## Pacific Ocean Interior Carbon Data Synthesis, PACIFICA, in Progress

by Masao Ishii, Toru Suzuki and Robert Key

Data managers and research groups that measure ocean  $\mathrm{CO}_2$  parameters and their related chemical and physical components at depths in the Pacific Ocean have been brought together under the PICES Section on *Carbon and Climate* (CC-S), co-chaired by Drs. James Christian (Canada) and Toshiro Saino (Japan). In 2006, CC-S started the activity of data synthesis for the interior of the Pacific Ocean. This activity and the data collection were later named "PACIFICA".

Natural seawater is a "salty soda pop", although it does not visibly evolve bubbles of CO2 because it is weakly basic (pH ~8), and CO<sub>2</sub> is mostly dissolved in the form of nonvolatile bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>) ions. The total content of these carbonate species in seawater, i.e., dissolved inorganic carbon (DIC) concentration, is around 2,000  $\mu$ mol  $kg^{-1}$  (1  $\mu$ mol = 1 × 10<sup>-6</sup> mole), roughly equivalent to a small spoonful of sodium bicarbonate powder, per kilogram of seawater. The total DIC in the world oceans, 40,000 PgC (1 PgC =  $1 \times 10^{15}$  gC), is about 50 times as much CO<sub>2</sub> as in the atmosphere. With this great ability to store DIC, the oceans also represent a key sink for CO<sub>2</sub> that is released by fossil fuel combustion and land use changes, and are thus contributing to global warming. However, the uptake of CO<sub>2</sub> by the oceans is chemically equivalent to the addition of carbonic acid (H<sub>2</sub>CO<sub>3</sub>), and causes a perturbation to the carbonate chemistry in seawater. This perturbation is commonly referred to as "ocean acidification" and is recognized as "the other CO<sub>2</sub> problem" (Doney et al., 2009) that threatens marine biology and ecosystems worldwide.

One challenge for oceanographers is to detect the tiny but important signals of anthropogenic DIC increase and acidification in seawater and their temporal evolution from observations. For this purpose, the tolerance allowed for DIC analysis is on the order of 1/1000, which is comparable to the ratio of a single krill to a blue whale in length. The acquisition of such high quality of DIC data became possible after development of the coulometric technique for DIC measurement (Johnson et al., 1985), the availability of certified reference materials (Dickson, 2001), and publication of a Guide to Best Practices for Ocean CO2 Measurements (DOE, 1994; Dickson et al., 2007). With growing social and scientific concerns about the carbon cycle and climate change, a significant volume of data were collected from more than 12,000 oceanographic stations in the world's oceans during the 1990s by international programs such as the Joint Global Ocean Flux Study (JGOFS), the World Ocean Circulation Experiment (WOCE) and related projects. These data have been synthesized to generate a unified data set in a cooperative effort of the Global Ocean

Data Analysis Project (GLODAP) (Key et al., 2004). Using this database with unprecedented quality and quantity, the distributions and total inventory of anthropogenic CO<sub>2</sub> as well as the natural component of DIC due to air—sea CO<sub>2</sub> exchange in the ocean was evaluated globally for the first time (Sabine et al., 2004; Sarmiento and Gruber, 2006). These scientists are further stimulating the development of forward and inverse ocean carbon cycle models. Among the most important aspects of GLODAP is that it has provided a benchmark against which future observational studies will be compared to understand changes related to the increasing anthropogenic CO<sub>2</sub> emission and climate change.

An activity to expand the ocean's interior CO<sub>2</sub> data collection, CARINA (Carbon Dioxide in the Atlantic Ocean), was also been initiated in Europe by Ludger Mintrop and Douglas Wallace as an informal project. Funded in 2005 as a component of the European Union's project CARBOOCEAN, the data collection in CARINA was expanded to the Arctic and Southern oceans. The database is now available from the Carbon Dioxide Information Analysis Center (CDIAC; http://cidiac.ornl.gov/oceans/CARINA/). It was in early 2007 that some researchers who were involved in CARINA and also in CC-S kicked off planning the expansion of data collection in the Pacific Ocean.

The activity for Pacific Ocean interior carbon data collection, PACIFICA, was cooperatively promoted at PICES-2007 (Victoria, Canada) and at PICES-2008 (Dalian, China). Collecting data sets and converting the data format were initiated after PICES-2007. Following these meetings, 2-to 3-day technical hands-on workshops were held three times: at PICES-2009 (Jeju, Korea), at the CC-S intersessional workshop in June 2010 (Tokyo, Japan), and at PICES-2010 (Portland, U.S.A.). At these workshops, the status of data collection was reviewed, details of method for data quality control were discussed, and its practices were advanced.

For data collection, we targeted cruises in the North Pacific and its marginal seas, and the South Pacific north of 30°S. First priority was given to the data sets of post-WOCE cruises with high-quality discrete hydrographic/chemical data such as DIC, total alkalinity (TA), pH, dissolved oxygen, nutrients (nitrate + nitrite, phosphate, silicic acid) and chlorofluorocarbons (CFCs). Historical data sets that had not been incorporated into GLODAP were merged into PACIFICA. Metadata that describes methods of analysis, information on quality control and list of related publications are also an important component of the database.

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Participants of the inter-sessional PACIFICA Workshop (June 2–4, 2010, JAMSTEC Office, Tokyo, Japan); 20 persons from 4 countries (Canada, Japan, Korea and U.S.A.) were in attendance.

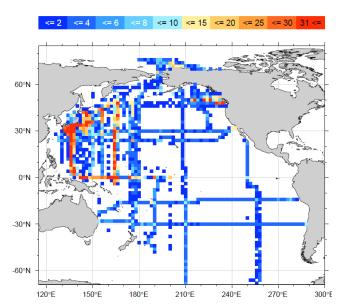


Fig. 1 Distribution and density of hydrographic/hydrochemical stations in the PACIFICA data collection in 2° x 2° pixels.

Data sets from a total of 305 cruises conducted between 1985 and 2009 were acquired (Fig. 1). The list of cruises is available at http://cdiac.ornl.gov/oceans/PACIFICA/ and http://pacifica.pices.jp/table/. Many of these data sets have already been publicly available from various data centers, research organizations and programs. As yet unopened high-quality data sets that the Principle Investigators gave permission to release have also been collected. The format of all these data sets has been converted to the "WHP-Exchange Format" (http://cchdo.ucsd.edu/WHP\_Exchange\_Description.pdf). The collection includes 16 CLIVAR Repeat Hydrography cruises conducted after 2001

that tracked the same sections as the WOCE Hydrographic Program in the 1990s. In spite of the growing concern for the acidification in marginal seas, the number of data sets from marginal seas is, so far, limited. Synthesizing the data of ocean CO<sub>2</sub> parameters in marginal seas will be the major subject for the next phase of expanding data collection.

One of the merits of PACIFICA is that it will go through a 2<sup>nd</sup> level quality control (2<sup>nd</sup> level QC). The 2<sup>nd</sup> level QC is an activity to correct for the systematic errors to develop a processed "new database" that is consistent among <u>cruises</u>. On the other hand, the 1<sup>st</sup> level QC is an activity that individual data providers should deal with to create an "original data set" that is consistent within a cruise. The 1<sup>st</sup> level QC includes works to assign questionable and bad data in the data set on the basis of the sampling and analytical conditions. Effectively, the 2<sup>nd</sup> level QC focuses on accuracy while the 1st level QC is focused on precision. Experience has shown that the 2<sup>nd</sup> level QC team has to redo the 1st level QC by examining vertical profiles, propertyproperty plots and so on. In fact, we have gone back and forth between the 1<sup>st</sup> and 2<sup>nd</sup> level QCs several times. Errors in data formatting have also been found during these processes. These data quality control measures are critical, but are usually tedious.

Data sets in PACIFICA are now undergoing a 2<sup>nd</sup> level QC using the method as developed by the CARINA team (Key *et al.*, 2010; Tanhua *et al.*, 2010) with some modifications to apply to the Pacific Ocean. This method is based on crossover analysis followed by the inversion of those results (Fig. 2). In crossover analysis, data in deep layers (>2000 m or >1500 m), where no change is expected over

the time period, are compared from two different cruises at nearby stations. Results of a huge number of crossover analyses are then analyzed by an inversion technique to determine the optimum systematic offset for each cruise and parameter. The inversion results are then examined by experts for each particular geographic region and type of measurement. Since the inversion technique will identify real temporal changes as well as measurement bias, care is taken to segregate the two signals. Finally, a table of "required" adjustments is accepted. In order to have an offset applied, the measurement offset must exceed a minimum bias amount that is different for each type of measurement. Three ad hoc groups were organized: for salinity, CO<sub>2</sub> parameters, and dissolved oxygen and nutrients. Since CFCs are usually not detectable in deep layers, a different method that is based on the relationship between CFC-11 and CFC-12 saturation levels in the surface layer (Steinfeldt et al., 2010) was used for the 2<sup>nd</sup> level OC.

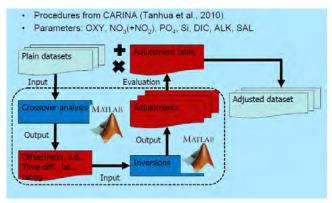


Fig. 2 Outline of the second level quality control (2<sup>nd</sup> level QC).

In the process of the 2<sup>nd</sup> level QC for PACIFICA, data sets from several WOCE cruises with basin-wide high-quality data and those from the Hawaii Ocean Time-series (HOT) have also been used to create a database consistent with GLODAP, HOT, and CARINA. Good news from applying the 2<sup>nd</sup> level QC is that, so far, the use of reference materials in fact helps us to obtain high-quality data (data of CO<sub>2</sub> parameters and nutrients from the cruises in which reference materials had been used are mostly consistent with each other, and no offset correction is needed for these cruises). These results demonstrate that it is critical to develop and appropriately use reference materials in collecting high-quality data for chemical components in the ocean.

Once the 2<sup>nd</sup> level QC for each parameter is completed, the accepted offsets will be applied to create the fully calibrated PACIFICA data product. PACIFICA, along with the original uncorrected data files, will be publicly available from the Marine Information Research Center (MIRC), Japan, and CDIAC.

We hope that PACIFICA, in conjunction with GLODAP and CARINA, will become a foundation to evaluate anthropogenic CO<sub>2</sub>, ocean acidification, and natural or climate change-driven variability in biogeochemical dynamics in the Pacific Ocean from regional to basin scales.

"Models come and go, but a good data set lasts forever." (Paul Quay, 2002: Science, 298, 2344).

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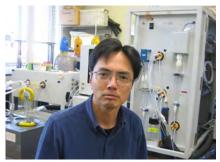
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Dr. Robert M. Key (key@princeton.edu) is Research Oceanographer in the Atmospheric and Oceanographic Sciences program at Princeton University. He has been heavily involved in all of the major U.S. programs designed to investigate ocean mixing, ventilation and carbon chemistry including Transient Tracers in the Ocean (TTONAS and TTOTAS), the South Atlantic Ventilation Experiment (SAVE), the World Ocean Circulation Experiment (WOCE) and the Repeat Hydrography portion of the Climate Variability and Predictability program (CLIVAR). During WOCE and CLIVAR, Bob has been lead PI for the U.S. radiocarbon program and participated actively in the carbon dioxide measurement programs. After completion of the WOCE field work, he was the lead investigator in producing the GLODAP data products and was strongly involved in subsequent determination of the global ocean anthropogenic CO<sub>2</sub> distribution and inventory. Bob had lead responsibility for assembly of the CARINA data, participated in the 2<sup>nd</sup> QC, and assembled the final data products. His research interests focus on large-scale ocean circulation and mixing problems, especially those critical to the global carbon cycle.

## 2011 PICES Calendar

- 5<sup>th</sup> Zooplankton Production Symposium on "Population connections, community dynamics and climate variability" (primary international sponsors: PICES and ICES), March 14–18, 2011, Pucón, Chile (www.pices.int/zooplankton2011.aspx);
- FUTURE Workshop on "Indicators of status and change within North Pacific marine ecosystems", April 26–28, 2011, Honolulu, U.S.A. (www.pices.int/meetings/descriptions.aspx#description4)
- ICES/PICES workshop on "Reaction of northern hemisphere ecosystems to climate events: A comparison", May 2–6, 2011, Hamburg, Germany (www.pices.int/meetings/descriptions.aspx#description5);
- Second ESSAS (Ecosystem Studies of Sub-Arctic Seas) Open Science Meeting on "Comparative studies of climate effects on polar and sub-polar ocean ecosystems: Progress in observation and prediction" and associated workshops, May 22–26, 2011, Seattle, U.S.A. (www.pices.int/essas2011.aspx);
- <sup>1</sup> 7<sup>th</sup> International Conference on "*Marine bioinvasions*" (co-sponsored by PICES), August 23–25, 2011, Barcelona, Spain (www.icmb.info/);
- Joint Theme Sessions at the 2011 ICES Annual Science Conference, September 19–23, 2011, Gdansk, Poland:
  - Atmospheric forcing of Northern hemisphere ocean gyres and their subsequent impact on the adjacent marine climate and ecosystems;
  - Atlantic redfish and Pacific rockfish: Comparing biology, ecology, assessment and management strategies for Sebastes spp.;
  - o Recruitment processes: Early life history dynamics from eggs to juveniles;
  - Surplus production models: Quantitative tools to manage exploited fisheries and compare the productivity of marine ecosystems;
- PICES Annual Meeting, October 14–23, 2011, Khabarovsk, Russia (www.pices.int/pices2011.aspx);
- International workshop on "Development and application of Regional Climate Models", October 11–12, 2011, Incheon, Korea (www.pices.int/meetings/descriptions.aspx#description8);
- International NPAFC-led workshop on "Explanations for the high abundance of pink and chum salmon and future trends" (co-sponsored by PICES), October 30–31, 2011, Nanaimo, Canada (http://www.npafc.org/new/events/workshops/2011Workshop1stAnnouncement.pdf).