine the mechanistic controls on ocean carbon distributions.

The single snapshot of the ocean provided by the GLODAP data product is not ideal for understanding the temporal patterns of variability in ocean uptake and storage. The most important component of an assessment of ocean biogeochemical change, whether of natural or anthropogenic origin, is high-quality observations. The WOCE/JGOFS data set provides an important point of reference for ocean carbon studies, but many other useful data sets exist or are being collected which have not been analyzed in such a context because there has not been a coordinated effort to bring these data together and no data management system to make navigation and exploitation of these data convenient. For example, the NOAA Climate Observations Division's (COD) Carbon Network (hydrographic sections, underway pCO<sub>2</sub>, and CO<sub>2</sub> moorings) is a valuable contribution to the Global Ocean Observing System (GOOS) and Global Climate Observing System (GCOS). It is not sufficient, however, simply to collect and archive the data if we expect the data to improve our understanding of the global carbon cycle and the role of the ocean in climate change. Although carbon scientists and oceanographers are the primary direct users of ocean carbon data, these scientists are working to produce meaningful products from these observations that a wide range of decision makers and the public can use to make informed decisions about current and future CO<sub>2</sub> emissions.

The goal of the Global Carbon Data Management and Synthesis Project is to work together with the COD carbon measurement projects as well as other national and international colleagues with high-quality ocean carbon data to take the fundamental carbon observations and turn them into products that are useful for scientists and the public for understanding the ocean carbon cycle and how it is changing over time. This effort ranges from ensuring that the observations are of the highest quality and are mutually consistent with each other to combining the observations into a common data set that is available and easy for the community to use and explore to evaluating the time rate of change in global ocean carbon uptake and storage. This project brings together ocean carbon measurement experts, information technology experts and data managers to ensure the most efficient and productive processing possible for the COD carbon observations.

## **2. Scientific Accomplishments**

The COD ocean carbon network makes two basic types of observations: surface CO<sub>2</sub> observations (with ships of opportunity and moorings) and water column carbon observations (with repeat hydrography cruises). The surface observations are aimed at understanding the exchange of CO<sub>2</sub> across the air-sea interface (i.e. ocean carbon uptake and release). The interior ocean observations help quantify the ocean carbon inventory and how it is changing with time (i.e. ocean carbon storage). Uptake is not necessarily the same as storage, because ocean transport can move carbon that is removed from the atmosphere in one place and store that carbon in another place. Although the spatial and temporal patterns of carbon uptake may be different from the storage patterns, these two measures of the ocean carbon cycle are closely related to each other. Integrated over large enough time and space domains, the net uptake should be reconcilable with the storage.

The Global Carbon Data Management and Synthesis Project addresses both observational approaches for understanding the role of the oceans in the global carbon cycle. Because surface observations are collected in a different manner and have different requirements for developing the final product than the repeat hydrography data, the data management and synthesis for these

two data types is discussed separately. The activities and accomplishments for both data types in FY2011 are discussed below.

While the COD ocean carbon network is primarily aimed at understanding the uptake and storage of ocean carbon, it also provides information on the consequences of that carbon on the chemistry of the oceans. When anthropogenic CO<sub>2</sub> is absorbed by seawater chemical reactions occur that reduce both seawater pH and the concentration of carbonate ions in a process known as “ocean acidification”. The pH of ocean surface waters has already decreased by about 0.1 units since the beginning of the industrial revolution (Caldeira and Wickett, 2003; Caldeira and Wickett, 2005), with a decrease of ~0.0018 yr<sup>-1</sup> observed over the last quarter century at several open ocean time-series sites (Bates, 2007; Bates and Peters, 2007; Santana-Casiano et al., 2007).

The COD ocean carbon observations and subsequent synthesis efforts through this project have played a significant role in highlighting to the scientific community and the general public the importance of ocean acidification and its consequences on marine life. The advancements in our understanding in ocean acidification made through this project are discussed in a section 2.3 below.

### **2.1. Surface Ocean CO<sub>2</sub>**

The surface ocean component of the Global Carbon Data Management and Synthesis Project involves continued processing of the carbon data generated from the COD volunteer observing ships and moorings, working with Taro Takahashi (LDEO) to generate updates to his air-sea CO<sub>2</sub> flux climatology, developing the algorithms to make seasonal CO<sub>2</sub> flux maps using satellite observations, and working with the international ocean carbon community on the Surface Ocean CO<sub>2</sub> Atlas (SOCAT) project. An important component of the effort is national and international outreach and coordination to improve data quality, and assemble data into coherent unified datasets. As described below the participants of the ocean carbon synthesis projects have been active participants and leaders of efforts such as SOCAT and RECCAP that provide critical data products for interpretation and testing/verification of models of ocean carbon dynamics and change. Each of these is very briefly discussed below.

#### ***Processing of New Data***

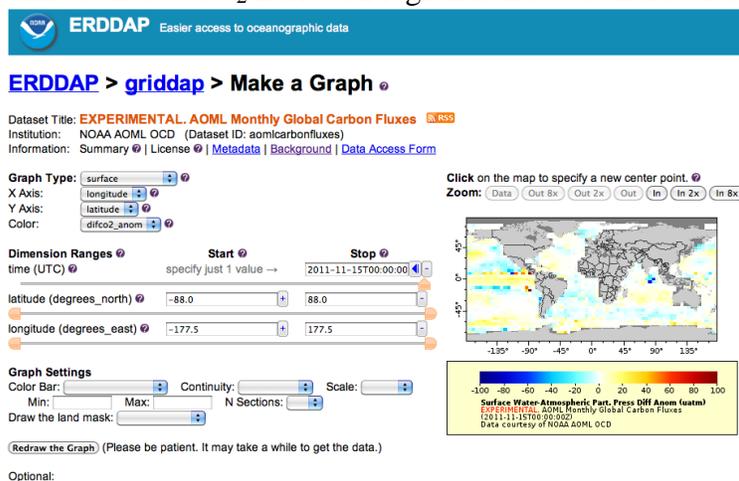
During FY2011, PMEL received daily underway CO<sub>2</sub> data files from 25 cruises in the Pacific Ocean on the following ships: Ka'imimoana (5), Bell Shimada (4), Oscar Dyson (2), RV Wecoma (1), Natalie Schulte(5), Hi'ialakai (8). Improvements were made to diagnostic software to autonomously quality control pCO<sub>2</sub>, temperature, salinity, barometric pressure, pumps, water flow and gas flow data. During the time in review, data from 22 cruises collected during FY2010 have been processed and submitted to CDIAC, and data from all cruises in FY2011 are in final processing. All current and previous underway pCO<sub>2</sub> data files are quality controlled using the data protocols outlined in Pierrot et al. (2008).

Data from 11 mooring sites were also processed at PMEL and submitted to CDIAC following the Pierrot et al. protocols. The processing included not only the latest data, but also a reprocessing of older data to ensure that all our mooring data are available in the agreed format. In total, we processed and submitted 34 buoy years of data in FY2011.

As detailed in the “pCO<sub>2</sub> from ships” report over 500,000 new underway pCO<sub>2</sub> data points have been processed by AOML following uniform data reduction and quality control. Data and plots are posted on the publically accessible website <http://www.aoml.noaa.gov/ocd/gcc/index.php>. Data and metadata are contributed to the global database at CDIAC, as well as direct submissions to the LDEO and SOCAT databases.

### Seasonal air-sea CO<sub>2</sub> Flux Maps

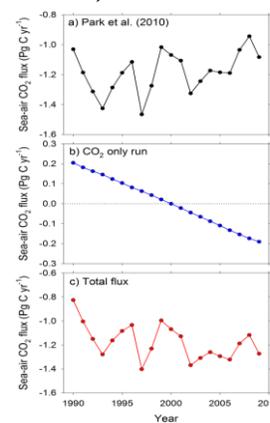
The work by Park et al. (2010a) has provided an improved approach for estimating air-sea CO<sub>2</sub> fluxes on seasonal timescales from historical pCO<sub>2</sub> data, sea surface temperature and wind speed. The algorithms provide a means to estimate air-sea CO<sub>2</sub> fluxes on regional and seasonal scales to the near-present. The global sea-air CO<sub>2</sub> flux maps are updated quarterly and served from a graphical user interface (**Figure 1**). The metadata for the approach is described in a NOAA data report (Park et al. 2010b). In addition to monthly global fluxes, monthly ΔpCO<sub>2</sub> and flux anomalies compared to the 30-year mean are provided.



**Figure 1.** Screen shot of the graphical user interface used to serve the monthly global estimates and pCO<sub>2</sub> and sea-air fluxes. The ΔpCO<sub>2</sub> anomaly map for Nov. 2011 is presented (from: <http://cwgcom.aoml.noaa.gov/erddap/griddap/aomlcarbonfluxes.graph>).

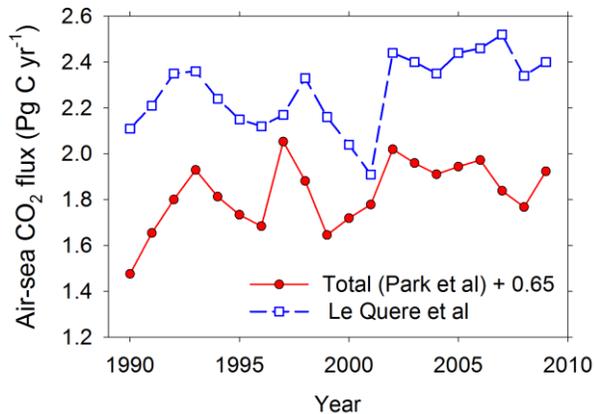
### Air-Sea Fluxes in the Regional Carbon Cycle Assessment and Processes (RECCAP)

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>. 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) (Ardizzone et al., 2009). We have recalculated the fluxes of Takahashi et al. (2009) with the new wind fields such that consistent regional and global estimates can be made over 19-years using the approach of Park et al. (2010a). In addition, we are including a model derived estimate of the changes in ocean uptake due to increasing atmospheric CO<sub>2</sub> levels. The impact of this is illustrated in **Figure 2**. An important aspect of the work is that the approach shows an increasing absolute uptake rate of CO<sub>2</sub> from the atmosphere but decreasing fractional uptake. This is in accord with numerical models, and has been referred to in the Southern Ocean as “saturation of the CO<sub>2</sub> sink” (LeQuere et al. 2009).



**Figure 2.** Net sea-air CO<sub>2</sub> fluxes based on the empirical approach of Park et al. (2010a) (top panel); the trend in sea-air CO<sub>2</sub> fluxes due to increasing atmospheric CO<sub>2</sub> levels normalized to year 2000, from a model simulation (middle panel); total net flux over the past two decades (bottom panel) from Wanninkhof et al. (2012, in preparation).

During FY2011 a comprehensive comparison of model-based and data-based estimates of sea-air CO<sub>2</sub> fluxes and trends over the past two decades was performed as part of RECCAP. There is good agreement of increasing uptake trends of about 0.15 Pg C decade<sup>-1</sup> with significant interannual variability driven by large-scale climate re-organizations such as ENSO. However, there are appreciable offsets in the absolute magnitudes. The empirical approach, numerical ocean biogeochemistry models such as those from NCAR, and atmospheric inverse models all show anthropogenic CO<sub>2</sub> uptake of 1.4-2 Pg C year<sup>-1</sup>. In contrast, global constraints and models adjusted to global constraints, such as the UEA model runs, show uptakes ranging from 2 to 2.5 Pg C year<sup>-1</sup> (**Figure 3**). A comprehensive analysis of model and data-based approaches of sea-air CO<sub>2</sub> fluxes over the last 2 decades is performed in Wanninkhof et al. (2012, in preparation).



**Figure 3.** Comparison of anthropogenic air-sea CO<sub>2</sub> fluxes based on a composite of ocean models (blue line with squares) and an empirical data based approach (red line and circles). Note, that the scale is reversed compared to Figure 2, and 0.65 Pg C year<sup>-1</sup> is added to the net air-sea CO<sub>2</sub> fluxes derived in the Park approach to reflect the anthropogenic CO<sub>2</sub> uptake.

### *Surface Ocean CO<sub>2</sub> Atlas (SOCAT)*

The past year, FY2011, was a banner year for Carbon Synthesis Project, capped by the public announcement and publication of the Surface Ocean CO<sub>2</sub> Atlas (SOCAT) dataset. SOCAT is an international effort to establish a global surface CO<sub>2</sub> data set that integrates together, in a common format, all publicly available surface CO<sub>2</sub> data for the surface oceans. The SOCAT data set was publically announced at the IOCCP Surface Ocean CO<sub>2</sub> Data-to-Flux Workshop in Paris in September. Two distinct SOCAT data products were produced: 1) an integrated, 2<sup>nd</sup>-level quality controlled, global surface ocean *f*CO<sub>2</sub> (fugacity of CO<sub>2</sub>) data set, following community-agreed procedures and regional review; and 2) several gridded summary fields derived from the cruise data on a 1° x 1° grid with no temporal or spatial interpolation, plus a similar analysis on a ¼° x ¼° grid to support coastal analyses.

Approximately half of the data provided in the first release of SOCAT were acquired and quality controlled by participants in the COD funded “pCO<sub>2</sub> on ships”, and “synthesis data management projects”. AOML and PMEL were actively involved with the quality control of the Tropical Atlantic data and the tropical Pacific data, respectively. A MATLAB program developed by A. Olsen of U. Bergen and D. Pierrot of AOML/CIMAS was used to compare cruises in the general vicinity of each other. The program includes the capability to adjust the pCO<sub>2sw</sub> data for expected temporal increases. We are also involved in preparation of the next release with Dr. Denis Pierrot joining the SOCAT steering group with Feely and Sabine.

In FY2009 PMEL launched a web portal to be a shared workplace supporting the SOCAT QC process. It provided a toolkit for assessing level 1 QC issues in the data, “suspending” a dataset (i.e. temporarily withdrawing it, pending corrections), collecting additional metadata and

documentation, tracking QC changes to a cruise's data, and applying 2<sup>nd</sup> level quality control ratings. This portal provided the centralized repository (a relational database) of SOCAT cruise observations together with visualization / analysis tools, and a system to collaboratively enter quality control evaluations and resolve conflicting assessments. During FY2010 this server was the focus of SOCAT activity, with 6374 scientist-provided QC assessments performed.

Once 2<sup>nd</sup> order quality control had been completed a public Web site had to be designed and deployed in preparation for September the public announcement of the collection. This effort began in June 2011. Heather Koyuk at PMEL was the primary author of the Web site that is the face of SOCAT at

<http://www.socat.info/>. Behind this Web site are data services at several locations. PMEL hosts the interactive data servers that provide the public with the ability to explore the collection as shown in **Figure 4**. CDIAC (at US DOE) and PANGAEA (in Germany) provide the secure, permanent archive of the data products, original cruise data and metadata for users who wish to download it. The SOCAT.info Web site also provides tutorial videos, FAQs and SOCAT project background information. Much of this content was developed at PMEL.



**Figure 4.** SOCAT.info main page

## 2.2. *Ocean Interior Carbon*

The ocean interior component of the Global Carbon Data Management and Synthesis Project involves continued processing and assessment of the CLIVAR/CO<sub>2</sub> Repeat Hydrography data, an international synthesis of high-quality carbon data for the period from GEOSECS to CLIVAR, and a global assessment of decadal changes in ocean carbon inventories. As with the surface data, an important component of the effort is national and international outreach and coordination to improve data quality, and assemble data into coherent unified datasets. As described below the participants of the ocean carbon synthesis efforts have been active participants and leaders of efforts such as CARINA, PACIFICA and RECCAP that provide critical data products for interpretation and testing/verification of models of ocean carbon dynamics and change. Each of these is very briefly discussed below.

### ***Processing Repeat Hydrography Data***

In FY2011, the NOAA DIC data from the S4P cruise, from Lyttelton-Punta Arenas along 67°S, were finalized and submitted to CDIAC. Data from the A10 cruise across the South Atlantic are currently being finalized and will be submitted to CDIAC shortly. PIs Millero and Dickson are finalizing the total alkalinity data collected on the CLIVAR S4P and A10 cruises. These data will be submitted to CDIAC and final cruise reports written and made publically available. Over the

past year CDIAC made DIC data from the following datasets available to the general public: I05\_2009, P06\_2009, P21\_2009, P15S\_2009, A13.5 (except for pH).

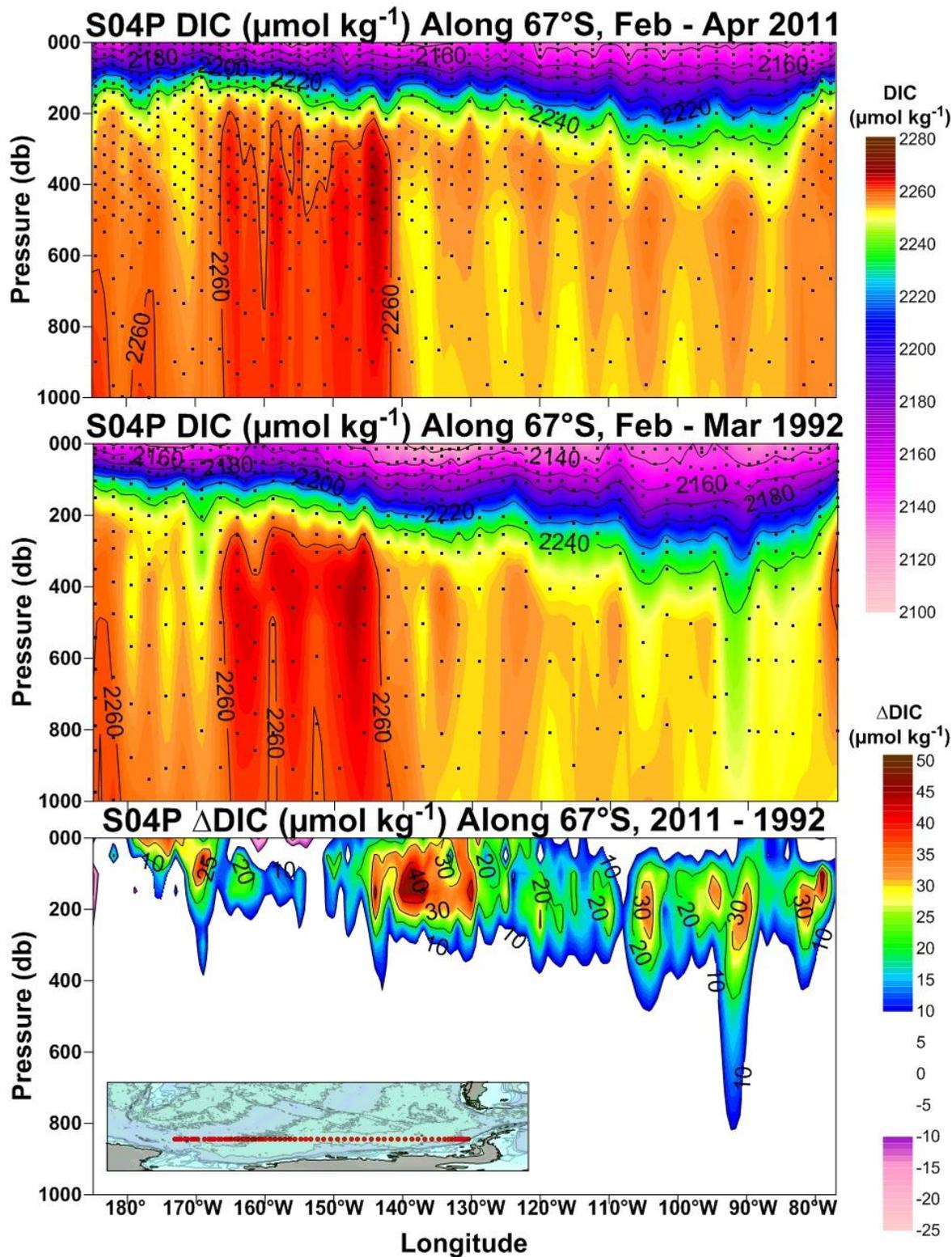
We have constructed an Atlantic, Pacific and Indian Ocean “CLIVAR” data product similar to GLODAP and CARINA. This data product is composed of very high quality cruise data collected since 1998. We have not distributed this data product because it includes several “preliminary” carbon data sets, a few proprietary data sets, and because several of these cruises have been included in other collections. We are using this product for in-house carbon change calculations (see below).

### ***Ocean Interior Data Synthesis***

With the completion of CARINA in 2010, the synthesis effort was shifted to the Pacific with a project led by PICES called PACIFICA. This is a data synthesis effort that is scientifically similar to CARINA in all aspects except that the data are primarily from the North Pacific. Over the past year the PACIFICA group, which includes several of the Global Carbon Data Management and Synthesis Project PIs collected and began assessing the quality of approximately 250 new cruises not previously available to the public. Princeton’s involvement in PACIFICA has been much less than it was for the prior data collection efforts primarily due to funding. Japanese scientists have assembled all of the data for the collection. They have also had the primary responsibility for 1<sup>st</sup> QC of the data. R. Key’s involvement has been limited to attending the data QC meetings and offering guidance. X. Lin (P.U.) has imported all of the PACIFICA data into the Princeton data system and has been checking 1<sup>st</sup> QC in collaboration with the PACIFICA group. Feely and Sabine are regional leaders in the QC process.

### ***Global Assessment of Decadal Changes in Ocean Carbon Storage***

An important component of the Global Carbon Data Management and Synthesis Project is the analysis of decadal changes in ocean carbon storage. These analyses are initially conducted along specific lines occupied as part of the CLIVAR/CO<sub>2</sub> Repeat Hydrography program. During the WOCE program, east-west cruise line S4P in the South Pacific along ca. 67°S was occupied in Feb-March 1992 and repeated this year in Feb. – April 2011 as part of the CLIVAR/CO<sub>2</sub> Repeat Hydrography program to investigate the temporal changes in total dissolved inorganic carbon (DIC) from 1992 to 2011 along this cruise line, The results are shown in **Figure 5**. The estimated DIC increases over the 19-year interval vary from about 0  $\mu\text{mol kg}^{-1}$  below 800 m to values greater than 40  $\mu\text{mol kg}^{-1}$  near 138°W with the main concentrations increases between the surface and 300m. Similar analyses using the extended multiple linear regression (eMLR) approach along the P06 line along 32°S by C. Sabine indicate that ocean carbon storage in this region has increased 30-50% over the last decade relative to the previous decade.

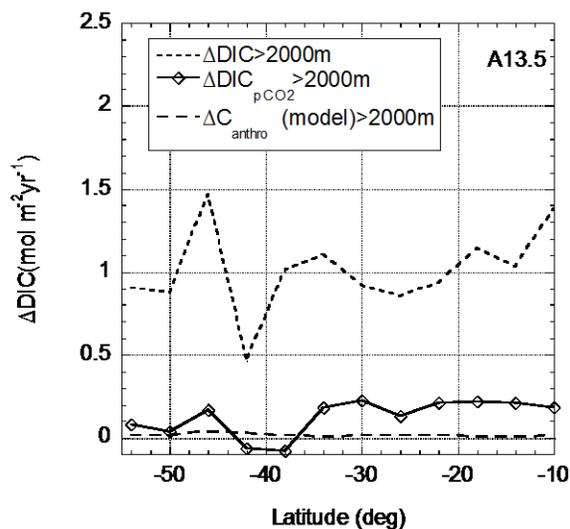


**Figure 5.** Sections of total dissolved carbon in Feb-April 2011 (top); Feb-Mar. 2022 (middle); and the 2011-1992 difference (bottom) in units of  $\mu\text{mol kg}^{-1}$ .

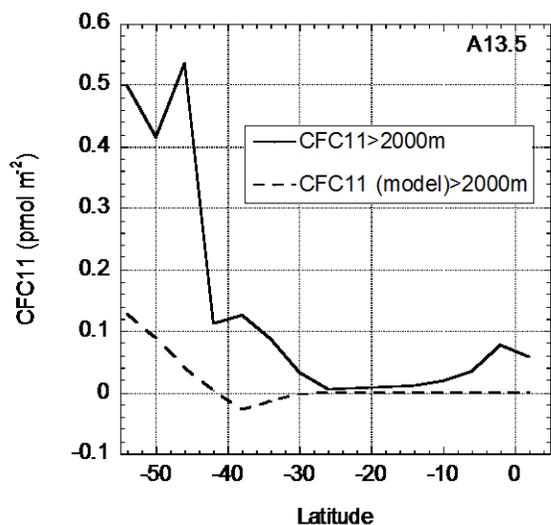
### ***Ocean Interior Carbon in the Regional Carbon Cycle Assessment and Processes (RECCAP)***

RECCAP is an international activity coordinated through the Global Carbon Project (GCP) with the goal of producing global and regional assessments of the sources and sinks of CO<sub>2</sub>. An important component of this effort is the evaluation of the global carbon inventories and how they are changing with time. Several of the COD carbon project PIs (Sabine, Feely, Wanninkhof, Key, Kozyr) are a part of this effort and are taking the lead on different aspects of the project. For example, as part of this project Sabine will be summarizing the various techniques for assessing natural and anthropogenic carbon inventories and their results. Initial work along these lines was recently published by Sabine and Tanhua (2010).

Detection and attribution of hydrographic and biogeochemical changes in the deep ocean ( $\approx > 2000$  m) is challenging due to limited accurate data. There are indications that anthropogenic and climate change signals are starting to manifest themselves at depth. During the performance period we determined the changes in deep water inorganic carbon content along meridional transects in the Atlantic and Pacific Ocean on decadal time scales using observations from the World Hydrographic Program in the 1980s and 1990's, and the CLIVAR/CO<sub>2</sub> repeat hydrography effort in the past decade. Decadal changes of DIC in deep water cannot currently be measured with confidence in the ocean interior removed from the outcrop regions. Changes based on discrete pCO<sub>2</sub> (20) measurement show appreciable rates of inventory change that are in general agreement with the age of water masses. The cruises in the Atlantic central basin show deep water changes at a rate of changes of 0.5 mol m<sup>-2</sup> yr<sup>-1</sup>, the South eastern South Atlantic basin shows changes of 0.12 mol m<sup>-2</sup> yr<sup>-1</sup> (**Figure 6**) and the Southeastern Pacific at 0.07 mol m<sup>-2</sup> yr<sup>-1</sup>. The changes are appreciably higher than the output of the NCAR CCSM-1 model but this model also shows less CFC11 at depth than measured CFC11 (**Figure 7**). The CFC11 ages based on the measured CFC11 concentrations indicate that the dissolved inorganic carbon (DIC) changes based on pCO<sub>2</sub>(20) measurements are plausible and from anthropogenic origin. The results indicate that appreciably more anthropogenic CO<sub>2</sub> is entering the ocean interior than several current observation based techniques indicate. However, the paucity in pCO<sub>2</sub>(20) data and largely uniform specific inventory changes  $\Delta$ DIC<sub>pCO<sub>2</sub></sub> with latitude (**Figure 6**) make the quantification of this signal tentative.



**Figure 6.** Specific inventory changes of  $\Delta$ DIC,  $\Delta$ DIC<sub>pCO<sub>2</sub></sub>, and  $\Delta$ C<sub>anthro</sub> (model) below 2000 m versus latitude for the A13.5 line from 54° S to 10° S between 1983 and 2010. The measured change in DIC is unrealistically large and attributed to offsets in the older data. The calculated DIC change based on pCO<sub>2</sub>(20),  $\Delta$ DIC<sub>pCO<sub>2</sub></sub>, is plausible.



**Figure 7.** Specific inventory for measured CFC11 and modeled CFC11 greater than 2000m for 2010 for the A13.5 line. The model data is systematically lower suggesting issues in (some) models with deep ventilation processes.

In related work R. Key has been working with M. Manizza to better understand the carbon system in the Arctic Ocean. This research is grounded with data assembled as part of the CARINA project and more recent cruises, and results from a numerical ocean model. The model suggests a regional uptake of  $59\text{TgC yr}^{-1}$  in agreement with the estimate from very limited data ( $29\text{-}199\text{TgC yr}^{-1}$ ). Because of limited circulation, broad shelf areas and numerous rivers, the carbon chemistry of this region is particularly interesting (Manizza et al. 2011). Later this year we plan to submit a proposal to NSF to develop an "ocean carbon state estimation" for the Arctic Ocean using a new regional adjoint model.

### 2.3. Ocean Acidification

The uptake of anthropogenic  $\text{CO}_2$  by the global ocean induces fundamental changes in seawater chemistry that could have dramatic impacts on biological ecosystems in the upper ocean. Based on measurements from the WOCE/JGOFS global  $\text{CO}_2$  survey, the CLIVAR/ $\text{CO}_2$  Repeat Hydrography Program in the Pacific Ocean, we have observed an average  $0.34\% \text{ yr}^{-1}$  decrease in the saturation state of surface seawater with respect to aragonite and calcite. The upward migrations of the aragonite and calcite saturation horizons, averaging about  $1$  to  $2 \text{ m yr}^{-1}$ , are the direct result of the uptake of anthropogenic  $\text{CO}_2$  by the oceans and regional changes in circulation and biogeochemical processes. The shoaling of the saturation horizon is regionally variable, with more rapid shoaling in the South Pacific where there is a larger uptake of anthropogenic  $\text{CO}_2$ . In some locations, particularly in the North Pacific Subtropical Gyre and in the California Current, the decadal changes in circulation can be the dominant factor in controlling the migration of the saturation horizon. If  $\text{CO}_2$  emissions continue as projected over the rest of this century, the resulting changes in the marine carbonate system would mean that many coral reef systems in the Pacific would no longer be able to sustain a sufficiently high rate of calcification to maintain the viability of these ecosystems as a whole and perhaps could seriously impact the thousands of species that depend on them for survival.

In the surface mixed layer (depths to  $\sim 100 \text{ m}$ ), the extent of pH change is consistent with that expected under conditions of seawater/ atmosphere equilibration, with an average rate of change

of  $-0.0017 \text{ yr}^{-1}$ . Future mixed layer changes can be expected to closely mirror changes in atmospheric  $\text{CO}_2$ , with surface seawater pH continuing to fall as atmospheric  $\text{CO}_2$  rises.

#### 2.4. References

- Ardizzone, J., Atlas, R., and Hoffman, R. N., 2009, New multiplatform ocean surface wind product available. *EOS Trans.*, 90(27): p. 231.
- Bates, N.R., 2007. Interannual variability of the oceanic  $\text{CO}_2$  sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades. *J. Geophys. Res.-Oceans*, 112(C9).
- Bates, N.R. and Peters, A.J., 2007. The contribution of atmospheric acid deposition to ocean acidification in the subtropical North Atlantic Ocean. *Mar. Chem.*, 107(4): 547-558.
- Caldeira, K. and Wickett, M.E., 2003. Anthropogenic carbon and ocean pH. *Nature*, 425(6956): 365-365.
- Caldeira, K. and Wickett, M.E., 2005. Ocean model predictions of chemistry changes from carbon dioxide emissions to the atmosphere and ocean. *J. Geophys. Res.-Oceans*, 110(C9).
- Canadell, J. G., C. Le Quere, et al., 2007. "Contributions to accelerating atmospheric  $\text{CO}_2$  growth from economic activity, carbon intensity, and efficiency of natural sinks." Proceedings Of The National Academy Of Sciences Of The United States Of America 104(47): 18866-18870.
- IPCC, 2007. Climate Change 2007: The Physical Science Basis: Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, United Kingdom, Cambridge University Press.
- Key, R.M. et al., 2004. A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP). *Global Biogeochemical Cycles*, 18(4).
- Le Quéré, C., et al., 2009. Trends in the sources and sinks carbon dioxide. *Nat. Geosci* 2, 831-836, doi:810.1038/ngeo1689.
- Manizza, M., M.J. Follows, S. Dutkiewicz, D. Menemenlis, J.W. McClelland, C.N. Hill, B.J. Peterson, R.M. Key, 2011. Modeling the Arctic Ocean carbon cycle, *J. Geophys. Res.*, 116,C12020, doi:10.1029/2011JC006998.
- Park, G.-H., Wanninkhof, R., Doney, S. C., Takahashi, T., Lee, K., Feely, R. A., Sabine, C., Triñanes, J., and Lima, I., 2010a. Variability of global net sea-air  $\text{CO}_2$  fluxes over the last three decades using empirical relationships. *Tellus*, 62B: 352-368.
- Park, G.-H., Wanninkhof, R., Trinanes, J., 2010b. Procedures to Create Near Real-Time Seasonal Air-Sea  $\text{CO}_2$  Flux Maps, Atlantic Oceanographic and Meteorological Laboratory NOAA Technical Memorandum-98, OAR AOML , Miami, p. 21.
- Prentice, I.C. et al., 2001. The carbon cycle and atmospheric  $\text{CO}_2$ . In: J.T. Houghton and D. Yihui (Editors), *Climate Change: The Scientific Basis, Contribution of working group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, Cambridge, UK, pp. 183-287.
- Sabine, C. L. and R. A. Feely (2007). The oceanic sink for carbon dioxide. *Greenhouse Gas Sinks*. D. Reay, N. Hewitt, J. Grace and K. Smith. Oxfordshire, UK, CABI Publishing: 31-49.
- Sabine, C.L., and T. Tanhua, 2010. Estimation of anthropogenic  $\text{CO}_2$  inventories in the ocean. *Annu. Rev. Mar. Sci.*, 2: 175–198.
- Santana-Casiano, J.M., Gonzalez-Davila, M., Rueda, M.J., Llinas, O. and Gonzalez-Davila, E.F., 2007. The interannual variability of oceanic  $\text{CO}_2$  parameters in the northeast Atlantic subtropical gyre at the ESTOC site. *Glob. Biogeochem. Cyc.*, 21(1).

- Takahashi, T., et al. 2009. Climatological mean and decadal change in surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans. *Deep-Sea Res. II*, 56(8–10), 554–577.
- Wallace, D.W.R., 2001. Storage and transport of excess CO<sub>2</sub> in the oceans: The JGOFS/WOCE Global CO<sub>2</sub> Survey. In: G. Siedler, J. Church and J. Gould (Editors), *Ocean Circulation and Climate: Observing and Modeling the Global Ocean*. Academic Press, San Diego, CA, pp. 489-521.
- Wanninkhof, R., et. al. 2012 Global ocean carbon uptake: Magnitude, variability, and trends. *Biogeosciences*, in preparation.

### 3. Education and Outreach

Synthesis Project investigators have been very active in educating the public about ocean carbon changes. Several of the PIs regularly teach graduate and undergraduate classes in ocean carbon chemistry. These classes incorporate the scientific results coming from this work. Several of the PIs have graduate students or post-docs that are exposed to the work accomplished through this project. Several of the Synthesis Project PIs also serve on a number of national and international science committees that help guide and coordinate ocean carbon research. Interactions with the general public include presentations to local schools, open public lectures (both in the US and abroad), public “webinars” (seminars broadcast as streaming video onto the web e.g. for World Oceans Day), laboratory tours for groups ranging from school kids to Congressional Representatives, and official congressional testimonies. We have also given numerous press interviews and have been quoted in printed and online media, radio, and television.

The R/V *Walton Smith* is used by the University of Miami Department of Marine Science to provide undergraduate students with at sea experience in marine chemistry. The pCO<sub>2</sub> 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 with Principal Investigators as First Author

- Feely, R.A., V.J. Fabry, A. Dickson, J.-P. Gattuso, J. Bijma, U. Riebesell, S. Doney, C. Turley, T. Saino, K. Lee, K. Anthony, and J. Kleypas, 2010. An international observational network for ocean acidification. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.cwp.29.
- Hankin, S., L. Bermudez, J. Blower, B. Blumenthal, K.S. Casey, M. Fornwall, J. Graybeal, R.P. Guralnick, T. Habermann, E. Howlett, B. Keeley, R. Mendelssohn, R.R. Schlitzer, R. Signell, D. Snowden, and A. Woolf, 2010. Data management for the ocean sciences—Perspectives for the next decade. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 1)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.pp.21.
- Hankin, S., J.D. Blower, T. Carval, K.S. Casey, C. Donlon, O. Lauret, T. Loubrieu, A. Srinivasan, J. Trinanes, Ø. Godøy, R. Mendelssohn, R. Signell, J. de la Beaujardiere, P. Cornillon, F. Blanc, R.

- Rew, and J. Harlan, 2010. netCDF-CF-OPeNDAP: Standards for ocean data interoperability and object lessons for community data standards processes. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.cwp.41.
- Millero, FJ, F. Huang, R.J. Woosley, R.T. Letscher, and D.A. Hansell, 2011. Effect of dissolved organic carbon and alkalinity on the density of Arctic Ocean waters, *Aquat. Geochem.* 17, 311-326, DOI 10.1007/s10498-010-9111-2.
- Millero, FJ, G.K. Ward, A. Lo Surdo and F. Huang, 2011. Effect of pressure on the dissociation constant of boric acid in water and seawater, *Geochim. Cosmochim. Acta* 76, 83-92, DOI: 10.1016/j.gca.2011.10.024.
- Sabine, C.L., Feely, R.A., Wanninkhof, R., Takahashi, T., Khatiwala, S., Park, G.-H., 2011. Global oceans: The global ocean carbon cycle. In: Blunden, J., Arndt, D.S., Baringer, M.O. (Eds.), *In State of the Climate in 2010*, Bulletin of the American Meteorological Society, pp. 92(96):S100-S105 ), doi:110.1175/1520-0477-1192.1176.S1171.
- Wanninkhof, R., Doney, S., Bullister, J.L., Levine, N.M., Warner, M.J., Gruber, N., 2010. Detecting anthropogenic CO<sub>2</sub> changes in the interior Atlantic Ocean between 1989 and 2005. *J Geophys. Res.* 115, C11028, doi:11010.11029/12010JC006251.
- Wanninkhof, R., Park, G.-H., Chelton, D., Resien, C., 2011. Impact of small-scale variability on air-sea CO<sub>2</sub> fluxes. In: Komori, S., McGillis, W., Kurose, R. (Eds.), *Gas transfer at water surfaces 2010*. Kyoto University Press, Kyoto, pp. 431-444.

#### **4.2. Publications with PI as co-author**

- Barbero, L., Boutin, J., Merlivat, L., Martin, N., Takahashi, T., Sutherland, S.C., Wanninkhof, R., 2011. Importance of water mass formation regions for the air-sea CO<sub>2</sub> flux estimate in the Southern Ocean *Tellus* 25, GB 1005, doi:1010.1029/2010GB003818.
- Blower, J.D., S.C. Hankin, R. Keeley, S. Pouliquen, J. de la Beaujardière, E. Vanden Berghe, G. Reed, F. Blanc, M.C. Gregg, J. Fredericks, and D. Snowden, 2010. Ocean data dissemination: New challenges for data integration. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 1)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.pp.05.
- Bond, N.A., M.F. Cronin, C. Sabine, Y. Kawai, H. Ichikawa, P. Freitag, and K. Ronnholm, 2011. Upper-ocean response to Typhoon Choi-Wan as measured by the Kuroshio Extension Observatory (KEO) mooring. *J. Geophys. Res.*, 116, C02031, doi: 10.1029/2010JC006548, 8 pp.
- Borges, A.V., S.R. Alin, F.P. Chavez, P. Vlahos, K.S. Johnson, J.T. Holt, W.M. Balch, N. Bates, R. Brainard, W.-J. Cai, C.T.A. Chen, K. Currie, M. Dai, M. Degrandpre, B. Delille, A. Dickson, W. Evans, R.A. Feely, G.E. Friederich, G.-C. Gong, B. Hales, N. Hardman-Mountford, J. Hendee, J.M. Hernandez-Ayon, M. Hood, E. Huertas, D. Hydes, D. Ianson, E. Krasakopoulou, E. Litt, A. Luchetta, J. Mathis, W.R. McGillis, A. Murata, J. Newton, J. Olafsson, A. Omar, F.F. Perez, C. Sabine, J.E. Salisbury, R. Salm, V.V.S.S. Sarma, B. Schneider, M. Sigler, H. Thomas, D. Turk, D. Vandemark, R. Wanninkhof, and B. Ward, 2010. A global sea surface carbon observing system: inorganic and organic carbon dynamics in coastal oceans. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25

- September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.cwp.07.
- Canadell, J., P. Ciais, K. Gurney, C. Le Quere, S. Piao, M. Raupach, and C. Sabine, 2011. An international effort to quantify regional carbon fluxes. *Eos Trans. AGU*, 92(10), doi: 10.1029/2011EO100001, 81–82.
- Cronin, M.F., N. Bond, J. Booth, H. Ichikawa, T.M. Joyce, K. Kelly, M. Kubota, B. Qiu, C. Reason, M. Rouault, C. Sabine, T. Saino, J. Small, T. Suga, L.D. Talley, L. Thompson, and R.A. Weller, 2010. Monitoring ocean-atmosphere interactions in western boundary current extensions. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.cwp.20.
- Drupp, P., E. Heinen De Carlo, F.T. Mackenzie, P. Bienfang, and C.L. Sabine, 2011. Nutrient inputs, phytoplankton response, and CO<sub>2</sub> variations in a semi-enclosed subtropical embayment, Kaneohe Bay, Hawaii. *Aquat. Geochem.*, 17(4–5), doi: 10.1007/s10498-010-9115-y, 473–498.
- Dugdale, R., F. Chai, R. Feely, C. Measures, A. Parker, and F. Wilkerson, 2011. The regulation of equatorial Pacific new production and pCO<sub>2</sub> by silicate-limited diatoms. *Deep-Sea Res. II*, 58(3-4), doi: 10.1016/j.dsr2.2010.08.008, 477–492.
- Emerson, S., C. Sabine, M.F. Cronin, R. Feely, S. Cullison, and M. DeGrandpre, 2011. Quantifying the flux of CaCO<sub>3</sub> and organic carbon from the surface ocean using in situ measurements of O<sub>2</sub>, N<sub>2</sub>, pCO<sub>2</sub> and pH. *Global Biogeochem. Cycles*, 25, GB3008, doi: 10.1029/2010GB003924, 12 pp.
- Garzoli, S. L., O. Boebel, H. Bryden, R.A. Fine, M. Fukasawa, S. Gladyshev, G. Johnson, M. Johnson, A. MacDonald, C.S. Meinen, H. Mercier, A. Orsi, A. Piola, S. Rintoul, S. Speich, M. Visbeck, and Wanninkhof, R., 2010, Progressing towards global sustained deep ocean observations. , in J. Hall, D.E. Harrison, and Stammer, D., eds., *OceanObs09: Sustained Ocean Observations and Information for Society (Volume 2)*, Volume WPP-306, 12 pp., European Space Agency Publication,, p. 12.
- Goodkin, N.F., Levine, N.M., Doney, S.C., Wanninkhof, R., 2011. Impacts of temporal CO<sub>2</sub> and climate trends on the detection of ocean anthropogenic CO<sub>2</sub> accumulation. *Global Biogeochem cycles* 25, GB3023, doi:3010.1029/2010GB004009.
- Gruber, N., A. Körtzinger, C.L. Sabine, M. Hood, M. Ishii, P. Monteiro, R. Wanninkhof, R.A. Feely, Y. Nojiri, A. Kozyr, U. Schuster, D.W.R. Wallace, S.C. Doney, H. Claustre, and A. Borges, 2010. Towards an integrated observing system for ocean carbon and biogeochemistry at a time of change. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 1)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.pp.18.
- Hamme, R.C., P.W. Webley, W.R. Crawford, F.A. Whitney, M.D. DeGrandpre, S.R. Emerson, C.C. Eriksen, K.E. Giesbrecht, J.F.R. Gower, M.T. Kavanaugh, M.A. Peña, C.L. Sabine, S.D. Batten, L.A. Coogan, D.S. Grundle, and D. Lockwood, 2010. Volcanic ash fuels anomalous plankton bloom in subarctic Northeast Pacific. *Geophys. Res. Lett.*, 37, L19604, doi: 10.1029/2010GL044629.
- Hood, M., M. Fukasawa, N. Gruber, G.C. Johnson, A. Körtzinger, C. Sabine, B. Sloyan, K. Stansfield, and T. Tanhua, 2010. Ship-based repeat hydrography: A strategy for a

- sustained global program. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.cwp.44.
- Jiang, L.-Q., W.-J. Cai, R.A. Feely, Y. Wang, X. Guo, D.K. Gledhill, X. Hu, F. Arzayus, F. Chen, J. Hartmann, and L. Zhang, 2010. Carbonate mineral saturation states along the U.S. East Coast. *Limnol. Oceanogr.*, 55(6), doi: 10.4319/lo.2010.55.6.2424, 2424-2432.
- Keul, N., Morse, J. W., Wanninkhof, R., Gledhill, D. K., and Bianchi, T. S., 2010, Carbonate Chemistry Dynamics of Surface Waters in the Northern Gulf of Mexico: Aquatic Geochemistry, v. 16, no. 3, p. 337-351, 310.1007/s10498-10010-19091-10492.
- Lee, K., C.L. Sabine, T. Tanhua, T.-W. Kim, R.A. Feely, and H.-C. Kim, 2011. Roles of marginal seas in absorbing and storing fossil fuel CO<sub>2</sub>. *Energy Environ. Sci.*, 4(4), doi: 10.1039/C0EE00663G, 1133–1146.
- Levine, N.M., Doney, S.C., Lima, I., Wanninkhof, R., Bates, N., Feely, R.A., 2011. The impact of the North Atlantic Oscillation on the uptake and accumulation of anthropogenic CO<sub>2</sub> by North Atlantic Ocean mode waters. *Global Biogeochem cycles* 25, GB3022, doi:3010.1029/2010GB00389.
- Michalak, A.M., R.B. Jackson, G. Marland, C. Sabine, and the Carbon Cycle Science Working Group, 2011. A U.S. Carbon Cycle Science Plan. A Report for The U.S. Climate Change Science Program, Washington D.C., <http://www.carboncyclescience.gov/USCarbonCycleSciencePlan-August2011.pdf>, 94 pp.
- Manizza, M., M.J. Follows, S. Dutkiewicz, D. Menemenlis, J.W. McClelland, C.N. Hill, B.J. Peterson, R.M. Key, 2011. Modeling the Arctic Ocean carbon cycle, *J. Geophys. Res.*, 116,C12020, doi:10.1029/2011JC006998.
- Marion, G.M., F.J. Millero, M.F. Camões, P. Spitzer, R. Feistel, C-T A. Chen, 2011. pH and Acidity of Natural Waters, *Mar. Chem.*, 126, 89-95.
- Monteiro, P., Schuster, U., Hood, M., Lenton, A., Metzl, N., Tilbrook, B., Sabine, C., Takahashi, T., Wanninkhof, R., Watson, A., Olsen, A., Bender, M., Yoder, J., and Rogers, K., 2010, A Global Sea Surface Carbon Observing System: Assessment of Changing Sea Surface CO<sub>2</sub> and Air-Sea CO<sub>2</sub> Fluxes, in Hall, J., D.E., H., and Stammer, D., eds., *Sustained Ocean Observations and Information for Society (Vol. 2)*, : Venice, Italy ESA Publication WPP-306.
- Park, G.-H., Wanninkhof, R., Doney, S. C., Takahashi, T., Lee, K., Feely, R. A., Sabine, C., Triñanes, J., and Lima, I., 2010. Variability of global net sea-air CO<sub>2</sub> fluxes over the last three decades using empirical relationships: *Tellus*, v. 62B, p. 352-368.
- Park, G.-H., Wanninkhof, R., Trinanes, J., 2010. Procedures to Create Near Real-Time Seasonal Air-Sea CO<sub>2</sub> Flux Maps, Atlantic Oceanographic and Meteorological Laboratory NOAA Technical Memorandum-98, OAR AOML , Miami, p. 21.
- Pawlowicz, P, D.G. Wright and F.J. Millero, 2011. The effects of biogeochemical processes on oceanic conductivity/salinity/density relationships and the characterization of real seawater, *Ocean Sci.* 7, 363-387.
- Peng, T.-H., and Wanninkhof, R., 2010. Increase of anthropogenic CO<sub>2</sub> in the Atlantic Ocean in last the two decades: *Deep -Sea Res I*, v. 57, p. 755-770, 710.1016/j.dsr.2010.1003.1008.
- Pierrot, D., Brown, P., Van Heuven, S., Tanhua, T., Schuster, U., Wanninkhof, R., and Key, R. M., 2010. Carina TCO<sub>2</sub> data in the Atlantic Ocean Earth System Science Data, p. ISSN: 1866-3508.

- Pierrot, D., Neil, C., Sullivan, K., Castle, R., Wanninkhof, R., Lueger, H., Johannson, T., Olsen, A., Feely, R.A., Cosca, C.E., 2009. Recommendations for autonomous underway pCO<sub>2</sub> measuring systems and data reduction routines. *Deep -Sea Res II* 56, 512-522.
- Pouliquen, S., S. Hankin, R. Keeley, J. Blower, C. Donlon, A. Kozyr, and R. Guralnick, 2010. The development of the data system and growth in data sharing. In *Proceedings of the "OceanObs'09: Sustained Ocean Observations and Information for Society" Conference (Vol. 1)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306, doi: 10.5270/OceanObs09.pp.30.
- Tanhua, T., Steinfeldt, R., Key, R. M., Brown, P., Gruber, N., Wanninkhof, R., Perez, F., Körtzinger, A., Velo, A., Schuster, U., van Heuven, S., Bullister, J. L., Stando, I., Hoppema, M., Olsen, A., Kozyr, A., Pierrot, D., Schirnick, C., and Wallace, D. W. R., 2010, Atlantic Ocean CARINA data overview and salinity adjustments: *Earth System Science Data*, v. 2, p. 17-34.
- Waters, J.F., F.J. Millero, and C.L. Sabine, 2011. Changes in South Pacific anthropogenic carbon, *Global Biogeochem. Cycles*, 25(4), GB4011, doi: 10.1029/2010GB003988.