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GLOBAL OCEAN SURFACE WATER PARTIAL PRESSURE OF CO_2 DATABASE: MEASUREMENTS PERFORMED DURING 1957–2015 (Version 2015)

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND ACRONYMS

AOML	Atlantic Oceanographic and Meteorological Laboratory
CDIAC	Carbon Dioxide Information Analysis Center
CLIVAR	Climate Variability (Program)
CO_2	carbon dioxide
CSIRO	Australian Commonwealth Scientific and Research Organization
DOE	U.S. Department of Energy
FTP	file transfer protocol
fCO_2	fugacity of CO_2
GEOSECS	Geochemical Ocean Sections Study
IGY	International Geophysical Year
JGOFS	Joint Global Ocean Flux Study
LDEO	Lamont-Doherty Earth Observatory
NCAR	National Center for Atmospheric Research
NCEP	National Centers for Environmental Prediction
NDP	numeric data package
NOAA	National Oceanic and Atmospheric Administration
NSF	National Science Foundation
ORNL	Oak Ridge National Laboratory
pCO_2	partial pressure of CO_2
PMEL	Pacific Marine Environmental Laboratory
SSS	sea surface salinity
SST	sea surface temperature
VOS	Volunteer Observing Ship
WOCE	World Ocean Circulation Experiment

ABSTRACT

Takahashi, T., S.C. Sutherland and A. Kozyr. 2016. Global Ocean Surface Water Partial Pressure of CO_2 Database: Measurements Performed During 1957–2015 (Version 2015). ORNL/CDIAC-161, NDP-088(V2015). Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee, doi: 10.3334/CDIAC/OTG.NDP088(V2015).

Approximately 10.5 million measurements of surface water pCO_2 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-CO_2 analyzer systems, and have been quality-controlled based upon the stability of the system performance, the reliability of calibrations for CO_2 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 pCO_2 in seawater are listed. The overall uncertainty for the pCO_2 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 pCO_2 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 CO_2, global carbon cycle, global ocean, equilibrator-CO_2 analyzer systems.

1. INTRODUCTION

Transfer of CO_2 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) $=10^{15}$ 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 CO_2 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 CO_2 concentrations in the atmosphere (Keeling et al. 1996; Bender et al., 2005; Manning and Keeling, 2006), sea-air differences in CO_2 partial pressure (Takahashi et al., 2002; Takahashi et al., 2009), distribution of carbon isotopes (^{12}C, ^{13}C and ^{14}C) (Gruber and Keeling, 2001; Quay et al, 2003), inversion of atmospheric CO_2 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 CO_2 emissions are absorbed annually by the oceans, and about 50% remains in the atmosphere. As a result, the atmospheric CO_2 concentration is increasing at a mean rate of about 1.9 ppm yr^{-1} (or 0.4% per year), and the concentration of CO_2 dissolved in surface ocean waters is also increasing, thus causing the acidification of ocean waters. Accurate documentation of changes that have occurred in the CO_2 chemistry of ocean waters is therefore important for understanding the fate of anthropogenic CO_2 released into the atmosphere as well as charting the future course of atmospheric CO_2 levels that would affect the earth's climate.

Carbon dioxide molecules react chemically with water to form bicarbonate (HCO_3^-) and carbonate ($CO_3^{=}$) ions, both of which do not communicate with the overlying air. Only about 0.5% of the total CO_2 molecules in seawater communicate with the air via gas exchange across the sea surface. This quantity is called the partial pressure of CO_2 (pCO_2), which represents the CO_2 vapor pressure. The seawater pCO_2 depends on the temperature, the total amount of CO_2 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 pCO_2 is smaller than the atmospheric pCO_2 (presently about 395 μatm), seawater takes up CO_2 from the overlying air; when it is greater than the atmospheric pCO_2, it emits CO_2 to the air. The rate of transfer of CO_2 across the sea surface is estimated by: (sea-air CO_2 flux) = (transfer coefficient) x (sea-air pCO_2 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 pCO_2 is much smaller than that for surface ocean water pCO_2, the magnitude of sea-air pCO_2 difference and hence the net flux is governed primarily by seawater pCO_2. Therefore, the interannual and seasonal variability for surface water pCO_2 is of particular interest.

The atmospheric CO_2 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 pCO_2, 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 pCO_2 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 pCO_2 and sea-air CO_2 flux (Takahashi et al., 1997) was based on about 0.25 million pCO_2 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 pCO_2 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 pCO_2 measurements were used to produce the climatological maps of pCO_2, total CO_2 concentration, alkalinity, pH, and degree of saturation for $CaCO_3$ 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.

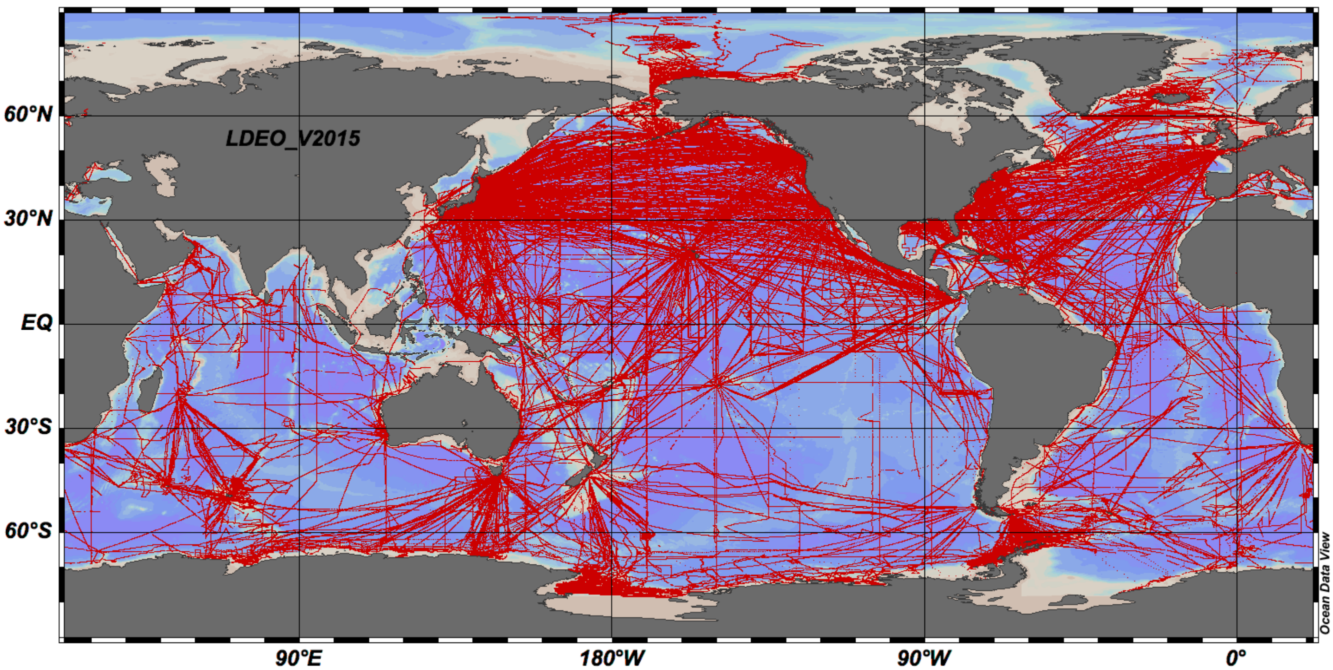

Fig. 1. Location of LDEO V2015 master database of sea surface pCO_2 observations.

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 CO_2 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 CO_2 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 CO_2 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-CO_2 analyzer systems and have been quality-controlled based on the stability of the system performance, the reliability of calibrations for CO_2 analysis, and the internal consistency of data. To allow re-examination of the data in the future, a number of measured parameters relevant to pCO_2 measurements are listed. The overall uncertainty for the pCO_2 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 CO_2 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-CO_2 analyzer systems and have been quality-controlled based on the stability of the system performance, the reliability of calibrations for CO_2 analysis, and the internal consistency of data. To allow re-examination of the data in the future, a number of measured parameters relevant to pCO_2 measurements are listed. The overall uncertainty for the pCO_2 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_{CO2} is same as X_{CO2}, 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, $(\partial \ln pCO_2/\partial T)_{Sal, Alk, TCO2}$ (Takahashi et al., 1993):

$$(pCO_2)_{sw} @T_{in\ situ} = [(pCO_2)_{sw} @\ T_{eq}]\ Exp\{0.0433\ (T_{in\ situ} - T_{eq}) - 4.35 \times 10^{-5}\ [(T_{in\ situ})^2 - (T_{eq})^2\ ]\ \}$$

where the "sw" and "eq" indicate the in situ and equilibrator conditions respectively. Throughout the computation, CO_2 gas is assumed to behave as an ideal gas that mixes with air and water vapor ideally. Although CO_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 pCO_2 differences in this report, we recommend the formula below for the computation of atmospheric pCO_2 and the corresponding value for sea-air pCO_2 difference.

$$(pCO_2)_{air} = (V_{CO2})_{air}\ (P_{baro} - P_{sw})$$

where P_{baro} is the barometric pressure at sea surface, and P_{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 pCO_2 difference, ΔpCO_2, is then computed using:

$$\Delta pCO_2 = (pCO_2)_{sw} - (pCO_2)_{air}$$

Since CO_2 is assumed to be an ideal gas for both $(pCO_2)_{sw}$ and $(pCO_2)_{air}$, the small effects of non-ideality should cancel due to differencing for ΔpCO_2. Positive ΔpCO_2 values indicate that the sea is a source for atmospheric CO_2, whereas negative values indicate that the sea is a sink.

Beginning with V2007 we added a column reporting the partial pressure of CO_2 in seawater in units of Pascals.

Values for the fugacity of CO_2 in seawater, fCO_2, have been submitted to LDEO by some investigators. In principle, the chemical potential of CO_2 should be represented by fCO_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_2-CO_2 molecular interactions is considered and/or that from CO_2-H_2O interactions is also included. The original determination of the solubility of CO_2 in seawater by Murray and Riley (1971), which was conducted by equilibrating 1 atmosphere total pressure of pure CO_2 gas, appears to include implicitly the effects of CO_2-H_2O interactions in gas phase above seawater samples, since the CO_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_2 solubility under 1 atmosphere CO_2 fugacity. However, while Weiss's results account primarily for the CO_2-CO_2 interactions, it is probable that the effect of CO_2-H_2O interactions in the gaseous phase is also included. Subsequently, Weiss and Price (1980) proposed a formulation for the CO_2-H_2O 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_2-H_2O non-ideality effect. Whether such a procedure may constitute a double correction for the CO_2-H_2O interactions is not clear. Because of these ambiguities, we have chosen to report pCO_2 values assuming ideality. Since the mole fraction concentrations of CO_2 in equilibrated gas samples, temperature and pressure of equilibration are also included in the file, anyone who wishes to compute fCO_2 will be able to compute it with one's preferred algorithm for fugacity.

Since fCO_2 values are always smaller than the corresponding pCO_2 values by 1 to 2 μatm and the differences are large enough with respect to the precision of measurements and the mean global sea-air pCO_2 difference of about 10 μatm, they should not be used interchangeably with pCO_2. On the other hand, the sea-air difference in fCO_2 is numerically indistinguishable with measurement errors from the sea-air pCO_2 difference (pCO_2) as long as fCO_2 in air and pCO_2 in air are computed in the same manner as fCO_2 and pCO_2 for the seawater respectively.

In all OISO data files, only fCO_2 values are reported without pCO_2 values or CO_2 concentrations in dried equilibrated gas. We had to convert the reported fCO_2 values to pCO_2 values to make the OISO data consistent with the rest of the database. Since formulations used for fCO_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 fCO_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 ($\partial \ln pCO_2 / \partial T$) 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-CO2 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.**

PI name*	Institution	Country
J. Akl	Integrated Marine Observing System (IMOS)	Australia
Thorarinn S. Arnarson	Marine Research Institute and University of Iceland	Iceland
Dorothee C. E. Bakker	School of Environmental Sciences, University of East Anglia	UK
Nicholas R. Bates	Bermuda Institute of Ocean Sciences	Bermuda
Richard Bellarby	Bjerknes Centre for Climate Research, University of Bergen	Norway
Wei-Jun Cai	School of Marine Science and Policy, University of Delaware	USA
Francisco Chavez	Monterey Bay Aquarium Research Institute	USA
Liqi Chen	Key Lab of Global Change and Marine Atmospheric Chemistry, Third Institute of Oceanography	China
David W. Chipman**	Lamont-Doherty Earth Observatory, Columbia University	USA
Cathy E. Cosca	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Bruno Delille	Universite de Liege, Liege	Belgium
Hein J. W. de Baar	Netherland Institute for Sea Research	Netherlands
Richard A. Feely	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
Gernot Friederich	Monterey Bay Aquarium Research Institute	USA
John Goddard**	Lamont-Doherty Earth Observatory, Columbia University	USA
Burke Hales	College of Oceanic and Atmospheric Sciences, Oregon State University	USA
Mario Hoppema	Alfred Wegener Institute for Polar and Marine Research	Germany
Masao Ishii	Meteorological Research Institute	Japan
Truls Johannessen	Bjerknes Centre for Climate Research, University of Bergen	Norway
J. Joao	National University of Ireland, Galway	Ireland
V. Kitidis	Plymouth Marine Laboratory	UK
C. D. Keeling***	Scripps Institution of Oceanography, University of California San Diego	USA
Arne Körtzinger	Leibniz Institute of Marine Sciences	Germany
Nicolas Metzl	Laboratoire d'Oceanographie et du Climat, Universite Pierre et Marie Curie	France
A. Kuwata	National Research Institute of Fisheries Science	Japan
Takashi Midorikawa	Meteorological Research Institute	Japan
Ludger Mintrop	MARIANDA marine analytics and data	Germany
Pedro M. S. Monteiro	CSIR, South Africa, Jan Cilliers St, Stellenbosch 7599	South Africa
P. P. Murphy	Pacific Marine Environmental Laboratory, National Oceanographic and Atmospheric Administration	USA
David R. Munro	Department of Atmospheric and Oceanic Sciences and Institute of Arctic and Alpine Research Laboratory, University of Colorado, Boulder, CO	USA
A. Nakadate	Pollutants Chemical Analysis Center, Marine Division, Japan Meteorological Agency	Japan

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"

CRUISE_ID*	Internal LDEO Cruise Number
STN*	Station number assigned in the LDEO File
LAT	Latitude in decimal degrees (North is positive)
LON	Longitude in decimal degrees (East is positive)
MONTH/DAY/YEAR	Date
JDATE	Julian Date in decimal notation. Convention is 0001 UTC 1 Jan = 1.0
VCO2_SW**	Mole fraction concentration of CO_2 (ppm) in dried air
PCO2_TMP	Temperature at which pCO_2 was measured in ºC
SST	Sea Surface Temperature in ºC
SSS	Sea Surface Salinity
PCO2_SST	Partial Pressure of CO_2 in seawater (in units of microatmospheres) at the temperature in the SST column
PCO2_SSTPA	Partial Pressure of CO_2 in seawater (in units of Pascals) at the temperature in the TEMP column
PCO2_TEQ	Partial Pressure of CO_2 in seawater (in units of microatmospheres) at the temperature in theTEMP_PCO2 column. This is ordinarily the value that is actually measured
EQ_PBARO	Pressure in the equilibration vessel in units of millibars
SHIPPBARO	Barometric pressure in the outside air from the ship's observation system in units of millibars

*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"

CruiseID	Internal LDEO File Name
LEG	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 many more than 9,999 observations we have broken the file into "legs."
SHIP/EXPERIMENT	The name of the ship or other platform used, and experiment, project
CRUISE_NAME	Cruise name
OBSERVER	A notation of the person making the observation or responsible for running the collection system
DEPARTURE_PORT	Port of Departure
DEPARTURE_DATE	Date of Departure
ARRIV_PORT	Port of Arrival
ARRIV_DATE	Date of Arrival
COMMENT*	Air data source and general information

*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/).

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