Uniform format surface fCO_2 database

Benjamin Pfeil and Are Olsen

Bjerknes Centre for Climate Research, Bergen, Norway

Introduction

Over the last few decades several million measurements of the surface ocean CO_2 concentration have been made, in particular following the advent of infrared based systems which determines the CO_2 concentration in an air headspace in equilibrium with a continuous stream of sea water. The concentration can be expressed as the mole fraction of CO_2 in the headspace (xCO_2), the CO_2 partial pressure (pCO_2), and the fugacity of CO_2 (fCO_2) in the headspace, which takes into account the non-ideal behavior of CO_2 gas. It is this latter which should be used for gas exchange calculations. Conversion between these can be carried out using a set of standard procedures (DOE, 1984, Dickson et al., 2007).

Unfortunately investigators have reported data differently. Some have reported xCO_2, some pCO_2, and some fCO_2 of the surface seawater. Given this, and given that the format of the files have varied it has always been a time consuming task to handle and use data from publicly available data repositories like CDIAC (Carbon Dioxide Information Analysis Center) for instance.

To alleviate this situation a uniform format global surface ocean fCO_2 data set has been developed, as encouraged by both SOLAS (at the International CO_2 Conference, Boulder 2005) and IOCCP (workshop on "Ocean Surface pCO_2 Data Integration and Database Development", Tsukuba 2004). This document briefly describes the work that has been done.

Equations

To ensure consistency we decided to recompute fCO_2 data whenever possible using a set of standard equations.

Calculations were carried out done according to *Recommendation for autonomous underway pCO_2 measuring systems and data reduction routines* by Pierrot et al, 2008, which follows the DOE handbook (DOE, 1994).

Unless otherwise specified, reported xCO_2 data were assumed to be dry mole fractions standardized by each investigator with respect to calibration gas runs. Calculation of CO_2 partial pressures from these data follows:

$$(pCO_2)^{wet}_{equT} = (xCO_2)^{dry}_{equT}(P_{equ} - pH_2O) \quad (1)$$

where $(xCO_2)^{dry}_{equT}$ is the CO_2 mole fraction and $pH_2O$is the water vapor pressure at equilibrator temperature.

Water vapor pressure is calculated according to Weiss and Price (1980):

$$pH_2O = \exp(24.4543 - 67.4509(100/T) - 4.8489\ln(T/100) - 0.000544S) \quad (2)$$

The correction for difference in intake and equilibrator temperatures was carried out using the emperical relationship derived by Takahahsi et al (1993)

$$(pCO_2)^{wet}_{SST} = (CO_2)^{wet}_{equT}\exp\{0.0423(SST - equT)\} \quad (3)$$

where SST is the sea surface temperature in the same units as *equ*T. If only fCO_2 at equilibrator temperature was provided, the conversion to in situ temperature was carried out on this.

Although several approaches are available (Copin- Montegut, 1988; Goyet et al., 1993; Takahashi et al., 1993; Weiss et al., 1982), the one of Takahashi et al. (1993) was preferred as it does not require knowledge of the alkalinity and TCO_2 of the waters and was determined for isochemical conditions, while the others were not.

The conversion of pCO_2 to fCO_2 values is carried out according to:

$$(fCO_2)^{wet}_{SST} = (pCO_2)^{wet}_{SST}\exp\left\{\frac{\left[B(CO_2,SST) + 2\left(1 - \left(x_{CO_2}\right)^{wet}_{equT}\right)^2\delta(CO_2,SST)\right]P_{equ}}{R \times SST}\right\} \quad (4)$$

where and P_{equ} is the and pressure (atm) of the equilibrator, and SST is the sea surface temperature (K). R = 82.0578 cm^3 atm mol^{-1} K^{-1}, and $B(CO_2,T)$ and $\delta(CO_2,T)$ are the virial coefficients for CO_2 (Weiss, 1974).

$B(CO_2,T)$ in cm^3 mol^{-1} is given by:

$$B(CO_2,T) = 1636.75 + 12.0408\,T - 3.27957\,10^{-2}T^2 + 3.16528\,10^{-5}T^3 \quad (5)$$

and $\delta(CO_2,T)$ in cm^3 mol^{-1} by:

$$\delta(CO_2,T) = 57.7 - 0188\,T \quad (6)$$

Implementation

The sea surface CO_2 concentration data in the files were reported in 11 different ways, and the large majority of the files contained data expressed in at least two different manners (e.g. xCO_2 and fCO_2).

Ideally we would like to have always computed or recomputed fCO_2 values from dry mole fractions along with reported equilibrator and intake temperatures, equilibrator pressure, and surface salinity using the set of equations given above. However, on many occasions not all of the required data were reported in the data files, and this necessitated the use of different starting points for our calculations and/or the use of data from external sources. In particular, atmospheric pressure and/or salinity data were sometimes missing. When pressure was missing we used 6 hourly sea level pressure data from the NCEP/NCAR reanalysis project (Kalnay et al., 1996). When salinity was not reported we used climatological monthly mean salinity data from the World Ocean Atlas 2005 (Antonov et al., 2005).

All in all this means that fCO_2 has been recomputed from different starting points and with different ancillary parameters. The different recomputed fCO_2 parameters are given in Table 1. Most times it was possible to recompute fCO_2 from different starting points in the same file, and we therefore provide the fCO_2 recommended value in each file (fCO2_rec). This is the recomputed fCO_2 value we recommend is

used. If two or more recomputed fCO_2 parameters is present, we recommend that the one calculated from closest to dry xCO_2 values is used, and this is fCO_2_rec in the data file. The order of preference is given in Table 1 as well. That is, if (1) was possible this was used as fCO2_rec, if (1) was not possible but (2) was, then (2) was used. If neither (1) nor (2) was possible but (3) was then this was used and so on. The philosophy behind this scheme was to (a) start out as close to dry xCO_2 values as possible and (b) to limit use of external data to those cases were absolutely required (i.e. when no in situ fCO_2 data could be obtained without resorting to WOA salinities or NCEP/NCAR pressures.). This also means for instance, that if fCO_2 data were provided, but no xCO_2 or pCO_2, like from for instance a CARIOCA bouy, the fCO_2 values were retained and are the fCO2_rec data in the file.

Finally, if either atmospheric pressure or NCEP/NCAR were used, 3 hPa were added to account for the overpressure normally maintained in ships (Takahashi and Sutherland, 2007)

Table 1: reported used for the recalculations in order of preference

Index[b]	CO_2 parameter	Number of cases	required extra var.
1	fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm	2250925	
2	fCO2_insitu_from_xCO2_water_sst_dry_ppm	204951	
3	fCO2_from_pCO2_water_water_equi_temp	724892	
4	fCO2_from_pCO2_water_sst_100humidity_uatm	334085	
5	fCO2_insitu_from_fCO2_water_equi_uatm	155969	
6	fCO2_insitu_from_fCO2_water_sst_100humidty_uatm	1978648	
7	fCO2_from_pCO2_water_water_equi_temp_ncep	26606	Pressure
8	fCO2_from_pCO2_water_sst_100humidity_uatm_ncep	1263959	Pressure
9	fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_woa	2281	Salinity
10	fCO2_insitu_from_xCO2_water_sst_dry_ppm_woa	2876	Salinity
11	fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_ncep	164	Pressure

12	fCO2_insitu_from_xCO2_water_sst_dry_ppm_ncep	5860	Pressure
13	fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_ncep_woa	776	Pressure, Salinity
14	fCO2_insitu_from_xCO2_water_sst_dry_ppm_ncep_woa		Pressure, Salinity

[b]Number is also used within the data file for identifying which reported CO_2 variable is used as the recommended one (fCO2_rec).

Reported data

All scripts and in- and output data have been made available along with this report. Transparency is essential for assuring the best quality data product and we encourage all to evaluate our calculations to identify errors, which may occur.

The data file contains all of the reported data, the NCEP/NCAR pressures and the WOA salinities. In addition bottom depth from ETOPO2 (http://www.ngdc.noaa.gov/mgg/global/global.html) has been included for identification of shelf and coastal data.

The file also contains an identifier which shows what input parameter was used. It should also be evident whether the original data were provided at equilibrator or intake temperature.

The following parameters are reported in the output file:

Abbreviation	Description	unit
cruise	Cruise name (the file name)	
sta	internal station number	
mon	month	
day	day	
yr	year	
hh	hour	
mm	minute	
long	longitude (0-360)	deg
lat	latitude (-90-90)	deg

bottomD	bottom depth as reported in file (can be deleted)	m
depth	intake depth used if no intake depth was reported	m
depthW	water intake depth as reported	m
temp	sea surface temperature	deg C
sal	sea surface salinity	PSU
XCO2_water_sst_wet_ppm	xCO_2 water at sea surface temperature in wet air	ppm
XCO2_water_equi_temp_wet_ppm	xCO_2 water at equilibrator temperature in wet air	ppm
XCO2_water_sst_dry_ppm	xCO_2 water at sea surface temperature in dry air	ppm
XCO2_water_equi_temp_dry_ppm	xCO_2 water at equilibrator temperature in dry air	ppm
fCO2_water_sst_100humidity_uatm	fCO_2 water at sea surface temperature in wet air (100 % humidity)	µatm
fCO2_water_corr25_uatm	fCO_2 water corrected to 25 deg C sea surface temperature in wet air	µatm
fCO2_water_corr_to_20	fCO_2 water corrected to 20 deg C sea surface temperature in wet air	µatm
fCO2_water_equi_atm	fCO_2 water at equilibrator temperature in wet air	µatm
pCO2_water_sst_100humidity_atm	pCO_2 water at sea surface temperature in wet air (100 % humidity)	µatm
pCO2_water_equi_temp	pCO_2 water at equilibrator temperature in wet air	µatm
pCO2_theta_SW_corrected_to_sst	pCO_2 water at sea surface temperature in wet air	µatm
Temperature_equi	temperature at equilibration	deg C
Pressure_atm	atmospheric pressure as reported	hPa
Pressure_equi	pressure in the equilibrator as reported	hPa
wind_direc_deg	wind direction as reported	deg
wind_speed	wind speed as reported	m/s
ship_speed	ship speed	knot

ship_direc	ship heading direction	deg
Humidity	humidity	%
woa_sss	salinity extracted from WOA 2005	PSU
woa_land_marker	0 sea 1 land	
ncep_slp	atmospheric pressure extracted from NCEP/NCAR 6 hourly data	hPa
speed_calc_knots	Ship speed calculated	knot
ETOPO2	Bottom depth extracted from ETOPO2	m
fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm	fCO_2 recomputed from xCO_2 water at equilibrator temperature in dry air; salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm
fCO2_insitu_from_xCO2_water_sst_dry_ppm	fCO_2 recomputed from xCO_2 water at sea surface temperature in dry air; salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm
fCO2_from_pCO2_water_water_equi_temp	fCO_2 recomputed from pCO_2 water at equilibrator temperature in wet air; salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm
fCO2_from_pCO2_water_sst_100humidity_uatm	fCO_2 recomputed from pCO_2 water at sea surface temperature in wet air (100 % humidity); salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm
fCO2_insitu_from_fCO2_water_equi_uatm	fCO_2 recomputed from fCO_2 water at equilibrator temperature in wet air; salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm
fCO2_insitu_from_fCO2_water_sst_100humidty_uatm	fCO_2 recomputed from fCO_2 water at sea surface temperature in wet air (100 % humidity); salinity and either atmospheric pressure or pressure at equilibration provided in the file	µatm

fCO2_from_pCO2_water_water_equi_temp_ncep	fCO_2 recomputed from pCO_2 water at equilibrator temperature in wet air, NCEP pressure used	µatm
fCO2_from_pCO2_water_sst_100humidity_uatm_ncep	fCO_2 recomputed from pCO_2 water at sea surface temperature in wet air (100 % humidity), NCEP pressure used	µatm
fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_woa	fCO_2 recomputed from xCO_2 water at equilibrator temperature in dry air, salinity from WOA used	µatm
fCO2_insitu_from_xCO2_water_sst_dry_ppm_woa	fCO_2 recomputed from xCO_2 water at sea surface temperature in dry air, salinity from WOA used	µatm
fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_ncep	fCO_2 recomputed from xCO_2 water at equilibrator temperature in dry air, NCEP pressure used	µatm
fCO2_insitu_from_xCO2_water_sst_dry_ppm_ncep	fCO_2 recomputed from xCO_2 water at sea surface temperature in dry air, NCEP pressure used	µatm
fCO2_insitu_from_xCO2_water_equi_temp_dry_ppm_ncep_woa	fCO_2 recomputed from xCO_2 water at equilibrator temperature in dry air, NCEP pressure and salinity from WOA used	µatm
fCO2_insitu_from_xCO2_water_sst_dry_ppm_ncep_woa	fCO_2 recomputed from xCO_2 water at sea surface temperature in dry air, NCEP pressure and salinity from WOA used	µatm
fCO2_rec	recoomended fCO_2	µatm
fCO2_source	Identifies which reported CO_2 value was used for calculations (see Table 1 for details)	

References

Antonov, J.I., Locarnini, R.A., Boyer, T.P., Mishonov, A.V., Garcia, H.E., 2006.

World Ocean Atlas 2005, Volume 2: Salinity. Levitus, S., ed, NOAA Atlas NESDIS 62, U.S. Government Printing Office, Washington, D.C., 182 pp.

Copin-Montegut, C., 1988. A new formula for the effect of temperature on the partial pressure of CO_2 in seawater. Marine Chemistry 25 (1), 29-37.

DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. Version 2, Dickson, A.G., Goyet, C., eds, ORNL/CDIAC-74.

Dickson, A.G., Sabine, C.L., Christian, J.R, 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3,191pp.

Goyet, C., Millero, F.J., Poisson, A., Shafer, D.K., 1993. Temperature dependence of CO_2 fugacity in seawater. Marine Chemistry 44 (2-4), 205-219.

Kalnay, E. et al, 1996. The NCEP/NCAR 40-year reanalysis project. Bulletin of American Meteorological Society 77, 437-470.

Pierrot, D., Neill, C., Sullivan, K., Castle, R., Wanninkhof, R., Lüger, H., Johannessen, T., Olsen, A., Feely R.A., Cosca, C.E., 2008. Recommendations for Autonomous Underway pCO2 Measuring Systems and Data Reduction Routines. Deep-Sea Research Part II. To be published.

Takahashi, T., Olafsson, J., Goddard, J.G., Chipman, D.W., Sutherland, S.C., 1993. Seasonal-Variation of CO_2 and Nutrients in the High-Latitude Surface Oceans – a Comparative-Study. Global Biogeochemical Cycles 7 (4), 843-878.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry 2, 203-215.

Weiss, R.F., Jahnke, R.A., Keeling, C.D., 1982. Seasonal effects of temperature and salinity on the partial pressure of CO_2 in seawater (Pacific Ocean). Nature 300 (5892), 511-513.

Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Marine Chemistry 8, 347–359.