Best practice data standards for discrete bottle based chemical oceanographic observations

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CISESS (UMD) & NOAA/NCEI

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(Jiang et al., 2022, doi: /10.3389/fmars.2021.705638)

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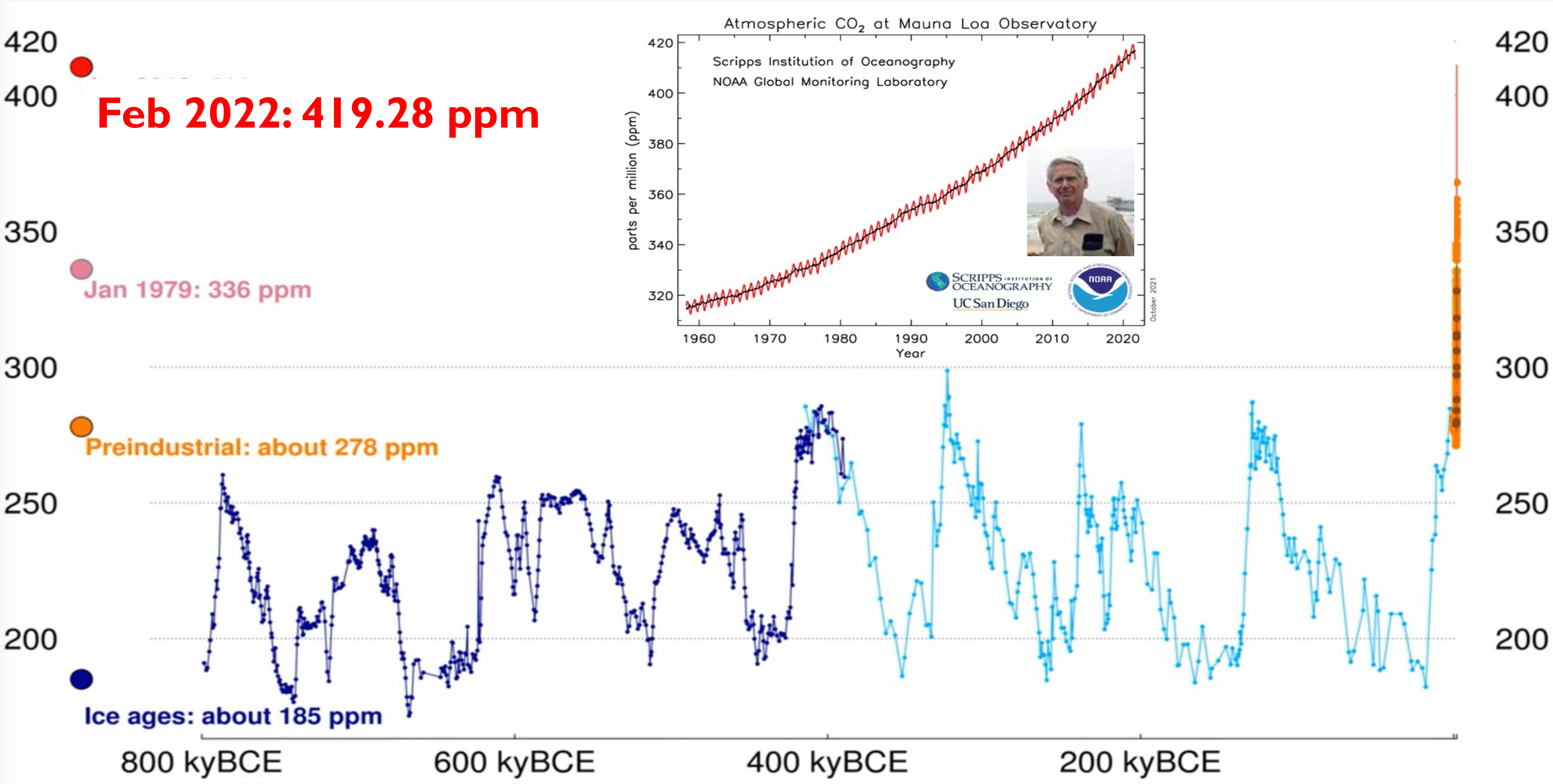
OUTLINE

- Background & introduction
- Column header standards
- Quality control flags
- A new TEOS-10 tool: GSW_Sys
- A new fCO2 tool: fCO2_Calc
- Upgraded CO2SYS tools
- Recommended CO2SYS constants
- Content vs Concentration
- Missing value indicators

Atmospheric CO_2 over the past 800,000 years

(Tans and Keeling, 2022)



Changing climate and ocean

Sources

34.8 $GtCO_2/yr$

89%

4.1 $GtCO_2/yr$

11%

Sinks

18.6 $GtCO_2/yr$

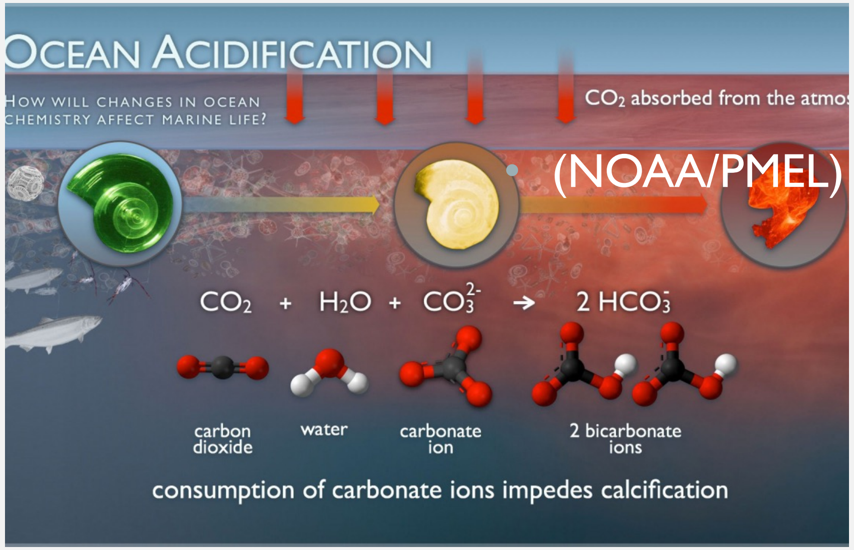
48%

11.2 $GtCO_2/yr$

29%

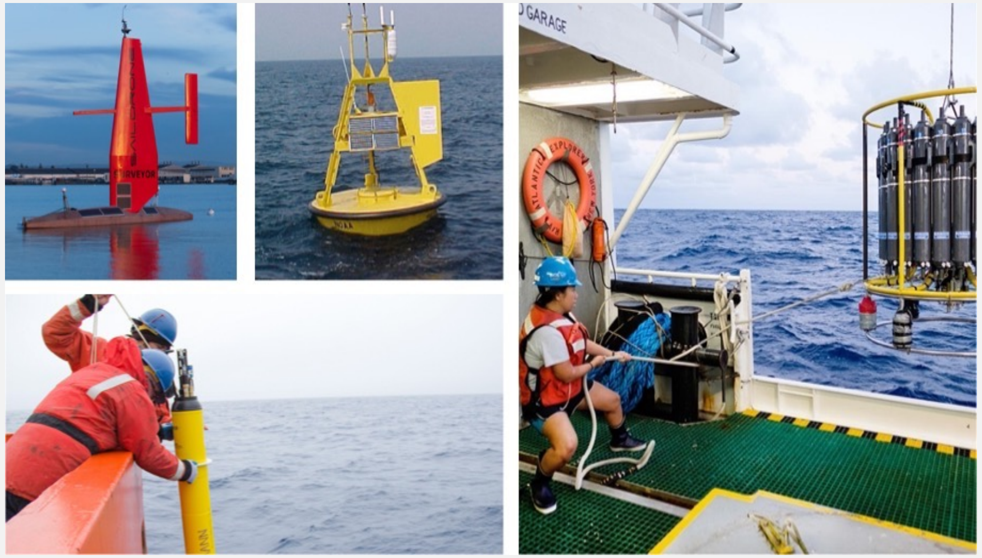
10.2 $GtCO_2/yr$

26%



(Friedlingstein et al 2021; Global Carbon Budget 2021)

From observations to mitigations & adaptions

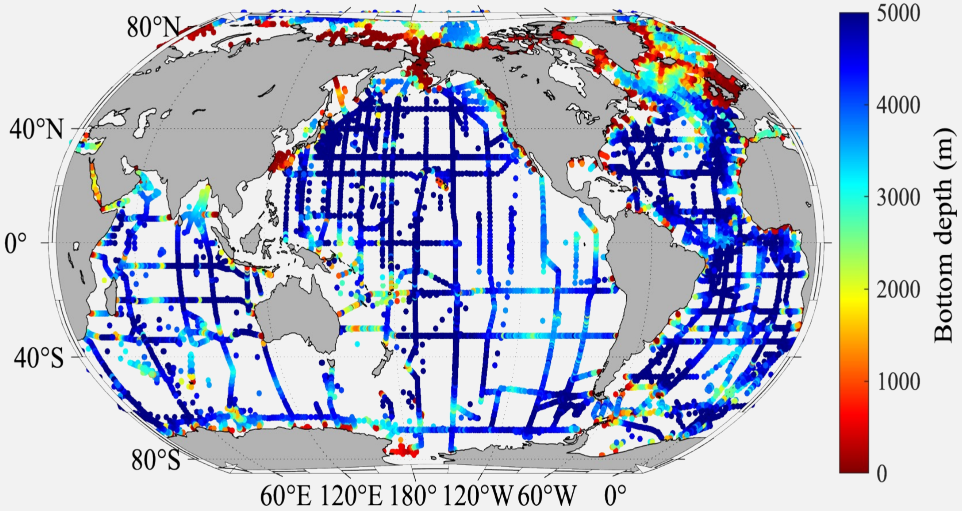


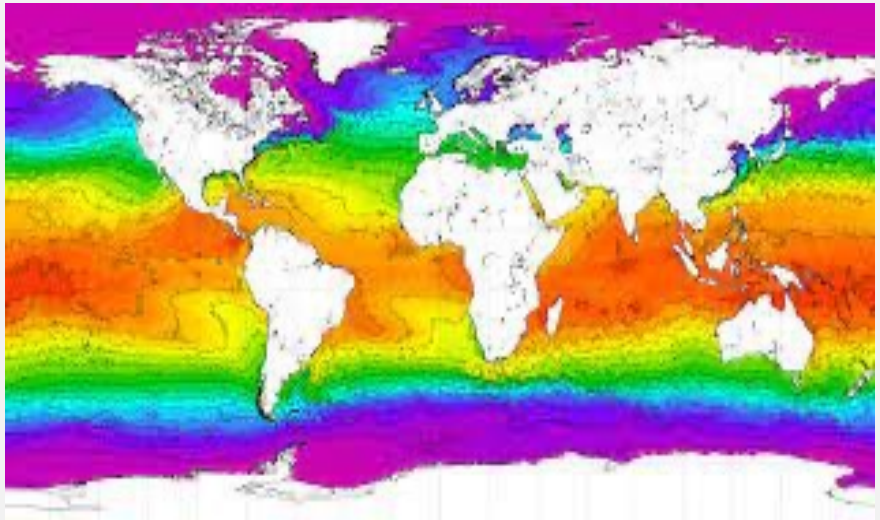
NATIONAL CENTERS FOR ENVIRONMENTAL INFORMATION

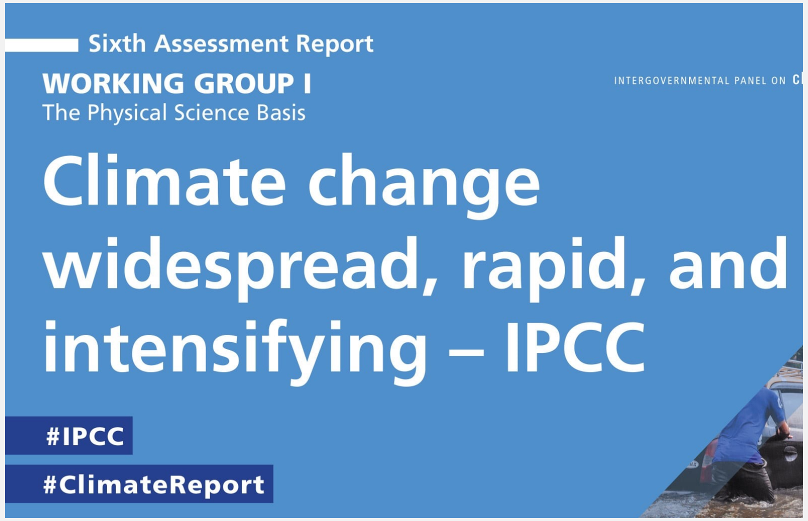
CCHDO
CLIVAR & Carbon Hydrographic Data Office

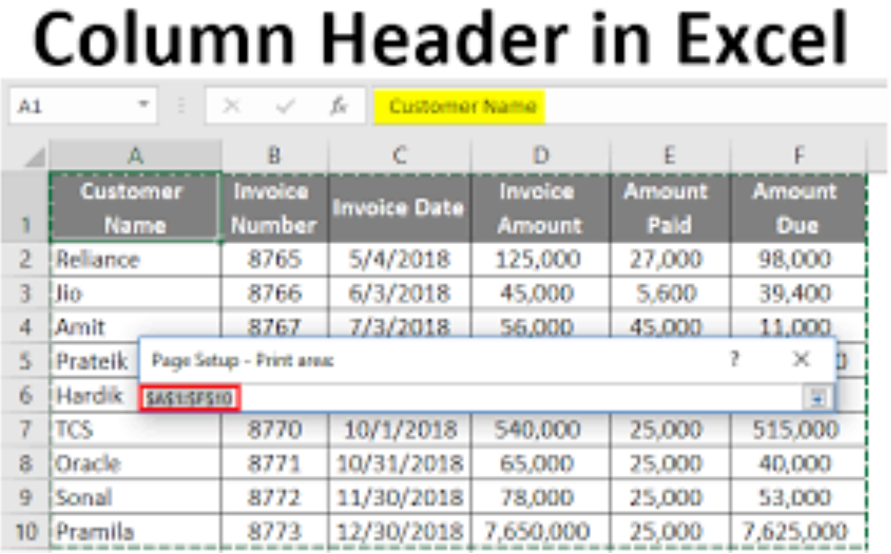
IAEA
Ocean Acidification International Coordination Centre
OA-ICC

(Lauvset et al. 2021)









	A	B	C	D	E	F
1	Customer Name	Invoice Number	Invoice Date	Invoice Amount	Amount Paid	Amount Due
2	Reliance	8765	5/4/2018	125,000	27,000	98,000
3	Jio	8766	6/3/2018	45,000	5,600	39,400
4	Amit	8767	7/3/2018	56,000	45,000	11,000
5	Prateik					
6	Hardik					
7	TCS	8770	10/1/2018	540,000	25,000	515,000
8	Oracle	8771	10/31/2018	65,000	25,000	40,000
9	Sonal	8772	11/30/2018	78,000	25,000	53,000
10	Pramila	8773	12/30/2018	7,650,000	25,000	7,625,000

$$s = \sqrt{\frac{\sum(x - \bar{x})^2}{n - 1}}$$

DATA STANDARDS

CCHDO WHP Exchange format

(Joyce and Corry, 1994; Swift and Diggs, 2008)

Exchange Format 1.2.0 documentation

Search

- Introduction
- Common Format Features
- Bottle Specific
- CTD Specific
- Quality Codes
- **Parameters**
- Changelog

- TCARBN
- ALKALI
- FCO2
- FCO2IN
- FCO2TMP
- PCO2
- PCO2TMP
- PH_TOT
- PH_SWS
- PH_TMP
- DOC
- TRITUM
- HELIUM
- DELHE3
- REFTMP
- REVPRS
- REVTMP
- CH4
- DMS
- N2
- CALCIUM
- ARGON
- 14C-DOC
- 13C-DOC
- D15N_NO3
- D15N_NO2+NO3
- D18O_NO2+NO3
- D18O_NO3
- UREA
- TOT_CHL_A
- TOT_CHL_B
- TOT_CHL_C
- ALPHA-BETA-CAR
- BUT-FUCO
- DCNS
- DELO17
- FUCO
- GALA
- GLUC
- MAN
- RHAM
- LAB_DEN
- PIGMENTS
- SALTREF
- SF5CF3
- DWNPRS
- DWNOXY
- SIG0
- SOMSAL
- HPLC
- MICROGELS

(Credit: https://exchange-format.readthedocs.io/en/latest/index.html)

Drivers of this new column header standard

I. Old technology & suboptimal headers

- *SALNTY* – Salinity
- *NITRAT* – Nitrate
- *TCARBN* – Total dissolved inorganic carbon content
- *ALKALI* – Total alkalinity content
- *BIONBR* – Sample identification number used by the Bedford Institute of Oceanography (BIO).
- *REVPRS* – *Sea water pressure as determined via a pair of reversing thermometers.*

III. Lack of broader international usage

- Need to publish the standards on a peer-reviewed paper
- Promote international usage

New Column Header standards

Abbreviation [unit]	Full unit	Decimal places	Description	Exchange format
DIC [umol/kg]	10^{-6} mol kg^{-1}	1	Total dissolved inorganic carbon content	TCARBN (UMOL/KG)
DIC_flag	N/A	N/A	Quality control flag for DIC (see Table 2)	TCARBN_FLAG_W
TA [umol/kg]	10^{-6} mol kg^{-1}	1	Total alkalinity content	ALKALI (UMOL/KG)
TA_flag	N/A	N/A	Quality control flag for TA	ALKALI_FLAG_W
pH_T_measured	N/A	4	pH measured on Total Scale (T) at measurement temperature	PH_TOT
TEMP_pH [deg_C]	degree Celsius	2	Temperature at which the pH_T_measured value is measured	PH_TMP (DEG_C)
pH_flag	N/A	N/A	Quality control flag for pH_T_measured.	PH_TOT_FLAG_W
Carbonate_measured [umol/kg]	µmol kg^{-1}	1	Dissolved carbonate ion content ($[CO_3^{2-}]$) at measurement temperature	N/A
TEMP_Carbonate [deg_C]	degree Celsius	2	Temperature at which the Carbonate_measured value is measured	N/A
Carbonate_flag	N/A	N/A	Quality control flag for Carbonate_measured	N/A

3 sets of WOCE QC flags

Niskin bottles

Flag	
1	Bottle info… …vailable
2	No proble…
3	Leaking
4	Did not tr…
5	Not repor…
6	Significar… …y in measured… …veen Gerard and Niski…
7	Unknown…
8	Pair did n… …tly.
9	Samples… …om this bottle

Discrete water samples

Flag	Meaning
1	Sample was drawn but analysis not received.
2	Acceptable measurement
3	Questionable measurement
4	Bad measurement
5	Not reported
6	Mean of replicate measurements
7	Manual chromatographic peak measurement
8	Irregular digital chromatographic peak integration
9	Sample not drawn for this measurement

Sensor measurements

Flag	Meaning
1	N…
2	A…
3	Q…
4	B…
5	N…
6	In… …al
7	D…
8	N…
9	Not sampled

Joyce and Corry (1994)

New consolidated QC flags

Flag	Meaning
2	Acceptable
3	Questionable
4	Known bad
6	Median of replicates
9	Missing value

TEOS-10

- 1980 International Equation of State of Seawater (EOS-80) standard (Millero et al., 1980; Millero and Poisson, 1981).
- In June 2009, the IOC, SCOR, and IAPSO adopted **International Thermodynamic Equations of Seawater 2010 (TEOS-10)** as a new standard for calculation of the thermodynamic properties of seawater.
- **Absolute Salinity S_A** (mass fraction of salt in seawater, unit: g/kg) as opposed to Practical Salinity S_P (a measure of the conductivity of seawater, unitless) to describe the salt content of seawater. Ocean salinities now have units of.
- **Conservative Temperature Θ** in place of potential temperature θ.

GSW_Sys

[A new tool for TEOS-10 related calculations]

- Depth from pressure,
- Absolute salinity,
- Conservative temperature,
- Density anomaly,
- AOU
- Oxygen saturation

START	START	START	START	START	START	START	Missing Data											
							-999											
Latitude (dec)	Longitude (dec)	● P (dbars) / ○ Depth (m)	Practical S (SP)(PSS-78)	t(oC) (ITS-90)	D.O. (µmol/kg))	Clear DATA <---	Depth (m)	Absolute S (SA)	θ(oC) potential @0dbar	Θ(°C) conservative	Density $(kg.m^{-3})$	Pot.Density @0dbar $(kg.m^{-3})$	σ_T $(kg.m^{-3})$	σ_θ $(kg.m^{-3})$	O2 Solub. (µmol/kg)	AOU (µmol/kg)	O2 Saturation (%)
27.390	-116.190	2496.6	34.657	1.83			2465.457	34.842	1.653	1.653	1039.191	1027.741	39.190991	27.741248	334.375		
27.390	-116.190	2001.4	34.632	2.14		Clear Results --->	1978.718	34.816	2.001	2.001	1036.905	1027.694	36.904912	27.693630	331.526		
27.390	-116.190	1500.7	34.582	2.86	200		1485.441	34.764	2.753	2.753	1034.504	1027.589	34.504343	27.588728	325.507	125.507	61.44
27.390	-116.190	1001.9	34.503	4.03			992.888	34.681	3.954	3.954	1032.019	1027.408	32.019261	27.407762	316.300		
27.390	-116.190	751.2	34.4	5.09			744.889	34.619	5.028	5.028	1030.688	1027.241	30.688290	27.241453	308.424		
27.39	-116.19	501.2	34.355	6.73			497.288	34.526	6.683	6.684	1029.248	1026.962	29.247891	26.961929	296.964		
27.39	-116.19	401.6	34.364	7.75			398.561	34.534	7.710	7.711	1028.648	1026.824	28.648266	26.824359	290.107		
27.39	-116.19	301.2	34.25	8.5	200		298.993	34.417	8.468	8.471	1027.985	1026.620	27.984648	26.620200	285.473	85.473	70.06
27.39	-116.19	200.9	34.343	10.45			199.476	34.509	10.426	10.428	1027.274	1026.371	27.273548	26.371298	273.382		
27.39	-116.19	150.3	34	10.46	200		149.253	34.163	10.442	10.451	1026.776	1026.100	26.775972	26.100259	273.958	73.958	73.00
27.39	-116.19	124.5	33.593	10.24			123.641	33.754	10.226	10.242	1026.380	1025.820	26.380395	25.819555	276.036		
27.39	-116.19	101.3	33.452	11.64			100.606	33.611	11.627	11.648	1025.915	1025.461	25.914557	25.461022	268.215		
27.39	-116.19	81.1	33.373	13.27			80.549	33.532	13.259	13.285	1025.447	1025.086	25.446516	25.085970	259.473		
27.39	-116.19	61.3	33.366	14.84	200		60.886	33.524	14.831	14.861	1025.025	1024.754	25.024790	24.754059	251.428	51.428	79.55
27.39	-116.19	49.9	33.409	16.07			49.565	33.567	16.062	16.094	1024.734	1024.515	24.734479	24.515212	245.367		
27.39	-116.19	40.8	33.451	16.99			40.527	33.609	16.983	17.016	1024.513	1024.335	24.513469	24.334849	240.994		
27.39	-116.19	30.4	33.448	17.42			30.197	33.606	17.415	17.449	1024.363	1024.230	24.363136	24.230257	239.031		
27.39	-116.19	20.6	33.48	18.04			20.463	33.638	18.037	18.071	1024.194	1024.105	24.194383	24.104553	236.201		
27.39	-116.19	11	33.482	18.08			10.927	33.640	18.078	18.113	1024.144	1024.096	24.143855	24.095890	236.014		

(Pierrot et al, 2021)

fCO2_Calc

[A new tool to calculate fCO_2 from xCO_2]

$$P_{H2O} = \exp[24.4543 - 67.4509 \times (100/T) - 4.8489 \times \ln(T/100) - 0.000544\ S]$$

$$pCO_2\_SW@TEMP\_EQU = xCO_2\_EQU \times (PRES\_EQU - P_{H2O})$$

$$pCO_2\_SW@SST = pCO_2\_SW@TEMP\_EQU \times \exp[0.0423\ (SST - Teq)]$$

$$B_{11} = -1636.75 + 12.0408\ T - 0.0327957\ T^2 + 3.16528 \times 10^{-5}\ T^3)$$

$$\sigma_{12} = 57.7 - 0.118\ T$$

$$fCO_2\_SW@SST = pCO2\_SW@SST \times exp(\frac{(B_{11} + 2\ \boldsymbol{\sigma}_{12}) \times P_{sea-surface}}{(82.0578 \times SST)})$$

START START START START START START START

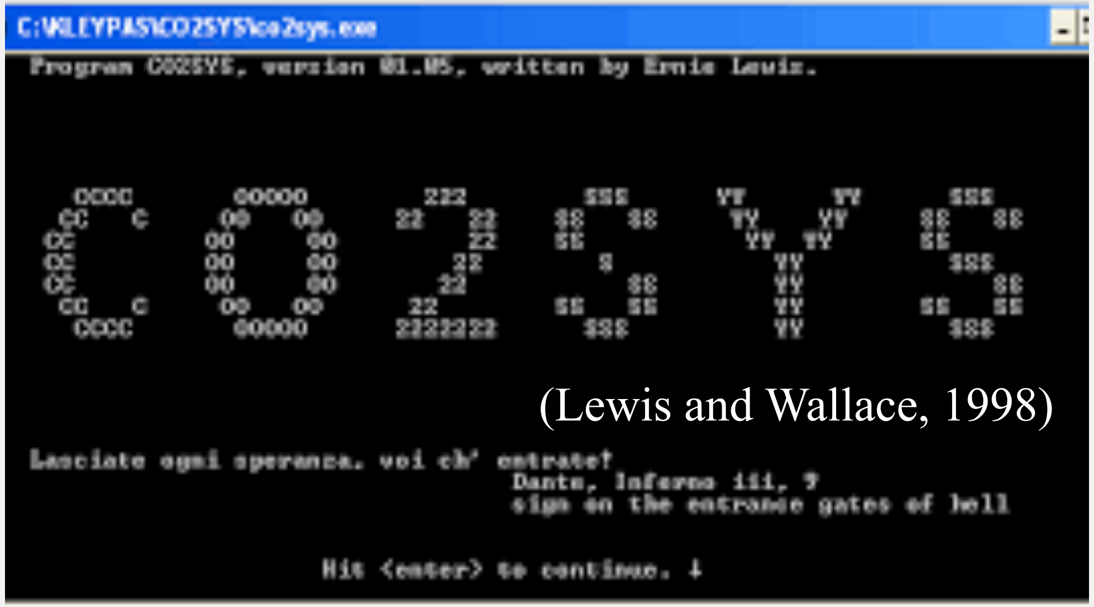
Barometer Height(m) = 0

SSS (PSS-78)	SST (oC)	xCO2 water (ppm)	xCO2 air (ppm)	t equ (oC)	P equ (mbar)	P air mbar		P air SeaLevel (mbar)	pH2O (@t_equ) (mbar)	pH2O (@SST) (mbar)	pCO2 (@t_equ) (µatm)	pCO2 (@SST) (µatm)	pCO2 air (µatm)	ΔpCO2(w-a) (µatm)	fCO2 (@t_equ) (µatm)	fCO2 (@SST) (µatm)	fCO2 air (µatm)	ΔfCO2(w-a) (µatm)
							Clear DATA <----											
33.907	1.629	401.249	381.906	1.992197	986.99646	985.69		985.69	6.9184	6.7409	388.11	382.20	368.98	13.22	386.49	380.60	367.43	13.17
33.908	1.645	400.111	381.949	1.948332	987.197876	985.61	Clear Results --->	985.61	6.8968	6.7486	387.10	382.17	368.99	13.18	385.49	380.57	367.44	13.13
35.231	10.000	420.000	381.949	10.000	987.197876	985.61		985.61	12.0332	12.0332	404.21	404.21	366.99	37.22	402.70	402.70	365.62	37.08
36.579	11.300	435.000	381.949	11.300	987.197876	985.61		985.61	13.1129	13.1129	418.19	418.19	366.59	51.60	416.64	416.64	365.24	51.41
36.350	12.500	449.000	381.949	12.500	987.197876	985.61		985.61	14.1955	14.1955	431.17	431.17	366.18	64.99	429.60	429.60	364.85	64.75
36.450	12.370	460	381.949	12.370	987.197876	985.61		985.61	14.0740	14.0740	441.78	441.78	366.22	75.56	440.18	440.18	364.89	75.28
36.387	16.700	320	381.949	16.700	987.197876	985.61		985.61	18.6210	18.6210	305.89	305.89	364.51	-58.62	304.84	304.84	363.26	-58.42
36.350	22.100	321	381.949	22.100	987.197876	985.61		985.61	26.0605	26.0605	304.49	304.49	361.71	-57.22	303.51	303.51	360.54	-57.03
36.670	23.500	256	381.949	23.500	987.197876	985.61		985.61	28.3641	28.3641	242.25	242.25	360.84	-118.59	241.48	241.48	359.70	-118.21
36.890	28.100	385	381.949	28.100	987.197876	985.61		985.61	37.2476	37.2476	360.95	360.95	357.49	3.46	359.87	359.87	356.42	3.45

(Pierrot et al, 2021)

Ocean carbon system parameters

- # 1 = Total Alkalinity
- # 2 = Dissolved inorganic carbon
- # 3 = pH
- # 4 = partial pressure (pCO_2)
- # 5 = fugacity (fCO_2)
- # ? = carbonate ion ($[CO_3^{2-}]$)



ELSEVIER
Marine Chemistry
Volume 209, 20 February 2019, Pages 70-80

Carbonate ion concentrations in seawater: Spectrophotometric determination at ambient temperatures and evaluation of propagated calculation uncertainties

Jonathan D. Sharp, Robert H. Byrne

College of Marine Science, University of South Florida, 140 7th Avenue South, St. Petersburg, FL 33701, USA

Upgraded CO2SYS and seacarb

Platform	Program	Version	New input variables	Link	Reference
MS Excel	CO2SYS_v3.0_Err.xlsm	3.0	$[CO_3^{2-}]$	https://github.com/dpierrot/co2sys_xl	Pierrot, 2021
MATLAB/ Octave	CO2SYS.m, errors.m	3.1.1	$[CO_3^{2-}]$, $[HCO_3^-]$, $[CO_2^*]$	http://doi.org/10.5281/zenodo.3950562	Sharp et al., 2021
Python	PyCO2SYS	1.8.0	$[CO_3^{2-}]$, $[HCO_3^-]$, $[CO_2^*]$, xCO_2	https://PyCO2SYS.readthedocs.io	Humphreys et al., 2021, 2022
R	seacarb	3.2.13	$[CO_3^{2-}]$, $[HCO_3^-]$, $[CO_2^*]$	https://CRAN.R-project.org/package=seacarb	Gattuso et al., 2021

Choice of dissociation constants

K_1 and K_2 dissociation constants of the ocean carbon system:

1 = Roy, 1993	T: 0-45 S: 5-45. Total scale. Artificial seawater.
2 = Goyet & Poisson	T: -1-40 S: 10-50. Seaw. scale. Artificial seawater.
3 = HANSSON	T: 2-35 S: 20-40. Seaw. scale.
4 = MEHRBACH	T: 2-35 S: 20-40. Seaw. scale.
5 = HANSSON and MEHRBACH	T: 2-35 S: 20-40. Seaw. scale.
6 = GEOSECS (i.e., original Mehrbach)	T: 2-35 S: 19-43. NBS scale. Real seawater.
7 = Peng	T: 2-35 S: 19-43. NBS scale. Real seawater.
8 = Millero, 1979, FOR PURE WATER	T: 0-50 S: 0.
9 = Cai and Wang, 1998	T: 2-35 S: 0-49. NBS scale. Real and artificial seawater.
10 = Lueker et al, 2000	T: 2-35 S: 19-43. Total scale. Real seawater.
11 = Mojica Prieto and Millero, 2002	T: 0-45 S: 5-42. Seaw. scale. Real seawater
12 = Millero et al, 2002	T: -1.6-35 S: 34-37. Seaw. scale. Field measurements.
13 = Millero et al, 2006	T: 0-50 S: 1-50. Seaw. scale. Real seawater.
14 = Millero 2010	T: 0-50 S: 1-50. Seaw. scale. Real seawater.
15 = Waters, Millero, & Woosley 2014	T: 0-50 S: 1-50. Seaw. scale. Real seawater.
16 = Sulpis et al, 2020	T: -1.7-32 S: 31-38. Total scale. Field measurements.

Recommended CO2SYS constants

Dissociation constants of carbonic acid:

- **Lueker et al. (2000)** [S_P: 19-43, and temperature (T): 2-35°C],
- **Waters et al. (2014)** [S_P: 1-50, T: 0-50°C].

The boron-salinity (B/S_P) ratio:

- **Lee et al. (2010)** is recommended over that of Uppström (1974).

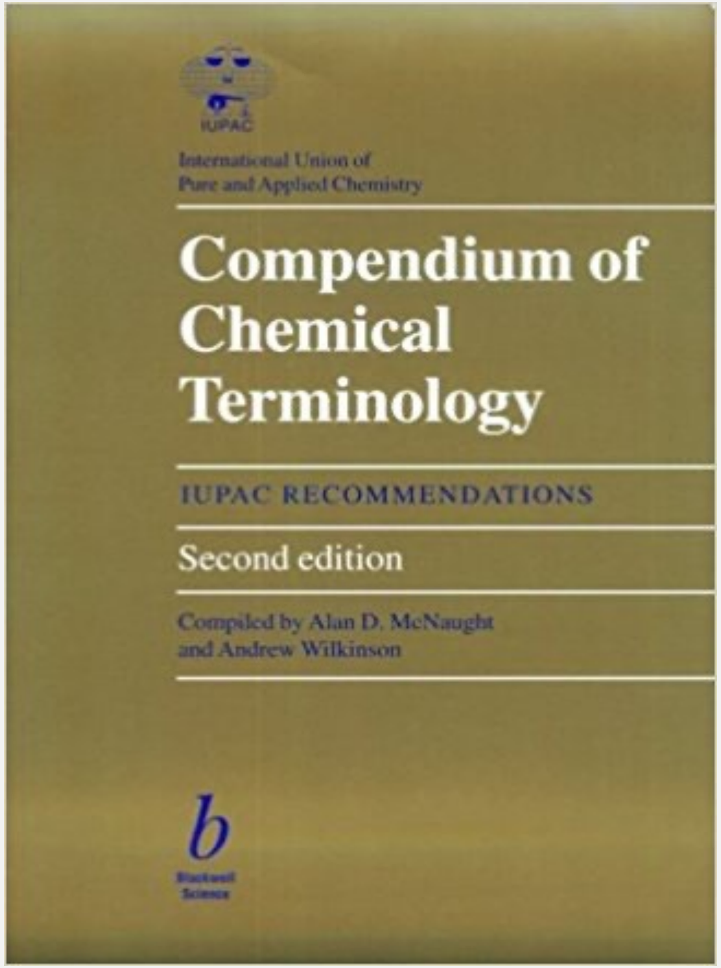
Dissociation constants of bisulfate (HSO_4^-)

- **Dickson (1990)** is recommended over Khoo et al. (1977).

Dissociation constants of hydrofluoric acid (HF),

- **Perez and Fraga (1987)** is recommended over Dickson and Riley (1979).

International Union of Pure and Applied Chemistry (IUPAC) Gold book



- **Concentration:** Quantities characterizing the composition of a mixture with respect to the **volume** of the mixture (doi: 10.1351/goldbook.C01222)
- **Content:** Amount-of-substance of a component divided by the **mass** of the system (doi: 10.1351/goldbook.S06073)

“Content” vs. “Concentration”

- Use of “content” (i.e., per kg-seawater), instead of “concentration” (i.e., per liter) for mass-based measurements.
- E.g., “**nitrate content**” or “**substance content of nitrate**”
- Variable (per kg SW) = Variable (per L) / Density (kg L^{-1})

Sample ID

- **Sample_ID** uniquely identifies a row of data during the subsequent QC and interpretation process
- Sample_ID = Station_ID × 10000 + Cast_number × 100
  + Rosette_position
- As an example, at station 15, the 2nd cast, a Rosette_position of 3 will have a Sample_ID of 150203.

Yearday vs. Julian Day

- **Yearday** refers to the day number in an annual cycle: Yearday = datefun(Y, M, D) – datefun(Y, 1, 1) + Time + 1
- Yearday is often incorrectly called Julian Day by oceanographers and meteorologists.
- **Julian Day** is the count starting from noon on January 1, 4713 BC (UTC), and starts with 0, instead of 1.
- As an example, January 5, 2021 has a Yearday_UTC of 5, but a Julian Day of 2,459,220.

Missing value indicator

"-999" or "NaN"

Acknowledgements

- The column header abbreviation standards presented here are based on the 30-year-old Exchange format of the World Ocean Circulation Experiment (WOCE) Hydrographic Programme (Joyce and Corry, 1994; Swift and Diggs, 2008) with updates and refinements by the Climate and Ocean-Variability, Predictability, and Change (CLIVAR) and the Carbon Hydrographic Data Office (CCHDO) of the Scripps Institution of Oceanography.
- Funding support from NOAA Ocean Acidification Program.

OAP

NOAA OCEAN ACIDIFICATION PROGRAM

Participating institutions

(in random order)

https://doi.org/10.3389/fmars.2021.705638