GLOBAL OCEAN SURFACE WATER PARTIAL PRESSURE OF CO$_2$ DATABASE:
MEASUREMENTS PERFORMED DURING 1957–2015

(Version 2015)

Contributed by
Taro Takahashi and Stewart C. Sutherland

Lamont-Doherty Earth Observatory, Columbia University, Palisades, NY 10964

Date Published: September 2007
Date Updated and Revised: April 2016

Prepared for the Climate Change Research Division
Office of Biological and Environmental Research
U.S. Department of Energy
Budget Activity Numbers KP 12 04 01 0 and KP 12 02 03 0

Prepared by
Alex Kozyr

Carbon Dioxide Information Analysis Center
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6335
managed by
UT-BATTTELLE, LLC
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725
CONTENTS

List of Figures........................................................................................................... v
List of Tables............................................................................................................... v
Abbreviations and Acronyms .................................................................................. vii
Abstract.................................................................................................................... ix

1. INTRODUCTION.................................................................................................... 1

2. OBJECTIVE........................................................................................................... 2

3. SUMMARY OF ADDITIONS AND CORRECTIONS IN ALL VERSIONS............. 3

4. METHODS OF COMPUTATION.......................................................................... 5

5. QUALITY CONTROL ............................................................................................ 7

6. DATA SOURCES .................................................................................................. 8

7. DATA LISTING .................................................................................................... 10

8. HOW TO OBTAIN THE DATA AND DOCUMENTATION............................... 12

9. ACKNOWLEDGEMENTS..................................................................................... 12

10. REFERENCES .................................................................................................... 12
LIST OF FIGURES

1 Location of LDEO V2015 master database of sea surface pCO₂ observations. ..............................2

LIST OF TABLES

1 List of data contributors to the global surface water pCO₂ LDEO database ..............................9
2 Data elements listed in the master data file “LDEO_Database_V2015.csv” ..............................11
3 Data elements listed in the metadata file “LDEO_Database_Metadata_V2015.csv” .................11
## ABBREVIATIONS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOML</td>
<td>Atlantic Oceanographic and Meteorological Laboratory</td>
</tr>
<tr>
<td>CDIAC</td>
<td>Carbon Dioxide Information Analysis Center</td>
</tr>
<tr>
<td>CLIVAR</td>
<td>Climate Variability (Program)</td>
</tr>
<tr>
<td>CO₂</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>CSIRO</td>
<td>Australian Commonwealth Scientific and Research Organization</td>
</tr>
<tr>
<td>DOE</td>
<td>U.S. Department of Energy</td>
</tr>
<tr>
<td>FTP</td>
<td>File transfer protocol</td>
</tr>
<tr>
<td>fCO₂</td>
<td>Fugacity of CO₂</td>
</tr>
<tr>
<td>GEOSECS</td>
<td>Geochemical Ocean Sections Study</td>
</tr>
<tr>
<td>IGY</td>
<td>International Geophysical Year</td>
</tr>
<tr>
<td>JGOFS</td>
<td>Joint Global Ocean Flux Study</td>
</tr>
<tr>
<td>LDEO</td>
<td>Lamont-Doherty Earth Observatory</td>
</tr>
<tr>
<td>NCAR</td>
<td>National Center for Atmospheric Research</td>
</tr>
<tr>
<td>NCEP</td>
<td>National Centers for Environmental Prediction</td>
</tr>
<tr>
<td>NDP</td>
<td>Numeric data package</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>NSF</td>
<td>National Science Foundation</td>
</tr>
<tr>
<td>ORNL</td>
<td>Oak Ridge National Laboratory</td>
</tr>
<tr>
<td>pCO₂</td>
<td>Partial pressure of CO₂</td>
</tr>
<tr>
<td>PMEL</td>
<td>Pacific Marine Environmental Laboratory</td>
</tr>
<tr>
<td>SSS</td>
<td>Sea surface salinity</td>
</tr>
<tr>
<td>SST</td>
<td>Sea surface temperature</td>
</tr>
<tr>
<td>VOS</td>
<td>Volunteer Observing Ship</td>
</tr>
<tr>
<td>WOCE</td>
<td>World Ocean Circulation Experiment</td>
</tr>
</tbody>
</table>
ABSTRACT


Approximately 10.5 million measurements of surface water pCO₂ made over the global oceans during 1957-2015 have been processed to make a uniform data file in this Version 2015. Measurements made in open oceans as well as in coastal waters are included. The data assembled include only those measured using equilibrator-CO₂ analyzer systems, and have been quality-controlled based upon the stability of the system performance, the reliability of calibrations for CO₂ analysis and the internal consistency of data. We have added about 1.4 million data points comprised of 461 leg/cruise segments in this version. A total of 200,000 of these were collected on the 5 ships in our current field program. The remainders were added from various web sites for Volunteer Observation Ships (VOS) operated by various agencies. Our ships operate primarily in high latitudes in both hemispheres and have built decades long records in these areas. R/V Nathaniel B. Palmer’s system has been operating since 1995, and R/V Laurence M. Gould’s system since 2001. Combined with the other three ships including USCGC Healy, R/V Sikuliaq and R/V M. Langseth, our contribution to this database through many years exceeds 2.3 million records primarily for the polar and sub-polar seas. These data have been corrected for the time-lag between the ship’s intake port and the pCO₂ system as described in the technical report by Takahashi and Sutherland (2015).

In order to allow re-examination of the data in the future, a number of measured parameters relevant to pCO₂ in seawater are listed. The overall uncertainty for the pCO₂ values listed is estimated to be ± 2.5 µatm on the average. The names and institutional affiliations of the contributors are listed in Table 1. The documentations for the previous versions (V1.0, V2007, V2008, V2009, V2010, 2011, V2012, V2013, and V2014) of our database are available at CDIAC http://cdiac.ornl.gov/ftp/oceans/LDEO_Database/

The global pCO₂ data set is available free of charge as a numeric data package (NDP) from the Carbon Dioxide Information Analysis Center (CDIAC). The NDP consists of the oceanographic data files and this printed documentation, which describes the procedures and methods used to obtain the data.

Keywords: carbon dioxide, partial pressure of CO₂, global carbon cycle, global ocean, equilibrator-CO₂ analyzer systems.
1. INTRODUCTION

Transfer of CO₂ from the atmosphere to the oceans is a critical process in the global carbon cycle, and is important for the future of the earth’s climate. During the past decade, 6 to 9 Pg-C yr⁻¹ (1 Pg (peta grams) = 10¹⁵ grams = 1 Giga ton) has been emitted into the atmosphere from various anthropogenic sources including the combustion of fossil fuels, cement production, deforestation, land use changes and others. The annual uptake rate of CO₂ by the oceans has been estimated to be about 2 Pg-C yr⁻¹ for the past decade on the basis of various independent scientific methods, including changes in oxygen and CO₂ concentrations in the atmosphere (Keeling et al. 1996; Bender et al., 2005; Manning and Keeling, 2006), sea-air differences in CO₂ partial pressure (Takahashi et al., 2002; Takahashi et al., 2009), distribution of carbon isotopes (¹³C, ¹²C and ¹⁴C) (Gruber and Keeling, 2001; Quay et al, 2003), inversion of atmospheric CO₂ distribution data using atmospheric circulation models (Baker et al., 2006; Patra et al., 2006), and various global carbon cycle models (Sarmiento et al., 2000; Gruber and Sarmiento, 2002; Matsumoto et al., 2004; Gruber et al., 2009). Thus, about 30% of the anthropogenic CO₂ emissions are absorbed annually by the oceans, and about 50% remains in the atmosphere. As a result, the atmospheric CO₂ concentration is increasing at a mean rate of about 1.9 ppm yr⁻¹ (or 0.4% per year), and the concentration of CO₂ dissolved in surface ocean waters is also increasing, thus causing the acidification of ocean waters. Accurate documentation of changes that have occurred in the CO₂ chemistry of ocean waters is therefore important for understanding the fate of anthropogenic CO₂ released into the atmosphere as well as charting the future course of atmospheric CO₂ levels that would affect the earth’s climate.

Carbon dioxide molecules react chemically with water to form bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions, both of which do not communicate with the overlying air. Only about 0.5% of the total CO₂ molecules in seawater communicate with the air via gas exchange across the sea surface. This quantity is called the partial pressure of CO₂ (pCO₂), which represents the CO₂ vapor pressure. The seawater pCO₂ depends on the temperature, the total amount of CO₂ dissolved in seawater and the pH of seawater. Over the global ocean, it varies from about 100 μatm to 1000 μatm (1 μatm = 10⁻⁶ atm = 0.101325 Pascal). When seawater pCO₂ is smaller than the atmospheric pCO₂ (presently about 395 μatm), seawater takes up CO₂ from the overlying air; when it is greater than the atmospheric pCO₂, it emits CO₂ to the air. The rate of transfer of CO₂ across the sea surface is estimated by: (sea-air CO₂ flux) = (transfer coefficient) x (sea-air pCO₂ difference). The transfer coefficient depends primarily on the degree of turbulence near the interface, and is commonly expressed as a function of the square of wind speed. Since the time-space variation for atmospheric pCO₂ is much smaller than that for surface ocean water pCO₂, the magnitude of sea-air pCO₂ difference and hence the net flux is governed primarily by seawater pCO₂. Therefore, the interannual and seasonal variability for surface water pCO₂ is of particular interest.

The atmospheric CO₂ concentrations observed at a number of locations over the globe is summarized in GLOBALVIEW-CO2 (2012) and TRENDS ON LINE (2011). On the other hand, no single data file for surface water pCO₂, that includes long term, global coverage has been made accessible to the general public. About 30 years ago, we started to assemble a global surface water pCO₂ data for time-space variability studies for the global oceans using the observations made by the Lamont-Doherty group. Many investigators from other institutions joined in and contributed their data to the database. The first publication on the global ocean pCO₂ and sea-air CO₂ flux (Takahashi et al., 1997) was based on about 0.25 million pCO₂ measurements; the second publication (Takahashi et al., 2002) about 1 million measurements. In the third publication in the Deep Sea Research (Takahashi et al., 2009), a dataset that consisted of about 3 million pCO₂ measurements plus a number of other measured supporting parameters, has been analyzed and summarized. In the fourth publication in Marine Chemistry (2014), about 6 million pCO₂ measurements were used to produce the climatological maps of pCO₂, total CO₂ concentration, alkalinity, pH, and degree of saturation for CaCO₃ over the global ocean.
Recently, an international consortium named SOCAT has been established for assembling surface ocean water pCO$_2$ data produced by many international research groups (Bakker et al., 2014). The LDEO database serves as a major source for such the effort.

**Fig. 1. Location of LDEO V2015 master database of sea surface pCO$_2$ observations.**

2. OBJECTIVE

Modern investigation of ocean water pCO$_2$ started during the International Geophysical Year (IGY), 1957 – 1960, with the introduction of infrared CO$_2$ gas analyzer and gas-water equilibrator aboard oceanographic research vessels (Takahashi, 1961; Keeling et al., 1965; Keeling, 1965; Broecker and Takahashi, 1966; Keeling and Waterman, 1968; Keeling, 1968; Waterman et al., 2006-a, b, c and d). Combined with high-accuracy CO$_2$-air gas mixtures that were made available for the calibrations of the analyzers at sea, the quality of seawater pCO$_2$ data was greatly improved from that obtained in the pre-World War II era. During major oceanographic programs that took place after IGY, the CO$_2$ analyzers and equilibrators have been steadily improved to give more frequent observations and better accuracy, although the principles of the measurement remained essentially unchanged. Computers that are used for system control and data logging contributed significantly to the data quality. The deployment of GPS system improved the location information significantly. The objective of this data file is to assemble high-quality pCO$_2$ data obtained using the equilibrator-analyzer method, and to reprocess the data using a standardized method of computation, that will be described below. Therefore, the pCO$_2$ values listed in this database may differ from the original listings prepared by respective investigators.
3. SUMMARY OF ADDITIONS AND CORRECTIONS IN VERSIONS

VERSION 2014:
This version is referred to as Version 2014, and includes data collected through 31 December 2014. In this update, a total of about 100,000 data points comprising 467 leg/cruise segments have been added. This version includes the results of reanalysis for approximately 2.3 million pCO$_2$ measurements which were made in the surface waters of the polar oceans aboard RVIB Palmer, RV Gould and USCGC Healy using an underway method developed and operated by the Lamont-Doherty Earth Observatory (LDEO) group. Although these data were reported to the CDIAC in a series of previous reports after the preliminary quality control, a reanalysis of the data has shown that these reported data call for corrections that account for the transit time of pumped sample water from the intake port near the bow to the pCO$_2$ system located some distance away. The corrections applied to each data point are up to about ±8 uatm for the Palmer and Gould data and ±16 uatm for the Healy data, while the mean of the corrections for each cruise is less than ±1 uatm.

VERSION 2013:
This version is referred to as Version 2013, and includes the data collected through 31 December 2013. In this update, a total of about 2,270,000 pCO$_2$ measurements made during 64 new cruise/ship files (including 170,770 new measurements made by the LDEO group) are added to the previous version 2012. A substantial number of files/data points from the participants of the NOAA sponsored Volunteer Observation Ships (VOS) were added. Several additional vessels as well as additional files from previously included vessels contributed significant number of the observations. When underway measurements were made across high SST gradient areas, errors up to about 5 µatm may occur due to time lag of sample water transit from the intake to the equilibrator (Section 5). Because of the lack of the necessary information, the errors due to time lag are not corrected in this version.

VERSION 2012:
This version is referred to as Version 2012, and includes the data collected through 31 December 2012. In this update, about 277,000 pCO$_2$ measurements made during 29 new cruise/ship files are added to the previous version 2011. The new additions include the new data from our field operations aboard L.M. Gould, N.B. Palmer, Marcus G. Langseth, US Coast Guard Cutter Healy. These data files from Gould, Palmer, Langseth, and Healy are also posted on our LDEO website: http://www.ldeo.columbia.edu/res/pi/CO2/. In addition, several files from the Volunteer Observation Ships (VOS) program, M/V Explorer of the Seas, and 3 NOAA ships., which have recently been released for years 2010 – 2012, are combined into the master file of CDIAC http://cdiac.ornl.gov/oceans/.

VERSION 2011:
This version is referred to as Version 2011 with approximately 6.4 million measurements of surface water partial pressure of CO$_2$, and includes the data collected through 31 December 2011. In this update, 209 new cruise/ship files are added to the previous version 2010. The new additions include the new data from our field operations aboard L.M. Gould, N.B. Palmer, Marcus G. Langseth, US Coast Guard Ship Cutter Healy. These individual data files are also posted on the CDIAC web site for Global Volunteer Observing Ship (VOS) Program: http://cdiac.ornl.gov/oceans/VOS_Program/ and LDEO website: http://www.ldeo.columbia.edu/res/pi/CO2/.

VERSION 2010:
Approximately 5.2 million measurements of surface water partial pressure of CO$_2$ obtained over the global oceans during 1957–2010 are listed in the Lamont-Doherty Earth Observatory (LDEO) database, which includes open-ocean and coastal water measurements. This version is referred to as Version 2010, and includes the data collected through 31 December 2010. In this update, 21 new
cruise/ship files are added to the previous Version 2009 (see NDP-088_V2009). Other than routine updates from our Vessel of Opportunity Program such as L.M. Gould, N.B. Palmer, and R/V Ronald H. Brown, there are two new sources of data: R/V Marcus G. Langseth, operated by Lamont-Doherty Earth Observatory, and S.A. Agulhas operated by CSIR, South Africa.

VERSION 2009:
This version is referred to as Version 2009, and includes the data collected through 31 December 2009. In this update, 42 new cruise/ship files are added to the previous version 2008 (see NDP-088r) including several files for the IGY expeditions in 1957–1963. Four files were received from Dr. Ralph F. Keeling at Scripps Institute of Oceanography containing the data from the late Dr. Charles D. Keeling's work on the “1957 Downwind” and “1961 Monsoon”, “1962 Lusiad” and “1963 Lusiad” Expeditions, re-edited by Lee Waterman, one of the original investigators, to improve their accuracy (Waterman et al., 2006-a, -b, -c and -d. See references for URL). The other file is for the 1957–1958 R/V Vema Expedition by Takahashi (1961). Based on his independent calibrations, he reported a mean atmospheric CO₂ value (in dry air) of 315.3 ± 1.4 ppm (N = 28) over the Atlantic Sector of the Southern Ocean (51°S-57°S; 41°W-02°E) during March 4-24, 1958. C. D. Keeling reported a mean value of 314.1 ppm for March, 1958, at the South Pole Station, and 0.3 ±0.1 ppm higher values at the Palmer and Amsterdam Island stations. These data sets are in agreement within their respective uncertainties, and therefore, no adjustment was made for the CO₂ values for gas samples equilibrated with seawater. All these data are reprocessed in a manner described below to maintain the consistency with the data in this database.

VERSION 2008:
This version is referred to as Version 2008, and includes the data collected through 31 December 2008. In this update, twenty-six new cruise/ship files are added to the previous version 2007. Dr. Nicolas Metzl of Universite Pierre et Marie Curie, Paris, kindly called our attention to discrepancies between his original and our data file listed in Version 2007. The discrepancies were caused by applying temperature correction to this data, that were already corrected to SST. Affected are a total of 13,981 records for the southern Indian Ocean in the file names OISO for years 1998 and 2000 (File Name OISO), which were published in Metzl (2009). The errors range from -29.6 µatm to + 1.3 µatm with an average of -9.27 ± 3.43 µatm. In Version 2008, these errors are corrected, and a total of 67,403 new OISO data spanning years 2000–2008 are added.

VERSION 2007:
More than 4.1 million measurements of surface water partial pressure of CO₂ obtained over the global oceans during 1968–2007 are listed in the Lamont-Doherty Earth Observatory (LDEO) database, which includes open-ocean and coastal water measurements. The data assembled include only those measured by equilibrator-CO₂ analyzer systems and have been quality-controlled based on the stability of the system performance, the reliability of calibrations for CO₂ analysis, and the internal consistency of data. To allow re-examination of the data in the future, a number of measured parameters relevant to pCO₂ measurements are listed. The overall uncertainty for the pCO₂ values listed is estimated to be ± 2.5 µatm on the average.

VERSION 1.0 (2006):
More than 3 million measurements of surface water partial pressure of CO₂ obtained over the global oceans during 1968–2006 are listed in the Lamont-Doherty Earth Observatory (LDEO) database, which includes open-ocean and coastal water measurements. The data assembled include only those measured by equilibrator-CO₂ analyzer systems and have been quality-controlled based on the stability of the system performance, the reliability of calibrations for CO₂ analysis, and the internal consistency of data. To allow re-examination of the data in the future, a number of measured parameters relevant to pCO₂ measurements are listed. The overall uncertainty for the pCO₂ values listed is estimated to be ± 2.5 µatm on the average.
4. METHODS OF COMPUTATION

The seawater pCO$_2$ data that are listed in this data file are based on direct measurements of seawater pCO$_2$ made using equilibrator-CO$_2$ analyzer systems. A large proportion of data listed is from semi-continuous underway pCO$_2$ systems with flow-through water, while many others are measurements for discrete water samples made at hydrographic stations along with measurements for other chemical and physical properties. Although different types of equilibrators (e.g., shower type, bubbling type, rotating disk type and membrane type in flow-through or closed circulation systems) and CO$_2$ gas analyzers (non-dispersive infrared analyzers and gas chromatographs of various designs) were employed, the results from different systems are accepted as long as analyzers were properly calibrated using validated CO$_2$-air gas mixtures and the carrier gas was equilibrated with seawater samples. Because of the diversity of methods used, it is not possible to present details of the method used by each research group who contributed data to this data file. Detailed methodology may be obtained directly from the original investigators who are listed in Table 1, or from the CDIAC reports for specific expeditions.

It is important to point out that the methods used for computing CO$_2$ concentrations in equilibrated gas varied among groups. For example, some groups computed a least-squares fit of output readings for three or more standard gas mixtures to a quadratic equation and used it to calculate concentrations in samples. Other groups used four or five standard gas mixtures for calibrations, and fitted the data to a 4$^{th}$ order polynomial equation. Others used an output from linearization circuits of infrared analyzer (provided by the manufacturer), and linearly regressed three or more standard gas readings to obtain sample CO$_2$ concentrations. The outputs from a gas chromatograph are a linear function of CO$_2$ concentration, and hence a linear regression is used for calibration. These different data reduction methods yield CO$_2$ concentrations varying ± 1.5 ppm (or ± 1.5 µatm in pCO$_2$). However, we did not re-compute the CO$_2$ values using a single uniform algorithm, and, instead, accepted CO$_2$ concentration values reported to us. Since different analyzers and different numbers of standard gas mixtures were used by respective groups, no single uniform data reduction scheme can be applied, and hence we relied on the judgment of each group for selecting the data reduction scheme most suited for their operational modes and skills. Measurements that were made using only one calibration gas mixture (not counting the CO$_2$-free air or nitrogen for establishing zero CO$_2$) are judged unreliable, and, hence, are not included in this database.

Using the reported CO$_2$ concentration values, the pCO$_2$ value in sample seawater at the equilibration temperature, (pCO$_2$)$_{eq}$, has been recomputed with the relationship:

$$(pCO_2)_{eq} = V_{co2} (P_{eq} - P_{water}),$$

where $V_{co2}$ is the mole fraction concentration of CO$_2$ in carrier gas ($V_{CO_2}$ is same as $X_{CO_2}$, which is often used in literature, and these qualities may be used interchangeably); $P_{eq}$ is the total pressure of gas in the equilibrator; and $P_{water}$ is the equilibrium water vapor pressure at temperature of equilibration, $T_{eq}$, and salinity. Since some equilibrators were operated open to the room air, $P_{eq}$ values may be equal to the ship’s interior pressure or to the barometric pressure outside the ship depending on the location of the equilibrator. When an equilibrator is located in an enclosed shipboard laboratory and is open to the room air, $P_{eq}$ is the ambient pressure in the laboratory. While an equilibrator operated in an enclosed space, only the barometric pressure at sea surface was reported in some data sets, but not $P_{eq}$. In such cases, $P_{eq}$ is assumed to be the reported barometric pressure at sea surface plus 3 mb, that represents an overpressure normally maintained inside a ship. This correction increases the (pCO$_2$)$_{sw}$ value by about 1 µatm. When the pressure was not reported, we used the climatological value in the nearest box from the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) Reanalysis II Project file for the month of the observation.

The pCO$_2$ at in-situ seawater temperature is computed using an integrated form of the temperature effect for isochemical seawater, ($\partial \ln pCO_2/\partial T$)$_{Sal, Alk, TCO_2}$ (Takahashi et al., 1993):
\begin{align*}
(p\text{CO}_2)_{\text{sw}} @ \text{in situ} &= [(p\text{CO}_2)_{\text{sw}} @ \text{eq}] \ \text{Exp}\{0.0433 \ (T_{\text{in situ}} - T_{\text{eq}}) - 4.35 \times 10^{-5} \ [(T_{\text{in situ}})^2 - (T_{\text{eq}})^2]\}
\end{align*}

where the “sw” and “eq” indicate the in situ and equilibrator conditions respectively. Throughout the computation, CO\textsubscript{2} gas is assumed to behave as an ideal gas that mixes with air and water vapor ideally. Although CO\textsubscript{2} fugacity is used in a number of published papers and data reports, we refrained from using the fugacity since it is computed differently from an investigator to another. Although we do not list the sea-air p\text{CO}_2 differences in this report, we recommend the formula below for the computation of atmospheric p\text{CO}_2 and the corresponding value for sea-air p\text{CO}_2 difference.

\begin{align*}
(p\text{CO}_2)_{\text{air}} &= (V_{\text{CO}_2})_{\text{air}} \ (P_{\text{baro}} - P_{\text{sw}})
\end{align*}

where \(P_{\text{baro}}\) is the barometric pressure at sea surface, and \(P_{\text{sw}}\) is the equilibrium water vapor pressure at the temperature and salinity for mixed layer water. The subscript “air” indicates the value for atmosphere samples.

The sea-air p\text{CO}_2 difference, \(\Delta p\text{CO}_2\), is then computed using:

\begin{align*}
\Delta p\text{CO}_2 &= (p\text{CO}_2)_{\text{sw}} - (p\text{CO}_2)_{\text{air}}
\end{align*}

Since CO\textsubscript{2} is assumed to be an ideal gas for both \((p\text{CO}_2)_{\text{sw}}\) and \((p\text{CO}_2)_{\text{air}}\), the small effects of non-ideality should cancel due to differencing for \(\Delta p\text{CO}_2\). Positive \(\Delta p\text{CO}_2\) values indicate that the sea is a source for atmospheric CO\textsubscript{2}, whereas negative values indicate that the sea is a sink.

Beginning with V2007 we added a column reporting the partial pressure of CO\textsubscript{2} in seawater in units of Pascals.

Values for the fugacity of CO\textsubscript{2} in seawater, \(f\text{CO}_2\), have been submitted to LDEO by some investigators. In principle, the chemical potential of CO\textsubscript{2} should be represented by \(f\text{CO}_2\). However, in practice, the fugacity values reported by various investigators are not clearly defined as to whether only the non-ideality arising from CO\textsubscript{2}-CO\textsubscript{2} molecular interactions is considered and/or that from CO\textsubscript{2}-H\textsubscript{2}O interactions is also included. The original determination of the solubility of CO\textsubscript{2} in seawater by Murray and Riley (1971), which was conducted by equilibrating 1 atmosphere total pressure of pure CO\textsubscript{2} gas, appears to include implicitly the effects of CO\textsubscript{2}-H\textsubscript{2}O interactions in gas phase above seawater samples, since the CO\textsubscript{2} gas above the sample water contained water vapor in equilibrium with the sample water at respective temperatures. Weiss (1974) refined their data and presented a formulation for the CO\textsubscript{2} solubility under 1 atmosphere CO\textsubscript{2} fugacity. However, while Weiss’s results account primarily for the CO\textsubscript{2}-CO\textsubscript{2} interactions, it is probable that the effect of CO\textsubscript{2}-H\textsubscript{2}O interactions in the gaseous phase is also included. Subsequently, Weiss and Price (1980) proposed a formulation for the CO\textsubscript{2}-H\textsubscript{2}O interactions based upon Pitzer’s correlations for interactions among gas molecules. Some researchers (e. g. Wanninkhof and Thoning, 1993) chose to correct Weiss’s fugacity values using, in addition, the Weiss-Price CO\textsubscript{2}-H\textsubscript{2}O non-ideality effect. Whether such a procedure may constitute a double correction for the CO\textsubscript{2}-H\textsubscript{2}O interactions is not clear. Because of these ambiguities, we have chosen to report p\text{CO}_2 values assuming ideality. Since the mole fraction concentrations of CO\textsubscript{2} in equilibrated gas samples, temperature and pressure of equilibration are also included in the file, anyone who wishes to compute \(f\text{CO}_2\) will be able to compute it with one’s preferred algorithm for fugacity.

Since \(f\text{CO}_2\) values are always smaller than the corresponding p\text{CO}_2 values by 1 to 2 \(\mu\text{atm}\) and the differences are large enough with respect to the precision of measurements and the mean global sea-air p\text{CO}_2 difference of about 10 \(\mu\text{atm}\), they should not be used interchangeably with p\text{CO}_2. On the other hand, the sea-air difference in \(f\text{CO}_2\) is numerically indistinguishable with measurement errors from the sea-air p\text{CO}_2 difference (p\text{CO}_2) as long as \(f\text{CO}_2\) in air and p\text{CO}_2 in air are computed in the same manner as \(f\text{CO}_2\) and p\text{CO}_2 for the seawater respectively.
In all OISO data files, only $f$CO$_2$ values are reported without pCO$_2$ values or CO$_2$ concentrations in dried equilibrated gas. We had to convert the reported $f$CO$_2$ values to pCO$_2$ values to make the OISO data consistent with the rest of the database. Since formulations used for $f$CO$_2$ calculation are not provided in their data report, it is not possible to re-compute pCO$_2$. Therefore, we use the following approximation for the conversion;

$$pCO_2 (\mu atm) = fCO_2 (\mu atm) \times [1.00436 - 4.669 \times 10^{-5} \times SST (°C)]$$

This yields pCO$_2$ values greater than $f$CO$_2$ by 0.8 to 1.8 µatm (about 1.3 µatm on the average) in the range of temperatures and pCO$_2$ values encountered in the OISO study areas in the southern Indian Ocean.

5. QUALITY CONTROL

Determination of surface water pCO$_2$ requires measurements for a number of parameters in addition to the concentration of CO$_2$ in the carrier gas equilibrated with seawater. With the broad range of data sources and continued evolution of the measurement systems, it has not been possible to ensure that the observations contain all the necessary data elements with desired precisions. In some cases, pCO$_2$ or fCO$_2$ was reported without $V_{CO2}$, sometimes with the pressure at the time of equilibration, sometimes not. Some files contained only the sea surface temperature and the pCO$_2$ at that temperature, but not the temperature and pCO$_2$ at equilibration. Ideally the incoming file should contain the mole fraction concentration of CO$_2$ in a parcel of dried air equilibrated with seawater ($V_{CO2}$), the temperature at the time of equilibration and the equilibration pressure. When the pressure was not reported, we used the climatological value in the nearest box from the NCEP/NCAR Reanalysis II Project file for the month of the observation. We accepted data points that contained pCO$_2$ and sea surface temperature with or without the pressure.

Field data obtained in earlier years do not necessarily have all the required supporting measurements. For example, the temperatures of equilibration and water samples were recorded by hand at intervals of a few to several hours, and hence these values are often interpolated linearly with time between measurements. The salinity is measured only at hydrographic stations, and these values were interpolated between stations. When salinity was not measured during some expeditions, climatological values were assigned. Some data were unrecoverable and lost as a result of changes in computer systems (hard and software). For the past decade, computer controlled systems for underway surface water pCO$_2$ measurements have been deployed widely, and more complete high quality data sets have been obtained. In constructing this data file, we exercised our personal judgment for accepting and rejecting data, especially those collected in earlier years. For more recent data sets, water flow rates through the equilibrator and the temperatures of equilibrator water are recorded for each pCO$_2$ measurement. They often served as important criteria for identifying satisfactory operation of the equilibrator. Measurements made at reduced or stopped water flow conditions were rejected, as were those made at unusually rapid changes in the temperature of the water in an equilibrator. CO$_2$ gas analyzers are commonly calibrated using three or more gas mixtures of different CO$_2$ concentrations. Those measurements made using only a single calibration gas mixture are subject to unspecified uncertainties, and hence are rejected.

All data points have been examined individually as they were integrated into this database. While not perfect, we have tried to edit out obvious problems, erring on the side of leaving IN questionable ones. Considering differences in equilibrator designs, calibration methods and some interpolated parameters, we estimate that the uncertainty of the pCO$_2$ data presented in this data file is about ± 2.5 µatm on the average.

We have rejected the use of data quality flags in our files. The original team who performed the measurements is in the best position to accept or reject individual measurements. With this in mind, we either accept or reject data, using our best judgment, and erring on the side of including data points.
The LDEO underway pCO$_2$ systems consist of an air-water equilibrator and IR CO$_2$ analyzer. The pCO$_2$ values measured at equilibrator temperatures are recorded every 3 minutes along with the temperatures of equilibration and in-situ temperatures (measured by TSG). The equilibrator temperatures lag behind the in-situ temperatures due to the transit time of pumped seawater from the bow of ship to the pCO$_2$ system. We have developed a simple statistical method for synchronizing TSG temperatures with equilibrator temperatures. The variance of the (Equilibrator temperature – TSG) temperature differences was minimized by advancing the equilibrator temperatures by one 3-minute time step at time. About 2.3 million pCO$_2$ data reported from the ships RVIB Palmer, RV Gould and USCGC Healy have been reanalyzed for the time lag using the method. The time lag is estimated to be about 3 to 6 minutes for the Palmer and the Gould, and up to 15 minutes for the Healy. The time lag introduced errors in the uncorrected (equilibration – in-situ) temperatures of up to ±0.5 °C for the Palmer and Gould, and up to ±1 °C for the Healy. We find that the standard deviation of the (equilibrator - in-situ) temperature differences for the corrected data set is about ±0.1 °C, which is consistent with the precision of temperature measurements. Accordingly, the seawater pCO$_2$ values, which were originally reported to CDIAC by assuming no time lag, are corrected by up to ±8 uatm (= 0.5 °C x 16 uatm °C$^{-1}$) using ($\partial \ln \text{pCO}_2 / \partial T$) of 0.0423 °C$^{-1}$, Takahashi et al., 1993) for the Palmer and Gould data and up to ±16 uatm (=1.0°C x 16 uatm °C$^{-1}$) for the Healy data. As a result of the corrections, the random errors in pCO$_2$ caused by the temperature-induced errors are reduced to within ±1 uatm. The mean of uncorrected pCO$_2$ values for each cruise is found to be virtually unchanged from that of the corrected values. The details of the method used and examples are described in CDIAC report by Takahashi and Sutherland (2015).

During some special expeditions (e.g. Hales and Takahashi, 2004), the time lag was determined precisely by using the arrival times of marker events (such as sharp temperature steps in water column), and the data were corrected for the measured time lag. Some of the pCO$_2$ data were obtained from bottled samples, in which the temperature and salinity were measured. Hence these data do not require time lag corrections. However, since most of the data listed in this database were obtained using underway systems, they may require time lag corrections unless the corrections were already applied by the data producers.

Seawater pCO$_2$ values that were computed using the alkalinity, total CO$_2$ concentration and pH data are not included in this data file because of their large uncertainties and potential biases resulting from different dissociation constants of carbonic, boric and other acids used for the computations.

During many cruises, atmospheric CO$_2$ concentrations were measured concurrently with surface water pCO$_2$. However, we suspect that many of them were contaminated by local sources (such as ship’s exhausts). Since atmospheric CO$_2$ concentrations vary from one air mass to another, especially in the northern hemisphere, distinguishing local contamination from natural variability is difficult. Hence, we decided to omit the atmospheric CO$_2$ data from this file. We recommend that the atmospheric CO$_2$ concentration data listed in the GLOBALVIEW-CO$_2$ for computing the sea-air pCO$_2$ difference.

### 6. DATA SOURCES

The LDEO database Version 2015 lists 10.5 million surface ocean pCO$_2$ observations made since 1957. A large portion of the data is composed of observations from the continuous underway systems, such as those used aboard the National Science Foundation icebreakers Nathaniel B. Palmer and Laurence B. Gould operating primarily in the Southern Ocean, and the research ships operated by the Atlantic Oceanographic and Meteorological Laboratory and the Pacific Marine Environmental Laboratory of the National Oceanic and Atmospheric Administration. The database also includes the observations made during a number of major national and international oceanographic programs such as Geochemical Ocean Sections Study (GEOSECS), Joint Global Ocean Flux Study (JGOFS), World Ocean Circulation Experiment (WOCE), Climate Variability (CLIVAR) Repeat Hydrography Project, Volunteer Observing Ships (VOS) Project and others, which were supported by the National Science Foundation, National
Oceanic and Atmospheric Administration, and Department of Energy. A significant number of data have been contributed by international colleagues from many countries including Japan, Germany, France, UK, Iceland, Australia, Canada, the Netherlands, Norway, and others. Table 1 lists the major contributors for the database.

Table 1. List of data contributors to the global surface water pCO$_2$ LDEO database.

<table>
<thead>
<tr>
<th>PI name</th>
<th>Institution</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Akl</td>
<td>Integrated Marine Observing System (IMOS)</td>
<td>Australia</td>
</tr>
<tr>
<td>Thorarinn S. Arnarson</td>
<td>Marine Research Institute and University of Iceland</td>
<td>Iceland</td>
</tr>
<tr>
<td>Dorothee C. E. Bakker</td>
<td>School of Environmental Sciences, University of East Anglia</td>
<td>UK</td>
</tr>
<tr>
<td>Nicholas R. Bates</td>
<td>Bermuda Institute of Ocean Sciences</td>
<td>Bermuda</td>
</tr>
<tr>
<td>Richard Bellarby</td>
<td>Bjerknes Centre for Climate Research, University of Bergen</td>
<td>Norway</td>
</tr>
<tr>
<td>Wei-Jun Cai</td>
<td>School of Marine Science and Policy, University of Delaware</td>
<td>USA</td>
</tr>
<tr>
<td>Francisco Chavez</td>
<td>Monterey Bay Aquarium Research Institute</td>
<td>USA</td>
</tr>
<tr>
<td>Liqi Chen</td>
<td>Key Lab of Global Change and Marine Atmospheric Chemistry, Third Institute of Oceanography</td>
<td>China</td>
</tr>
<tr>
<td>David W. Chipman</td>
<td>Lamont-Doherty Earth Observatory, Columbia University</td>
<td>USA</td>
</tr>
<tr>
<td>Cathy E. Cosca</td>
<td>Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration</td>
<td>USA</td>
</tr>
<tr>
<td>Bruno Delille</td>
<td>Universite de Liege, Liege</td>
<td>Belgium</td>
</tr>
<tr>
<td>Hein J. W. de Baar</td>
<td>Netherland Institute for Sea Research</td>
<td>Netherlands</td>
</tr>
<tr>
<td>Richard A. Feely</td>
<td>Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration</td>
<td>USA</td>
</tr>
<tr>
<td>Gernot Friederich</td>
<td>Monterey Bay Aquarium Research Institute</td>
<td>USA</td>
</tr>
<tr>
<td>John Goddard</td>
<td>Lamont-Doherty Earth Observatory, Columbia University</td>
<td>USA</td>
</tr>
<tr>
<td>Burke Hales</td>
<td>College of Oceanic and Atmospheric Sciences, Oregon State University</td>
<td>USA</td>
</tr>
<tr>
<td>Mario Hoppema</td>
<td>Alfred Wegener Institute for Polar and Marine Research</td>
<td>Germany</td>
</tr>
<tr>
<td>Masao Ishii</td>
<td>Meteorological Research Institute</td>
<td>Japan</td>
</tr>
<tr>
<td>Truls Johannessen</td>
<td>Bjerknes Centre for Climate Research, University of Bergen</td>
<td>Norway</td>
</tr>
<tr>
<td>J. Joao</td>
<td>National University of Ireland, Galway</td>
<td>Ireland</td>
</tr>
<tr>
<td>V. Kitidis</td>
<td>Plymouth Marine Laboratory</td>
<td>UK</td>
</tr>
<tr>
<td>C. D. Keeling</td>
<td>Scripps Institution of Oceanography, University of California San Diego</td>
<td>USA</td>
</tr>
<tr>
<td>Arne Körtzinger</td>
<td>Leibniz Institute of Marine Sciences</td>
<td>Germany</td>
</tr>
<tr>
<td>Nicolas Metzl</td>
<td>Laboratoire d’Oceanographie et du Climat, Universite Pierre et Marie Curie</td>
<td>France</td>
</tr>
<tr>
<td>A. Kuwata</td>
<td>National Research Institute of Fisheries Science</td>
<td>Japan</td>
</tr>
<tr>
<td>Takashi Midorikawa</td>
<td>Meteorological Research Institute</td>
<td>Japan</td>
</tr>
<tr>
<td>Ludger Mintrop</td>
<td>MARIANDA marine analytics and data</td>
<td>Germany</td>
</tr>
<tr>
<td>Pedro M. S. Monteiro</td>
<td>CSIR, South Africa, Jan Cilliers St, Stellenbosch 7599</td>
<td>South Africa</td>
</tr>
<tr>
<td>P. P. Murphy</td>
<td>Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration</td>
<td>USA</td>
</tr>
<tr>
<td>David R. Munro</td>
<td>Department of Atmospheric and Oceanic Sciences and Institute of Arctic and Alpine Research Laboratory, University of Colorado, Boulder, CO</td>
<td>USA</td>
</tr>
<tr>
<td>A. Nakadate</td>
<td>Pollutants Chemical Analysis Center, Marine Division, Japan Meteorological Agency</td>
<td>Japan</td>
</tr>
</tbody>
</table>
Shin-ichiro Nakaoka  National Institute for Environmental Studies, Tsukuba  Japan
Craig Neill  Integrated Marine Observing System (IMOS)  Australia
Timothy Newberger  Lamont-Doherty Earth Observatory, Columbia University  USA
Yukihiro Nojiri  Dept. of Earth & Environment Sciences, Hirosaki University and National Institute for Environmental Studies, Tsukuba  Japan
Jon Olafsson  Marine Research Institute and University of Iceland  Iceland
Are Olsen  Bjerknes Centre for Climate Research, University of Bergen  Norway
Tsueno Ono  National Research Institute of Fisheries Science  Japan
Christopher L. Sabine  Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration  USA
S. Saito  Marine Division, Global Environment and Marine Department, Japan Meteorological Agency  Japan
Ute Schuster  School of Environmental Sciences, University of East Anglia, Norwich  UK
Tobias Steinhoff  Leibniz Institute of Marine Sciences  Germany
Stewart C. Sutherland  Lamont-Doherty Earth Observatory, Columbia University  USA
Peter Salomeh  Scripps Institution of Oceanography  USA
Colm Sweeney  Earth System Research Laboratory, National Oceanographic and Atmospheric Administration  USA
Taro Takahashi  Lamont-Doherty Earth Observatory, Columbia University  USA
Bronte Tilbrook  Australian Commonwealth Scientific and Research Organization (CSIRO) Marine and Atmospheric Research  Australia
B. Ward  National University of Ireland, Galway, IRELAND  Ireland
Rik Wanninkhof  Atlantic Oceanographic and Meteorological Laboratory, National Oceanographic and Atmospheric Administration  USA
Lee S. Waterman**  Scripps Institution of Oceanography, University of California San Diego  USA
Andrew Watson  School of Environmental Sciences, University of East Anglia  UK
Ray F. Weiss  Scripps Institution of Oceanography, University of California San Diego  USA
C. S. Wong  Institute of Ocean Sciences  Canada
H. Yoshikawa-Inoue  Graduate School of Environmental Earth Science, Hokkaido University  Japan

*The PI names are given in the alphabetical order.
**Retired
***Deceased

7. DATA LISTING

This NDP consists of two files: the file called “LDEO_Database_V2015.csv” contains all the numerical data, and the file “LDEO_Database_Metadata_V2015.csv” contains information on the data source, credit, institution, etc. The data elements in “LDEO_Database_V2015.csv” and their units are listed in Table 2; and those in “LDEO_Database_Metadata_V2015.csv” are explained in Table 3. Detailed cruise documentation (such as names of ship and ports and dates for departure and arrival) may be obtained directly from the respective PI’s.
Table 2. Data elements listed in the master data file “LDEO_Database_V2015.csv”

<table>
<thead>
<tr>
<th>Field</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRUISE_ID</td>
<td>Internal LDEO Cruise Number</td>
</tr>
<tr>
<td>STN*</td>
<td>Station number assigned in the LDEO File</td>
</tr>
<tr>
<td>LAT</td>
<td>Latitude in decimal degrees (North is positive)</td>
</tr>
<tr>
<td>LON</td>
<td>Longitude in decimal degrees (East is positive)</td>
</tr>
<tr>
<td>MONTH/DAY/YEAR</td>
<td>Date</td>
</tr>
<tr>
<td>JDATE</td>
<td>Julian Date in decimal notation. Convention is 0001 UTC 1 Jan = 1.0</td>
</tr>
<tr>
<td>VCO2_SW**</td>
<td>Mole fraction concentration of CO₂ (ppm) in dried air</td>
</tr>
<tr>
<td>PCO2_TMP</td>
<td>Temperature at which pCO₂ was measured in ºC</td>
</tr>
<tr>
<td>SST</td>
<td>Sea Surface Temperature in ºC</td>
</tr>
<tr>
<td>SSS</td>
<td>Sea Surface Salinity</td>
</tr>
<tr>
<td>PCO2_SST</td>
<td>Partial Pressure of CO₂ in seawater (in units of microatmospheres) at the temperature in the SST column</td>
</tr>
<tr>
<td>PCO2_SSTPA</td>
<td>Partial Pressure of CO₂ in seawater (in units of Pascals) at the temperature in the TEMP column</td>
</tr>
<tr>
<td>PCO2_TEQ</td>
<td>Partial Pressure of CO₂ in seawater (in units of microatmospheres) at the temperature in the TEMP_PCO2 column. This is ordinarily the value that is actually measured</td>
</tr>
<tr>
<td>EQ_PBARO</td>
<td>Pressure in the equilibration vessel in units of millibars</td>
</tr>
<tr>
<td>SHIPPBARO</td>
<td>Barometric pressure in the outside air from the ship’s observation system in units of millibars</td>
</tr>
</tbody>
</table>

*Cross reference fields to the internal LDEO file name in case problems are discovered

**Missing data have the value -999.9

Table 3. Data elements listed in the metadata file “LDEO_Database_Metadata_V2015.csv”

<table>
<thead>
<tr>
<th>CruiseID</th>
<th>Internal LDEO File Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>LEG</td>
<td>Leg Number. This is an arbitrary designation in many files because of our limit of four characters for a station number. For surface underway files that normally have more than 9,999 observations we have broken the file into “legs.”</td>
</tr>
<tr>
<td>SHIP/EXPERIMENT</td>
<td>The name of the ship or other platform used, and experiment, project</td>
</tr>
<tr>
<td>CRUISE_NAME</td>
<td>Cruise name</td>
</tr>
<tr>
<td>OBSERVER</td>
<td>A notation of the person making the observation or responsible for running the collection system</td>
</tr>
<tr>
<td>DEPARTURE_PORT</td>
<td>Port of Departure</td>
</tr>
<tr>
<td>DEPARTURE_DATE</td>
<td>Date of Departure</td>
</tr>
<tr>
<td>ARRIV_PORT</td>
<td>Port of Arrival</td>
</tr>
<tr>
<td>ARRIV_DATE</td>
<td>Date of Arrival</td>
</tr>
<tr>
<td>COMMENT*</td>
<td>Air data source and general information</td>
</tr>
</tbody>
</table>

*Additional information may be available for a particular file if needed.
8. HOW TO OBTAIN THE DATA AND DOCUMENTATION

The LDEO database NDP-088(V2015) is available free of charge from CDIAC. The complete documentation and data can be obtained from the CDIAC oceanographic web site (http://cdiac.ornl.gov/oceans/LDEO_Underway_Database/).

Contact information:

Carbon Dioxide Information Analysis Center
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6335
USA
Telephone: (865) 574-3645
Telefax: (865) 574-2232
E-mail: cdiac@ornl.gov
Internet: http://cdiac.ornl.gov/

9. ACKNOWLEDGEMENTS

Many national and international investigators contributed their observations to this database. The efforts by the investigators and supporting staff at sea and on land are acknowledged. We appreciated the encouragements offered by Richard A. Feely (PMEL/NOAA) and Rik Wanninkhof (AOML/NOAA) for establishing a compilation of surface water pCO$_2$ data over the global oceans obtained since the modern investigation of surface water pCO$_2$ started. We gratefully acknowledge that the continued support and encouragements by Joel M. Levy, David M. Legler and Kathy Tedesco from the Office of Global Programs of the National Oceanic and Atmospheric Administration has made this compilation possible. The field study of T. Takahashi and his associates have been supported by the grants from the National Science Foundation, the National Oceanic and Atmospheric Administration, the U. S. Department of Energy, EXXON Research and Engineering Company, Ford Motor Company, and the Comer Science & Educational Foundation.

10. REFERENCES


GLOBALVIEW-CO2. Cooperative Atmospheric Data Integration Project—Carbon Dioxide. CD-ROM, NOAA CMDL, Boulder, Colorado (also available on Internet via anonymous FTP to ftp.cmdl.noaa.gov, Path: ccg/co2/GLOBALVIEW).


http://scrippsc02.ucsd.edu/data/seawater_pco2/pco2_monsoon_1961.csv

http://scrippsc02.ucsd.edu/data/seawater_pco2/pco2_lusiad_1962.csv

http://scrippsc02.ucsd.edu/data/seawater_pco2/pco2_lusiad_1963.csv
