



Workshop – A Practical introduction to marine
monitoring hardware and procedures
Trieste 15-17 September 2015

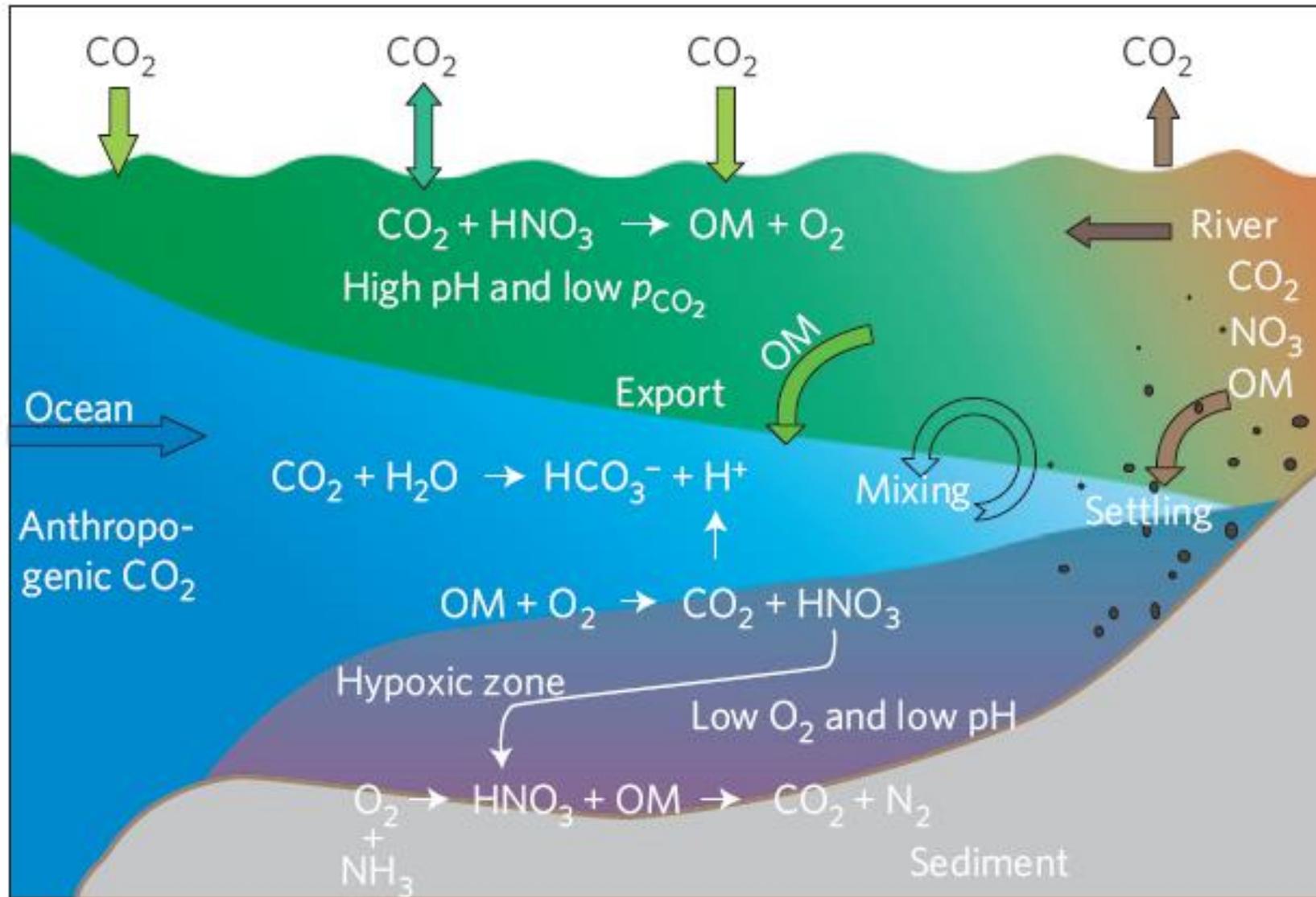


pCO₂: Instrument and laboratory measurements

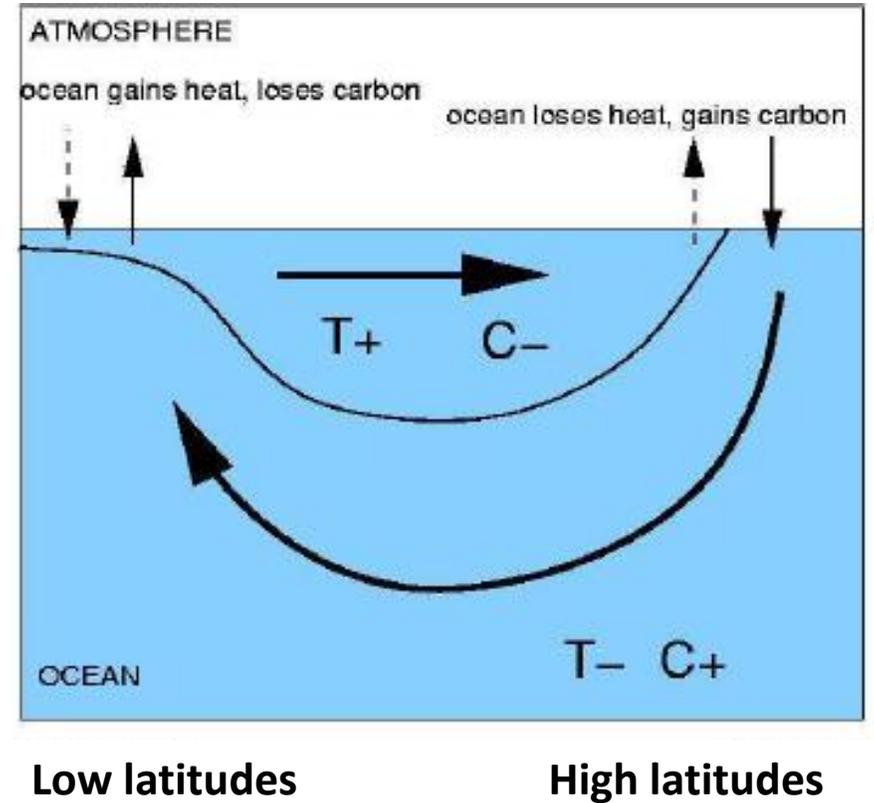
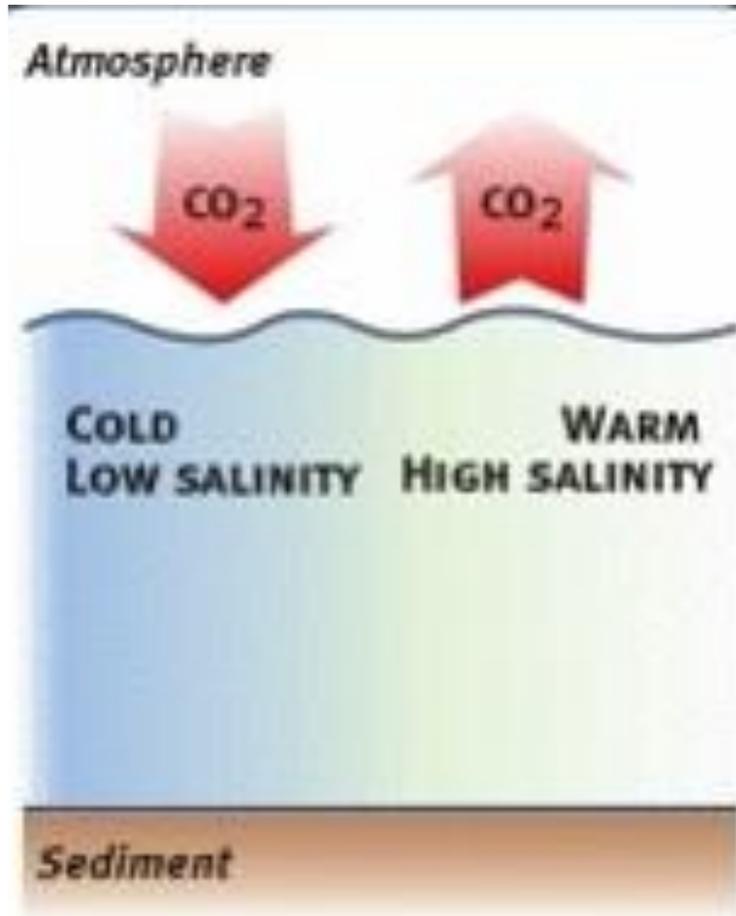
Michele Giani & Lidia Urbini

Marine Biogeochemistry and Ecosystem Research group

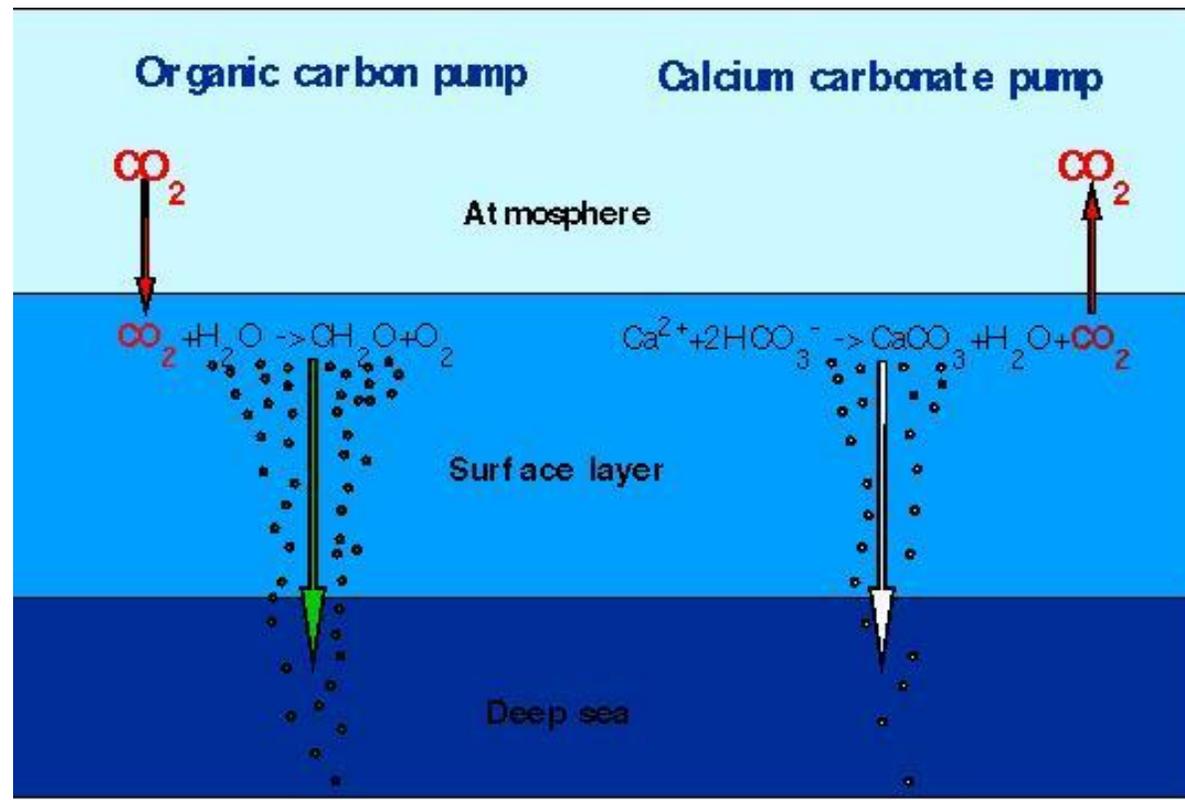
Carbon cycling in coastal waters



The physical carbon pump



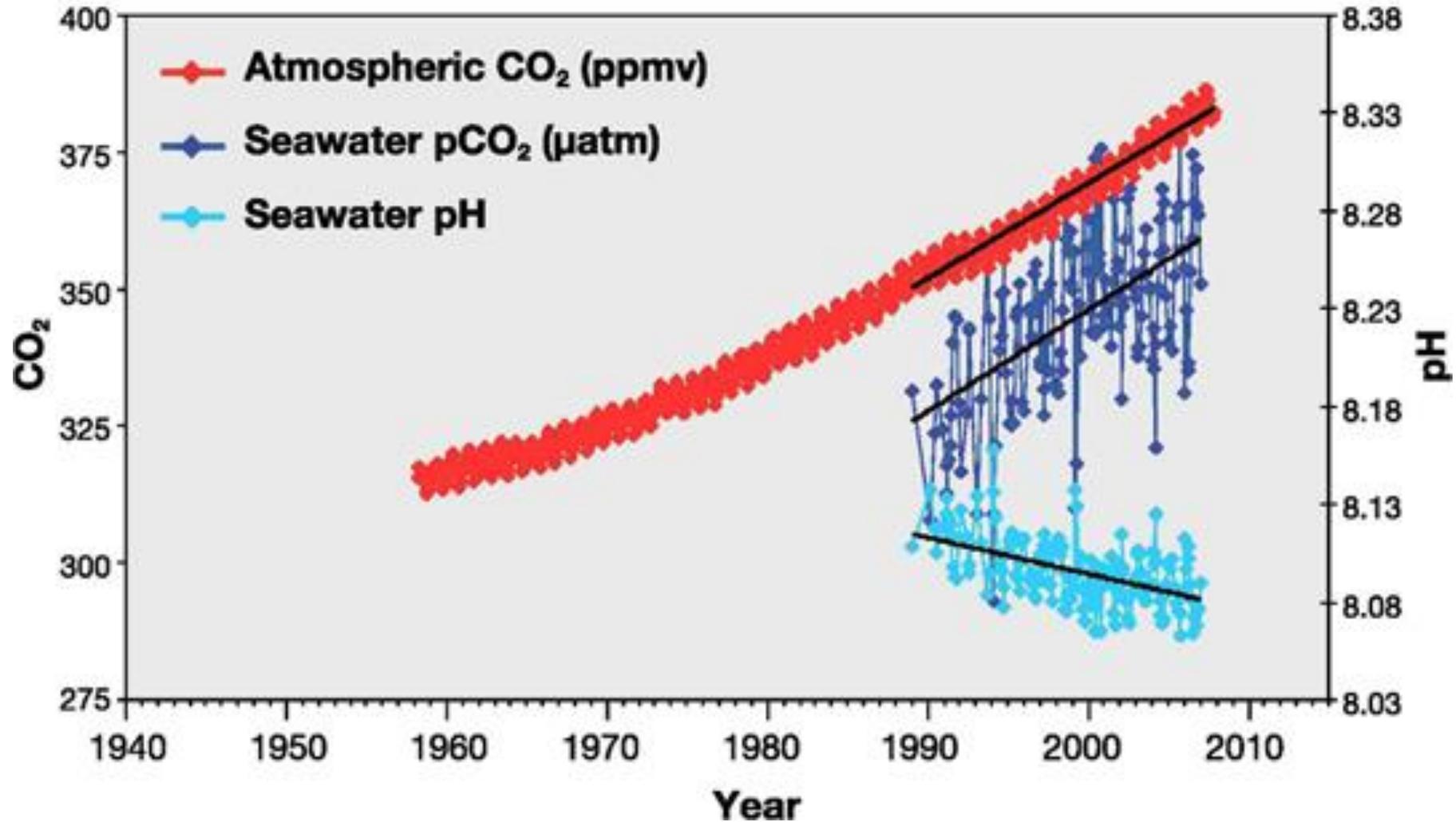
The colder seawater is, the more CO_2 is dissolved in it. The oceans in tropical and subtropical regions release CO_2 into the atmosphere, whereas large amounts of CO_2 are in solution in the polar seas.



Photosynthetic carbon fixation and the flux of organic matter to depth, termed **organic carbon pump**, generates a CO_2 sink in the ocean.

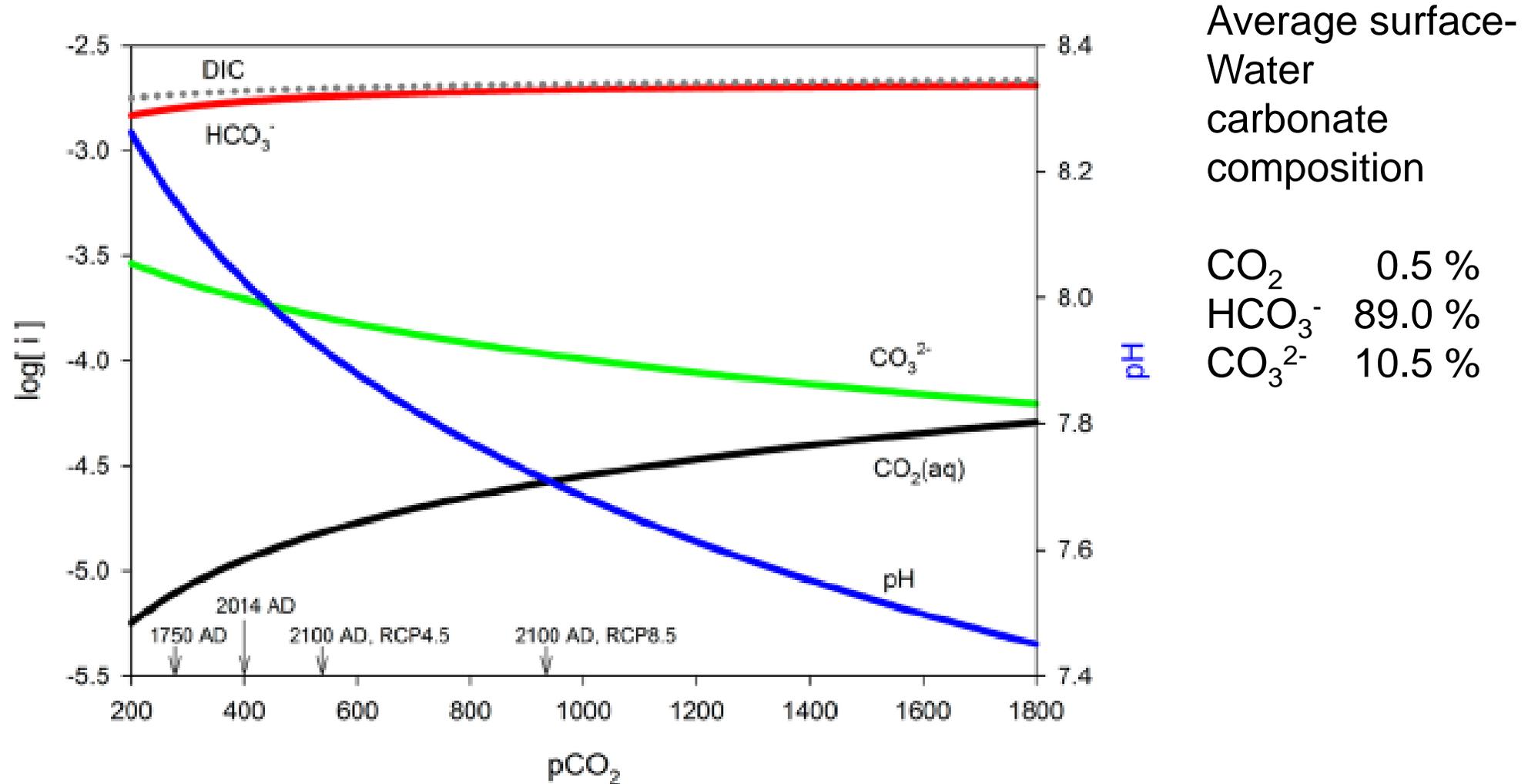
In contrast, calcium carbonate production and its transport to depth, referred to as the **carbonate pump**, releases CO_2 in the surface layer.

CO₂ and pH time series in the North Pacific Ocean



Credit: Richard A. Feely, Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, USA, with atmospheric data from Pieter Tans and seawater data from David Karl. Adapted from Feely (2008) in Levinson and Lawrimore (eds), Bull. Am. Meteorol. Soc, 89(7): S58.

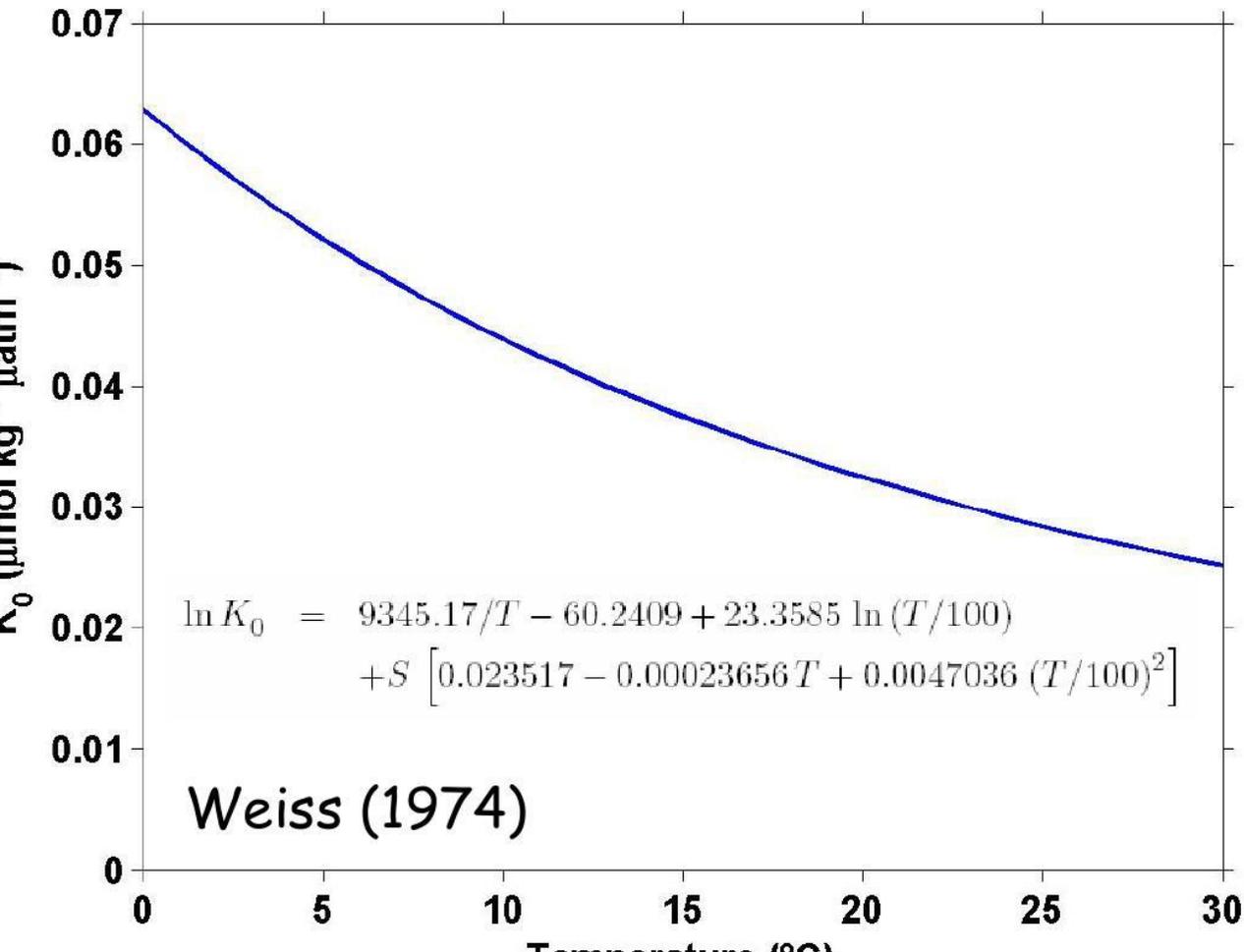
Modeled concentrations of carbon species in surface seawater (AT=2200 $\mu\text{mol kg}^{-1}$) equilibrated with atmospheric pCO_2



From Byrne, 2014

Henry's law — solubility of CO₂

$$\text{Henry's Law: } [\text{CO}_2] = K_0(T,S) \cdot f\text{CO}_2$$



- [CO₂]: concentration of CO₂ in surface waters
- fCO₂: fugacity (» partial pressure) of CO₂ in surface waters
- K₀: equilibrium constant as function of T and S.
- If the surface ocean is in equilibrium with the atmosphere. than atm
- pCO₂ is controlling surface pCO₂. [CO₂] out of Henry's Law.
- Colder waters store more CO₂!

Mole fraction and partial pressure

Mole fraction of a gas

$x_{\text{CO}_2} = n_{\text{CO}_2} / \sum_i n_i$ is usually expressed in $\mu\text{mol mol}^{-1}$

The partial pressure of a gas is proportional to its mole fraction

$$p_{\text{CO}_2} = x_{\text{CO}_2} P$$

where P = total pressure of the mixture

The CO_2 partial pressure assigned to a seawater sample refers to the partial pressure of CO_2 in the gas phase that is in equilibrium with that seawater. Once the p_{CO_2} , or more precisely the fugacity f_{CO_2} , has been determined, with the Henry's law $\Rightarrow [\text{CO}_2]_{\text{aq}}$ can be calculated

The fugacity of a pure gas

Partial pressure is a concept appropriate for ideal gases.

The **chemical potential** of a gas is:

$$\mu_i = \mu_i^0 + RT \ln p_i \quad (\text{ideal gas}) \quad p_i = \text{partial pressure of the gas species } i$$

μ_i^0 = standard potential, R= gas constant, T= absolute temperature

$$\mu_i = \mu_i^0 + RT \ln f_i \quad (\text{real gas}) \quad f_i = \text{fugacity of the gas species } i$$

In infinitely dilute gas mixture:

$$f_i / p_i \rightarrow 1 \text{ as } p \rightarrow 0$$

$$f_{\text{CO}_2} = p_{\text{CO}_2} \exp \left(\frac{P}{RT} \frac{B+2\delta}{RT} \right) \quad B \text{ (m}^3 \text{ mol}^{-1}) = (-1636.75 + 12.0408T - 3.27957 \cdot 10^{-2} T^2 + 3.16528 \cdot 10^{-5} T^3) \cdot 10^{-6}$$

$$\delta \text{ (m}^3 \text{ mol}^{-1}) = (57.7 - 0.118T) \cdot 10^{-6}$$

P= total pressure in Pa (1 atm = 101325 Pa)

f_{CO_2} and p_{CO_2} in μatm , R= 8.314 J K⁻¹mol⁻¹ (gas constant), T= absolute temperature

Saturation vapor pressure of water

- The air equilibrated with seawater is assumed to be at 100% humidity

$$p\text{CO}_2 = x\text{CO}_2 (P - p\text{H}_2\text{O})$$

$P(\text{atm})$ = total pressure

$p\text{H}_2\text{O}(\text{atm})$ = saturation vapor pressure of water

For a gas sample with $x\text{CO}_2 = 360 \mu\text{mol mol}^{-1}$ at 100% humidity and $p = 1 \text{ atm}$, at 25°C and $S = 35$ $p\text{H}_2\text{O} \approx 0.03 \text{ atm}$

$$p\text{CO}_2 = 349 \mu\text{atm}$$

in dry air ($p\text{H}_2\text{O} = 0$) $p\text{CO}_2 = x\text{CO}_2$

Table 1.4.9: The different quantities used to describe CO₂ in the gas phase.

Quantity	Symbol used in literature	Unit	Value ^a	Remark
mole fraction	$x\text{CO}_2$	$\mu\text{mol mol}^{-1}$	360.0	in dry air
mixing ratio/ concentration ^b	$x\text{CO}_2$	ppmv	360.0	in dry air
partial pressure	$p\text{CO}_2$	μatm	349.0 ^c	at 100% humidity
fugacity	$f\text{CO}_2$	μatm	347.9 ^d	at 100% humidity

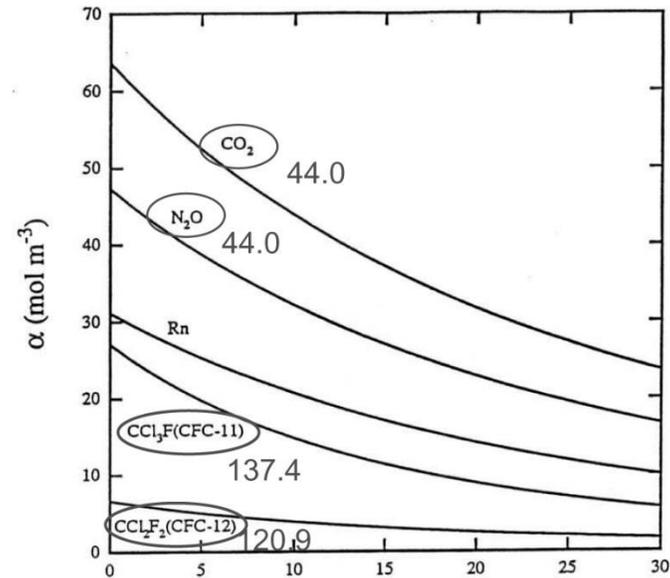
^a Values refer to, or are calculated from $x\text{CO}_2 = 360 \mu\text{mol mol}^{-1}$ measured in dry air.

^b Also used for mole fraction, assuming that all gases in the mixture behave perfectly.

^c At $T = 25^\circ\text{C}$ and $S = 35$.

^d At $T = 25^\circ\text{C}$.

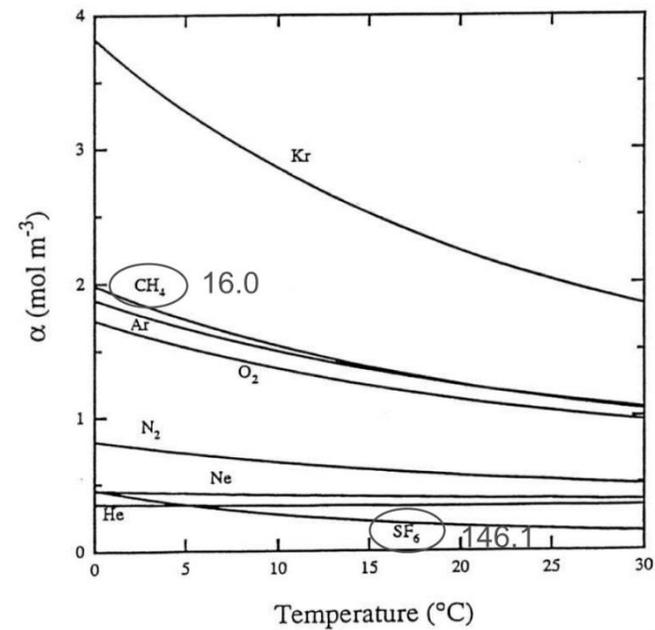
SOLUBILITY OF GASES VERSUS TEMPERATURE



NON-IDEAL GASES

gas	molecular weight
CO ₂	44.0
N ₂ O	44.0
CFC-11	137.4
CFC-12	120.9
CH ₄	16.0
SF ₆	146.1

↑
Increasing solubility



IDEAL GASES

gas	molecular weight
Rn	222.0
Kr	83.8
Ar	39.9
O ₂	32.0
N ₂	28.0
Ne	20.2
He	4.0

↑
Increasing solubility

Figure 3.2.1

Temperature effect on seawater pCO₂

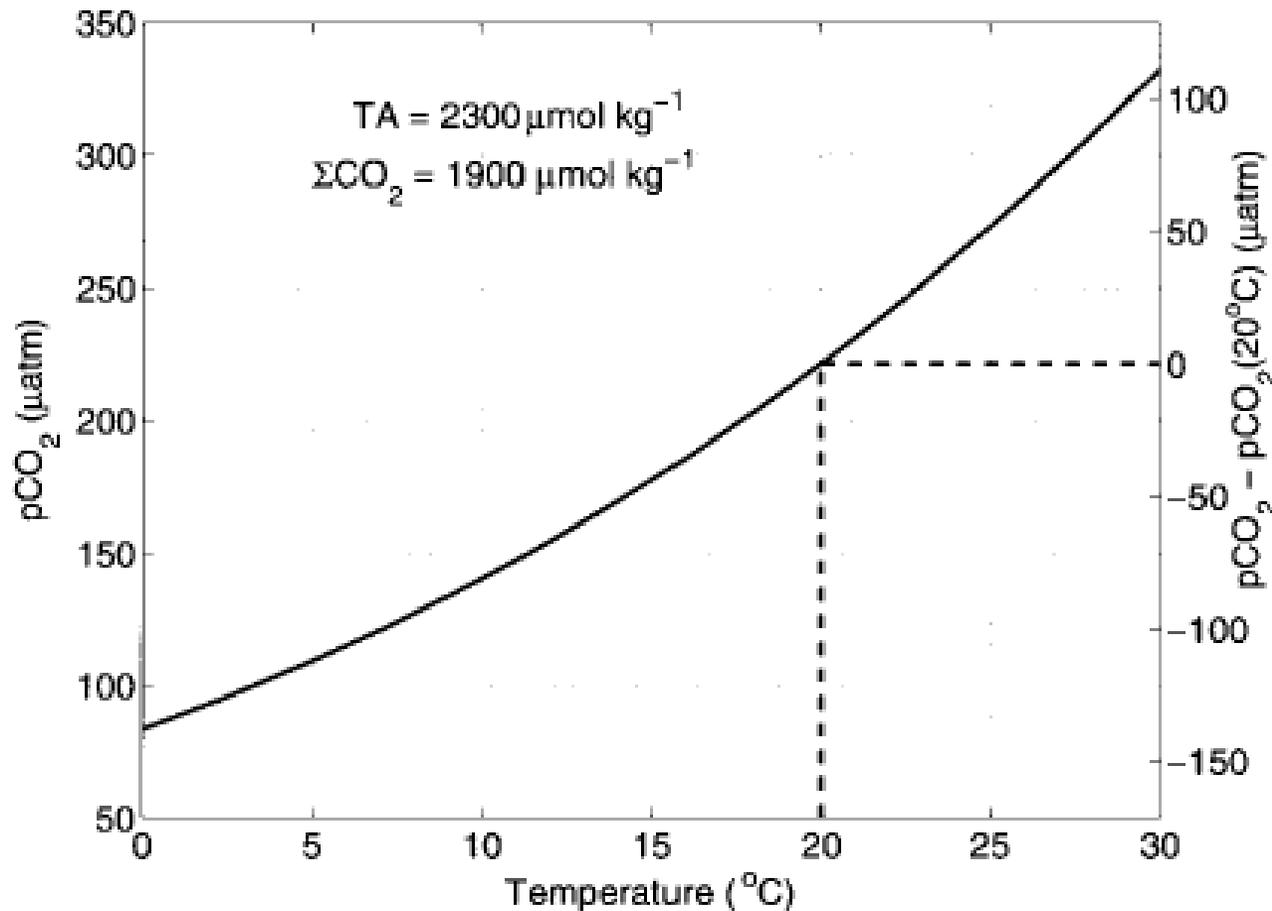


Figure 1.4.18: Seawater $p\text{CO}_2$ as a function of temperature (T). If measurements are made at 20°C (so-called discrete systems), large corrections may have to be applied to calculate $p\text{CO}_2$ at *in situ* T (cf. Goyet et al., 1993). The problem is less severe in so-called continuous systems where equilibration and *in situ* T are similar.

Measurement of CO₂

The main principle of pCO₂ measurement is based on the equilibration of a carrier gas phase with a seawater sample and subsequent determination of the CO₂ in the carrier gas by an infrared analyser.

As the pCO₂ in seawater strongly varies with temperature a correction is necessary to compensate for the difference between equilibration temperature and the in-situ seawater temperature. The equilibrated surface water values should be accurate within 2 μatm. This will necessitate pressure measurements within 0.2 mBar and water temperature measurements with an accuracy of 0.01 C

Seawater pCO₂ measurement based on different equilibration principles and detection methods

Liquid – Gas equilibration and direct absorption measurement

- *Equilibrators:*

 - » water \leftrightarrow gas

 - » water \leftrightarrow membrane \leftrightarrow gas

- *Detectors:* NDIR, Laser, Wavelength-Scanned Cavity Ring Down Spectroscopy

Liquid – Liquid equilibration

- *Equilibrator:* semipermeable membrane

- *Detector:* spectrophotometric pH determination of dye solution

Liquid – “Solid” equilibration

- *Equilibrator:* semipermeable membrane (dye embedded)

- *Detector:* dye based fluorescence quenching

Seawater pCO₂ sensors

Table 1 The various designs of pCO₂ sensors

Equilibrator	Measured phase	Determination	References
direct contact of water-gas	gas	NDIR	ACT (2009a); Nemoto et al. (2009)
gas permeable interface	gas	NDIR	Kayanne et al. (2002); Fiedler et al. (2012); Saderne et al. (2013), this study
gas permeable interface	indicator solution	electrode	Shitashima 2010
gas permeable interface	indicator solution	fluorescence	Goyet et al. (1992); Tabacco et al. (1999); Rubin and Ping Wu (2000)
gas permeable interface	indicator solution	spectrophotometry	Degrandpre (1993); Lefèvre et al. (1993); Degrandpre et al. (1995; 1999); Wang et al. (2002; 2003); Nakano et al. (2006); Lu et al. (2008)

Indirect determination of $p\text{CO}_2$ through spectrophotometric pH determination

Equilibration with colorimetric
pH indicator solution in a gas
permeable tube membrane

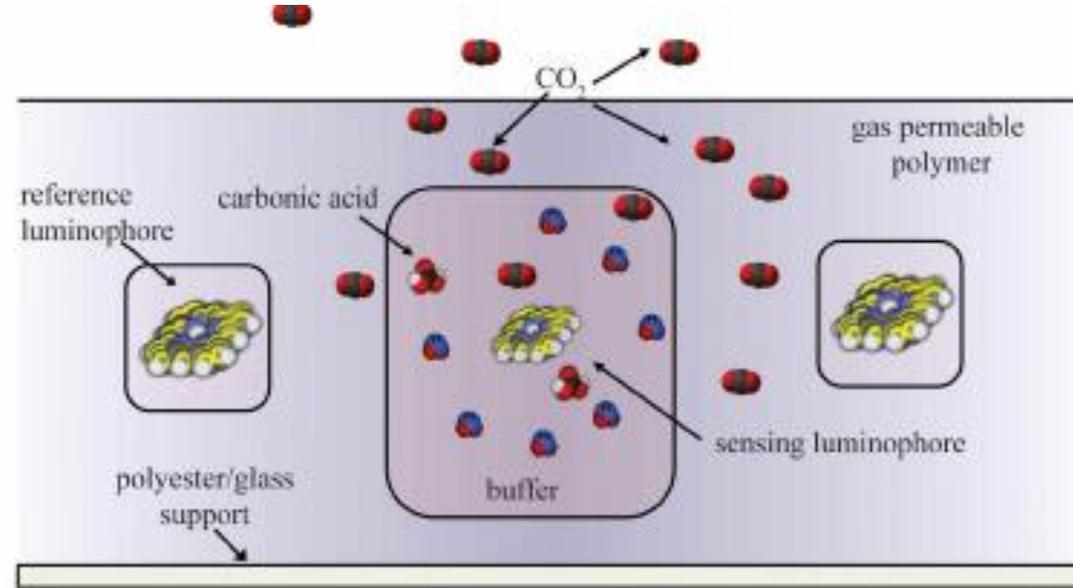
pH shift in indicator solution is
related to $p\text{CO}_2$



pCO₂ Optodes

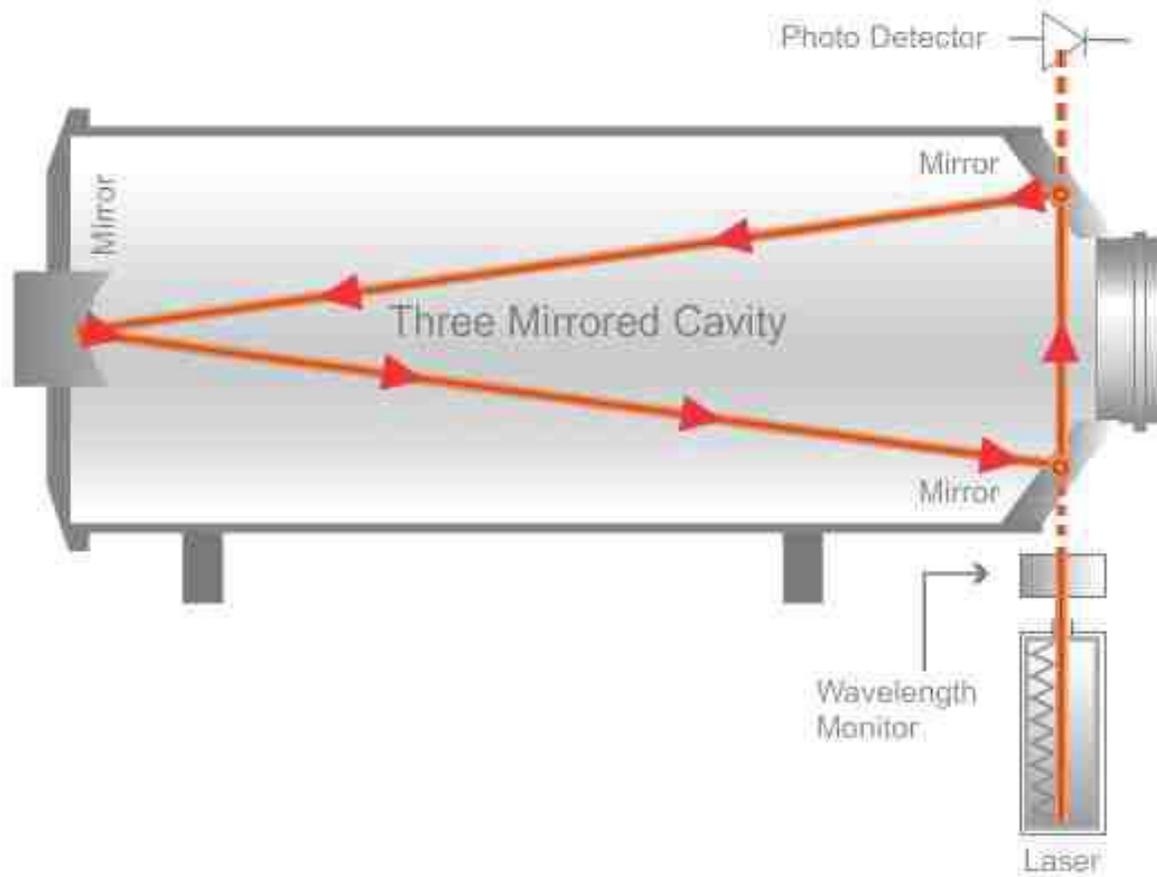
Dye based fluorescence
quenching à DLR

- Dye is embedded into a sensing foil which is in equilibrium with water CO₂
- Comparison of the phase shift between the sensing and the reference luminophore



From Atamanchuk et al., 2014

Cavity Ring Down Spectroscopy: time, not absorbance



CRDS utilizes the unique infrared absorption spectrum of gas-phase molecules to quantify the concentration and isotopic composition of H₂O (and other molecules, e.g., CO₂, CH₄, N₂O, H₂S, etc.)

Measure decay rate, rather than absolute absorbance

Small 3-mirrored cavity ~ 35 cc

Long effective path-length (> 10 km)

Time-based measurement

Laser is switched on and off, and scanned across wavelengths

G2301 measure CO₂ CH₄ H₂O

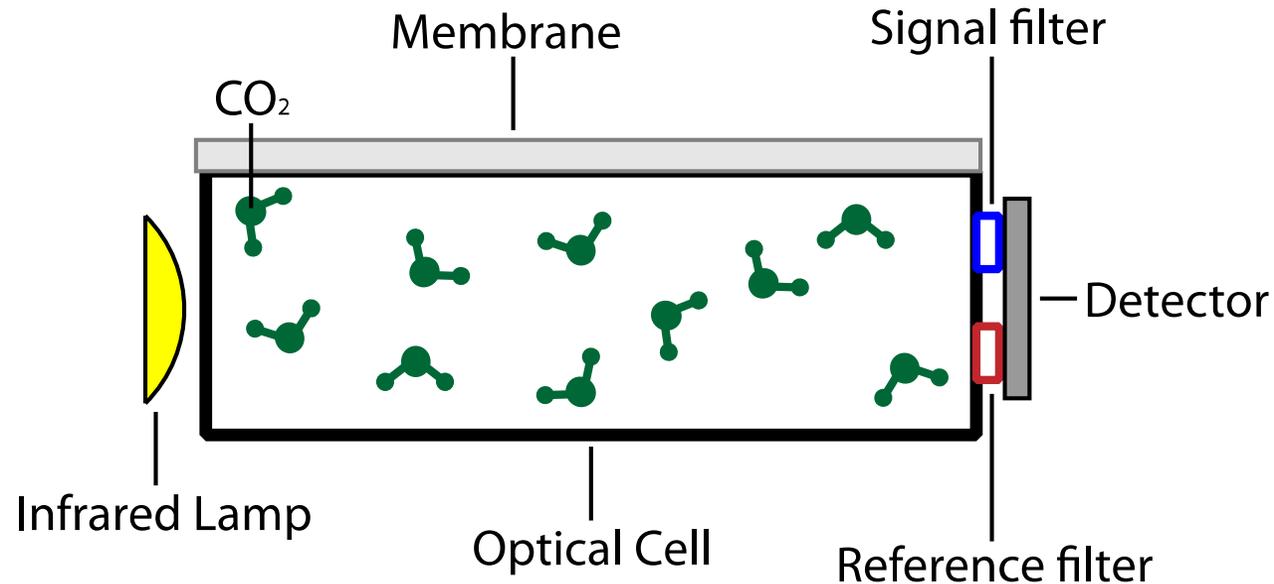
Commercial Instruments for in situ seawaters CO₂ measurements

Instrument	Description	Platforms
Pro-OCEANUS Systems Inc.: CO ₂ -Pro-CO ₂ -Pro CV	pCO ₂ by IR detection featuring automatic zero point calibration High sampling rate; pumped interface; low cost; long term stability	underway systems, moorings, profiling floats
General Oceanics GO _p CO ₂ system	pCO ₂ by LICOR IR detection. Designed for longterm installation and unattended use on research vessels or VOS ships	underway systems
Apollo scitech inc. p _p CO ₂ system (as-p2)	Water sample is forced into the equilibrator by a shipboard pump. Equilibrated air is drawn from the equilibrator and dried with an electronic cooling system. It is then quantified with an infrared CO ₂ analyzer (LI7000) before sending back to the equilibrator. The shower-head equilibrator is effective (response time 2 min). The equilibrator is completely sealed from the outside room air.	underway systems
Sunburst Sensors: SAMI-CO ₂	Autonomous indicator-based sensors for measurement of the partial pressure of CO ₂ of seawater. Temperature is also measured. Low power for long-term (>1 year) deployments	underway systems, moorings, drifters
Sunburst Sensors: Superco ₂ system	designed for automated shipboard analysis of seawater and atmospheric CO ₂ . Built around LI-COR 840A, analyzes CO ₂ levels every 2 seconds. The system periodically runs 3-4 standard gases to calibrate NDIR system. Can support a Seabird thermosalinograph and other analog output sensors by special order.	underway systems
Sunburst Sensors: AFT-CO ₂	Based on the same technology as the SAMI-CO ₂ , packaged to be plumbed into a line on a research vessel. Runs autonomously with own data logging interface or can be connected to a PC if real-time data is required. Uses colorimetric reagent method with traceable accuracy of +/- 3 µatm.	underway systems, moorings, drifters
CONTROS HydroC™ CO ₂ Sensor	Optical, headspace-based underwater sensor for the measurement of the partial pressure of carbon dioxide (pCO ₂). Within the HydroC™ a headspace is realized in the form of an equilibrated gas stream in which the CO ₂ concentration is measured optically by means of non-dispersive infrared (NDIR) absorption spectrometry. Latest developments using an external pump have decreased response time to 60s. The HydroC™ has an internal zeroing procedure, is pressure resistant to 6.000m water depth	AUVs, ROVs, Gliders, Moorings
CONTROS HydroC™ CO ₂ Flow Through Sensor	Water is pumped through the flow head. Dissolved gases diffuse through a specialized thin film composite membrane into the internal gas circuit leading to a detector chamber, where the partial pressure of CO ₂ is determined by means of IR absorption spectrometry. Concentration dependent IR light intensities are converted into the output signal, which is either transmitted by cable or saved on an internal data logger.	underway systems
Picarro CO ₂ System	The Picarro G1200 CO ₂ /H ₂ O Analyzer is a real time, trace gas monitor capable of measuring these gases parts-per-billion (ppbv) sensitivity. The analyzer is based on Picarro's unique Wavelength-Scanned Cavity Ring Down Spectroscopy (WS-CRDS), a time-based measurement utilizing a near-infrared laser to measure a spectral signature of the molecule	underway, surface mooring
Marianda Company SUNDANS system	The Surface UNderway carbon Dioxide prtial pressure ANalySer (SUNDANS) measures pCO ₂ by LICOR IR detection (sea surface + atmosphere), barometric pressure, position (GPS);	underway systems on research vessels
SubCtech OceanPack System	Flow through pCO ₂ system for underway measurements with high performance dual beam NDIR detector behind a silicon membrane. Resolution < 1 uatm; accuracy +/- 3uatm, time response 1 minute.	underway systems

CO₂ measurement

- Non-Dispersive Infrared (NDIR) detection
- **Measures xCO₂ and dissolved gas pressure to allow calculation of pCO₂**
- Measures the absorbance of a specific infrared wavelength by CO₂ molecules in a gaseous headspace
- The measurement can be affected by:
 - Temperature of the NDIR detector
 - Gas stream pressure
 - Gas stream humidity
 - Detector ageing effects
 - Accurate calibration

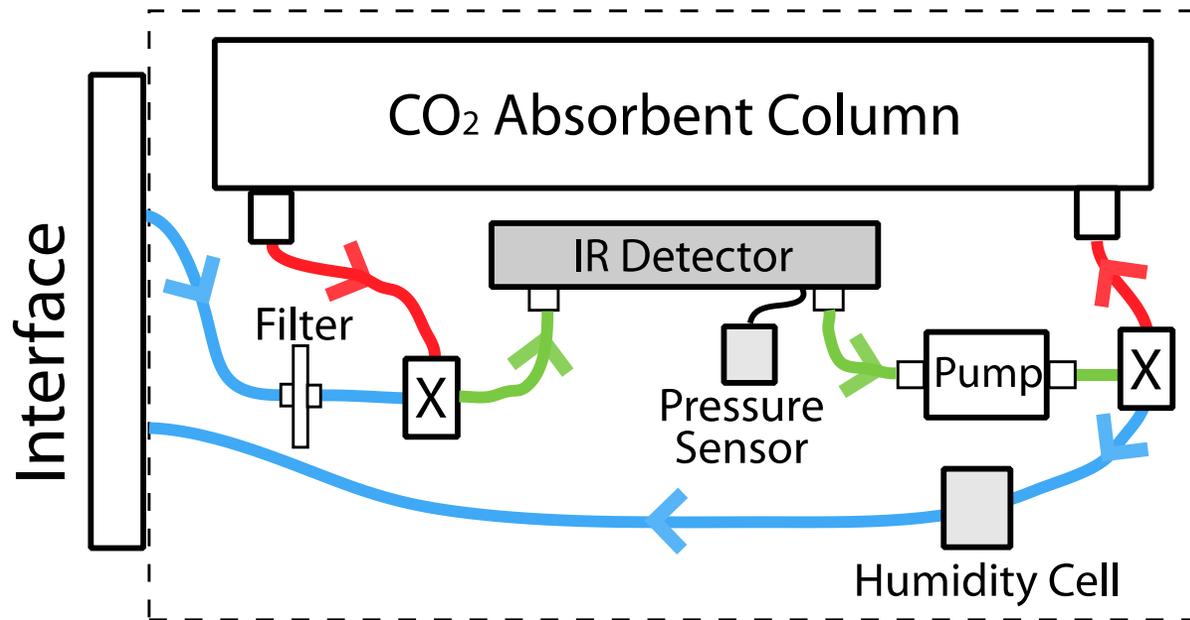
Infrared Detection



- Gases diffuse from water through the membrane into an optical cell where CO₂ is detected using IR detection

Infrared Sensor Operation

- Gas flows through cell in contact with the semi-permeable membrane (blue and green)
- When a zero measurement is made, the gas stream is routed through an absorption column (red and green)



Accuracy and stability

- Detector temperature
 - Requires stable and accurate temperature measurement
 - Measured to ± 0.1 Celsius
 - Kept well above ambient to prevent condensation in the detection cell and to keep thermal stability when water temperature changes

Accuracy and stability

- Gas Stream Pressure
 - Needs to be known in the detector as increased cell temperature can alter gas pressure in the cell
 - Increased pressure leads to an apparent increase in concentration
 - Compensation of the signal is provided on board
- The gas pressure signal is used to calculate $p\text{CO}_2$
- Many factors affect the total dissolved gas pressure, TDGP, in natural waters so it must be measured

Accuracy and stability

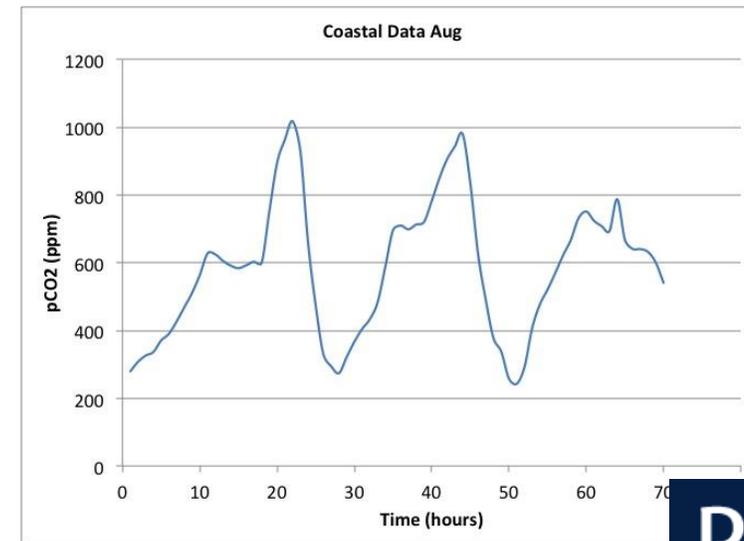
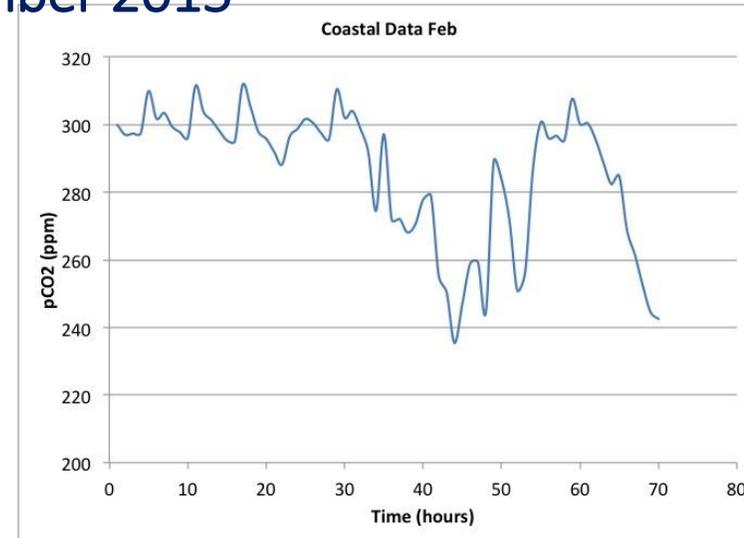
- Gas Stream Humidity
 - Water molecules absorb infrared at the same wavelength used to measure CO₂
 - Ratio of signal is minimized at 4.26 um
 - Still must be accounted for using an inline humidity cell
 - Onboard correction for this effect

Accuracy and stability

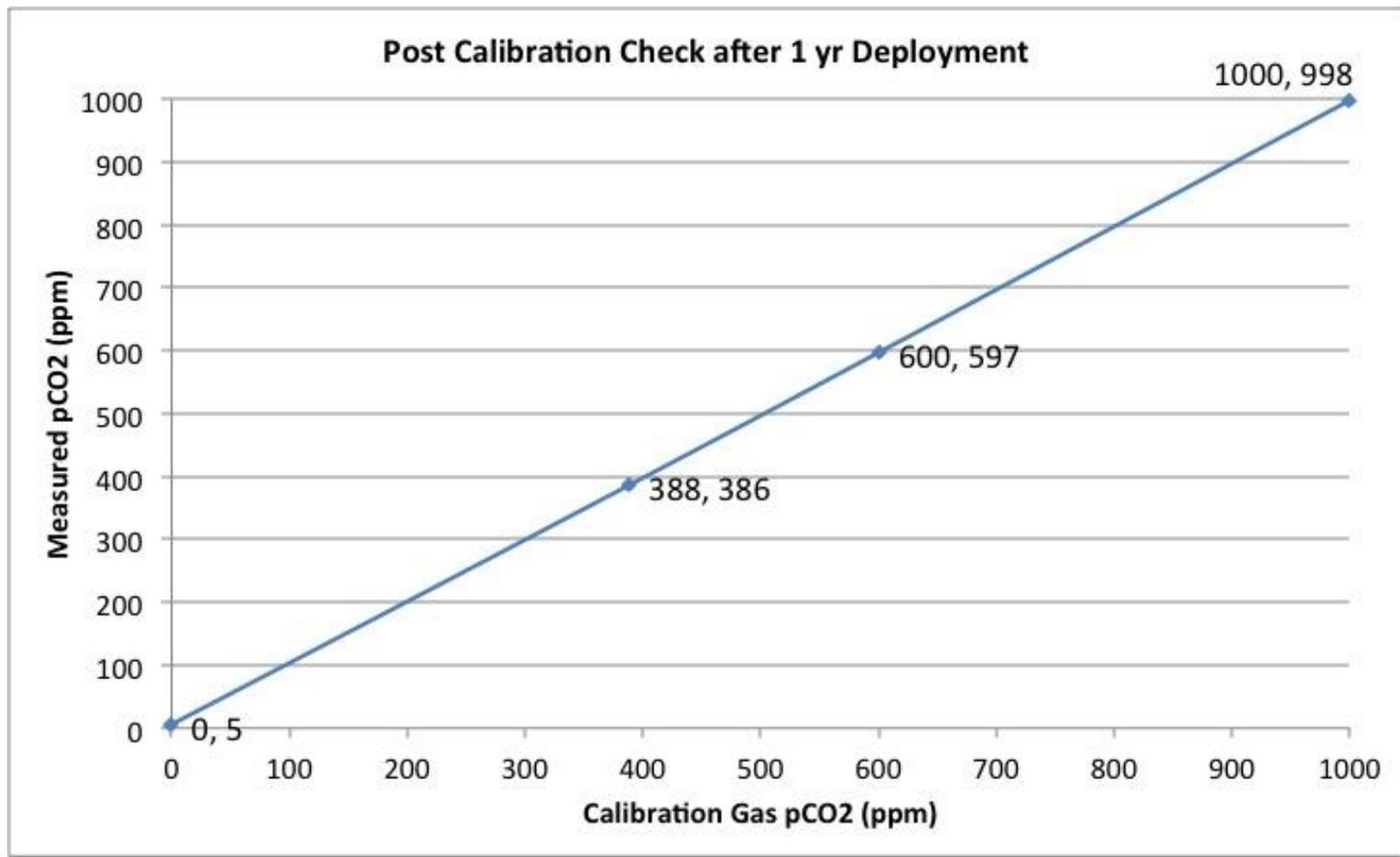
- Detector Ageing Effects
 - Affects the performance through signal drift
 - CO₂-Pro models use an Automatic Zero Point Compensation, AZPC
 - Absorption of CO₂ from detector gas stream allows for frequent measurement and correction for detector zero drift
 - Correction is automatic and in real-time, no post-deployment correction of data needed

Accuracy and stability

- Automatic Zero Point Compensation
- Example: instrument measured hourly for a period of one year
- Factory calibration check before and after showed minimal change
- Provided reliable data for a year with no intervention



Accuracy and stability



Accuracy and stability

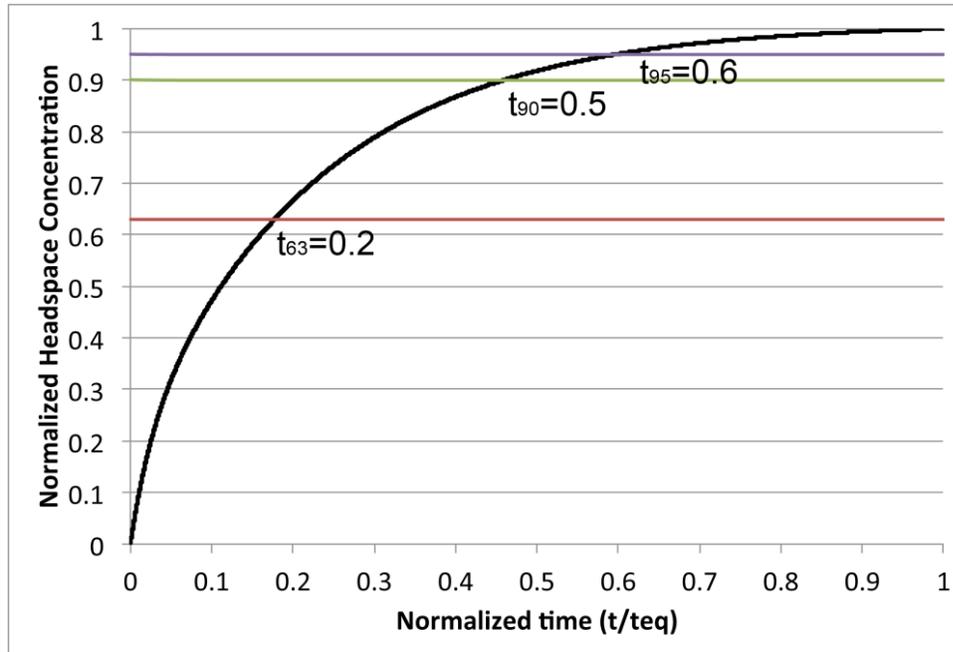
- Accurate Calibration
 - Pro-Oceanus uses NOAA standard gases and NOAA traceable gases
 - Minimum 5 point gas calibration using a polynomial curve fit
 - Gas pressure sensor calibration
 - Many years of testing have led to major improvements in all aspects listed
 - Improved temperature stability, internal corrections for pressure and humidity means NO post-corrections required

Semi-Permeable Membrane

- The only barrier between the water being measured and the detector
- Integrity of the membrane is key to proper functioning of the instrument
- Membrane should not be touched by fingers or other solid objects
- Options for copper biofouling prevention

Equilibration Time

- The equilibration of gas across the instrument membrane is governed by the laws of diffusion



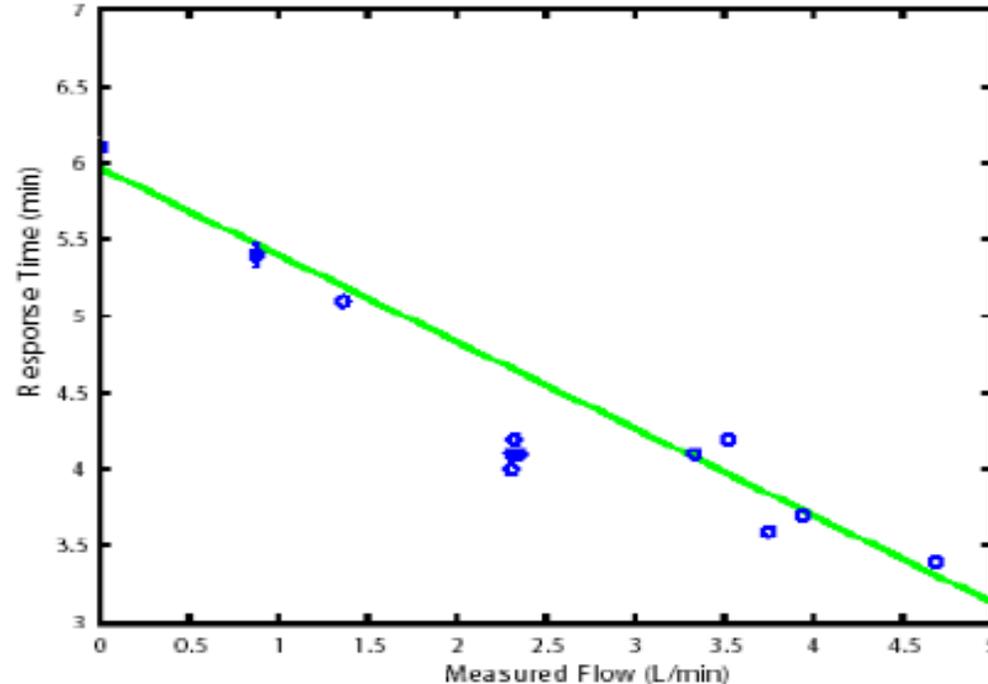
t_{63} is taken as one fifth of the total time to equilibrate,

t_{90} is approximately half the time to equilibrate,

t_{95} is roughly 60% of the time to equilibrate.

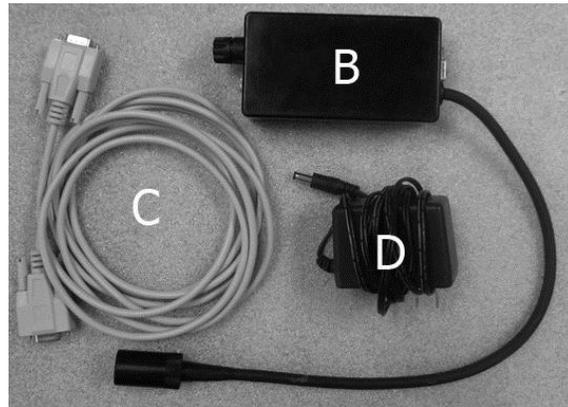
t_{99} is taken as t_{eq} .

Effect of the flow rate on the equilibration time



*Time constant for equilibration of CO₂ across the supported interface
as a function of sample water flow rate.*

Standard Equipment for CO₂-Pro CV



- Sensor (A) comes with a bench top deck box (B) and 120 V AC wall plug to 12 V DC power supply (D).
- Deck box contains a 2 meter underwater cable and plug for connection to the sensor.
- A 2 meter RS-232 cable is also supplied (C) for communication to computer via serial port.

Specifications

Parameter	Specification
Accuracy	$\pm 2 \mu\text{atm}$ (0 – 600 μatm range)
Power Consumption	220 mA (750 mA during warmup)* (Average current draw for standard water conditions)
Input Voltage	12-18 VDC
Signal Output	RS-232, ASCII String 0-5 VDC Analog Signal available (or 4-20 mA)
Water Temperature Range	-2 to 20 °C Water Temp. (Arctic) 0 to 30 °C Water Temp. (Standard) 15 to 40 °C Water Temp. (Tropical)
Equilibration time constant (t_{63})	2 minutes
Detector	Non-Dispersive Infrared (NDIR)
Warm up Time	3-5 minutes (dependent on water temperature)
Housing Material	Acetal Plastic (Titanium optional)

Instrument Operation

- The sensor may be operated in any orientation however:
 - Placing the instrument **horizontally** is ideal
 - Sediment and particles can accumulate on the membrane when the sensor head is oriented upwards
 - Biofouling is more prevalent on the up side of the sensor in shallow waters – membrane should not point up for extended deployments
 - Gas bubbles can become trapped along the membrane during submersion when the membrane head is facing downwards

Communication to sensor

- Communication is achieved using an RS-232 terminal program
- Many functions the same with or without the internal datalogger
- Protocols supplied for non-datalogging version
- Datalogger
 - Stores up to 2 Gb of data
 - User friendly program to set logging frequency, zero interval

Datalogger and controller

----- Oceanus Logger Main Menu -----

FW Version 4.1.0w

Pro Oceanus Inc.

Date: 2012/11/09 Time: 14:53:53

- | | |
|----------------------|------------------------|
| 1) Record Data Now | 5) Auto Start Settings |
| 2) View Logged Data | |
| 3) Erase Logged Data | 6) Sleep Now |
| 4) Change Clock Time | 7) Display Live Data |

Datalogger and controller

#2012/10/02 11:06:33, M, 44500, 41628, 481.444, 40.7, 22.814, 23.840, 1010, 40.3, 41.0,
#2012/10/02 11:06:35, M, 44500, 41628, 481.276, 40.7, 22.883, 23.800, 1010, 40.4, 41.0,
#2012/10/02 11:06:36, M, 44500, 41627, 481.211, 40.7, 22.814, 23.840, 1010, 40.4, 41.0,
#2012/10/02 11:59:56, M, 44502, 41575, 492.394, 40.7, 24.135, 24.920, 1010, 40.4, 40.9,
#2012/10/02 11:59:58, M, 44502, 41576, 492.369, 40.7, 23.998, 24.920, 1010, 40.4, 41.0,
#2012/10/02 17:59:56, M, 44495, 40906, 639.356, 40.7, 25.776, 25.360, 1013, 40.5, 40.9,
#2012/10/02 17:59:58, M, 44495, 40907, 639.458, 40.7, 25.913, 25.360, 1013, 40.4, 40.9,

Color	Corresponding Value
Dark Grey	Zero A/D [counts] of most recent autozero sequence
Light Blue	Current A/D [counts]
Dark Blue	Measured CO ₂ [ppm]
Red	Average IRGA temperature [°C]
Orange	Humidity [mbar]
Yellow	Humidity sensor temperature [°C]
Green	Gas stream pressure [mbar]
Purple	IRGA detector temperature [°C]
Light Grey	IRGA source temperature [°C]

As the actual measurement is made on gas which is nearly saturated with water vapor,
The output is the mole fraction of CO₂ in wet air (wCO₂) and
 $p\text{CO}_2 = w\text{CO}_2 * P_{\text{wet}}$

where P_{wet} = measured total pressure of the internal gas which includes water vapor pressure

Maintenance

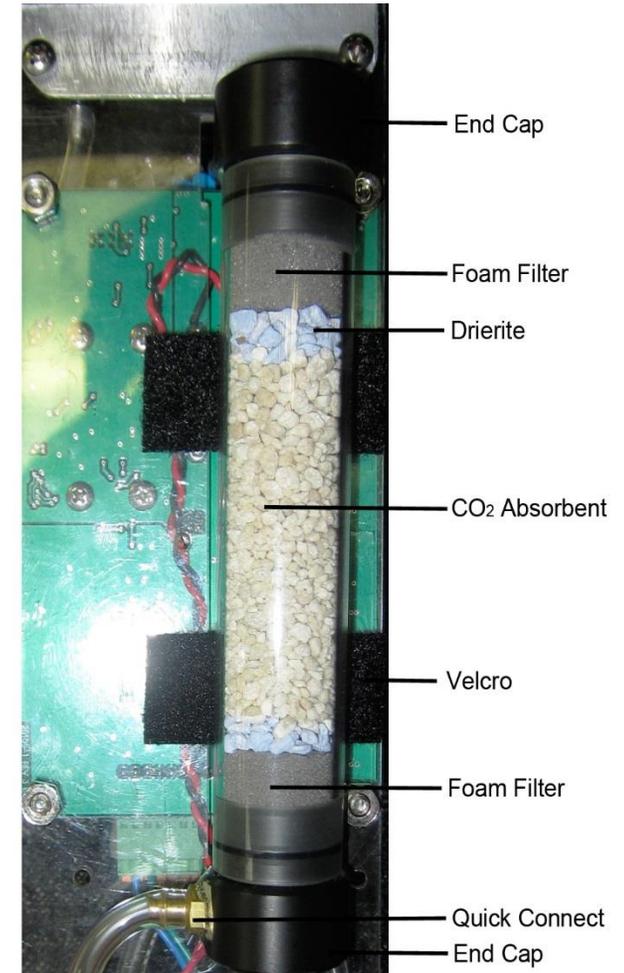
- The instrument requires minimal maintenance
- Cleaning the membrane is all that is typically needed
- Biofilms can not only slow down the time to equilibrate, but also result in false readings due to either the consumption or production of CO₂ by biofilm organisms

Membrane Cleaning

- It is not advised to touch the membrane at any time to avoid scratches and premature wear
- The preferred method is using a dilute solution of oil-free laundry detergent in water, diluted 1:100 to 1:200
- Use a small submersible pump in the solution and direct the water flow directly onto the membrane face for 30 minutes. Place the pump 6 inches from the interface and direct water onto the instrument face
- Follow this by using clean water and the water pump for 15 minutes to fully rinse any soap residue from the membrane
- Air dry the membrane and place the protective cap over the end of the instrument for storage

Internal Maintenance

- CO₂ Absorption Column
- Replacing the Absorbent
 - Either Ascarite II or Soda Lime, *Ascarite requires a small amount of Drierite on either end to remove moisture
 - Both change color when exhausted
- Open the Instrument via the Mason ring lock-down collar
- Pull out the electronics tray and disconnect the column
- Discard used absorbent and replace with new
- Lightly grease O-Ring Seal and reassemble



Biofouling Prevention

- Solid copper helps prevent biofouling
- Copper tape should not be placed on the semi-permeable membrane or in contact with dissimilar metals
- Apparently duct tape works too!



MAMBO buoy
Surface cage
27 august 2015
Maintenance

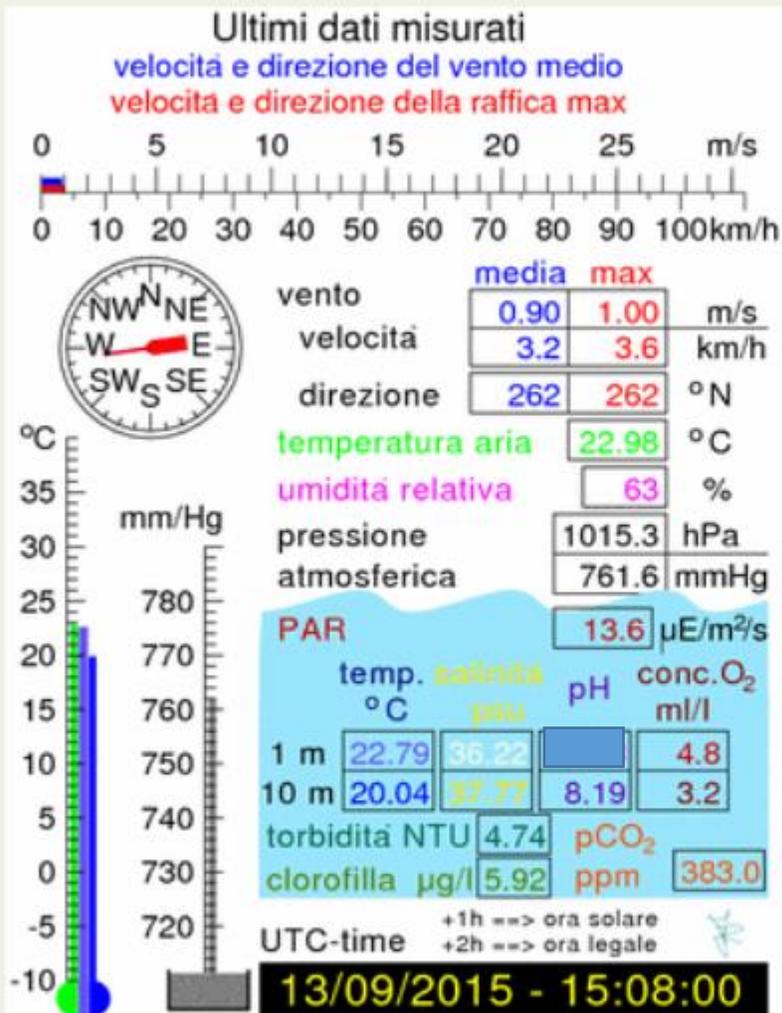


Factory Maintenance

- Factory calibration checks, 5 point standard
 - Recommended every 12-18 months
 - Re-calibration of sensor if required
- Replacement of membrane interface
 - Recommended every 2-3 years
 - Dependent on application



MAMBO Buoy



cliccare la figura per ingrandire

Monitoraggio AMBIentale Operativo
Boa MAMBO-1

45°41.86'N - 13°42.50'E
È situata ai limiti della Riserva Naturale Marina di Miramare nel Golfo di Trieste.

Con cadenza semi-oraria effettua misure meteo-marine i cui dati sono accessibili in NEAR REAL TIME

I grafici disponibili sul sito presentano le serie temporali relative ai periodi indicati. L'utilizzo dei dati MAMBO-1 è consentito per fini **no profit** previa citazione della fonte (**Dati MAMBO-1, OGS**).

Per l'eventuale richiesta dei dati contattare: NODC



Ritmare

La ricerca italiana per il mare

diagramma in formato .PDF

Dati storici da 1999: diagrammi mensili formato .pdf)

NEWS



C1-LTER

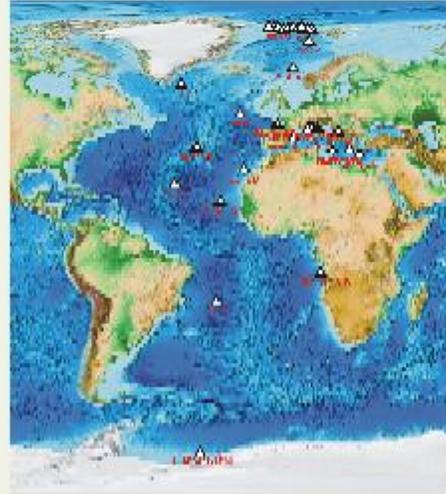
Collegamento alla Boa di Pir

SAILOR - Southern Adriatic Interdisciplinary Laboratory for Oceanographic Research

E2-M3A buoy



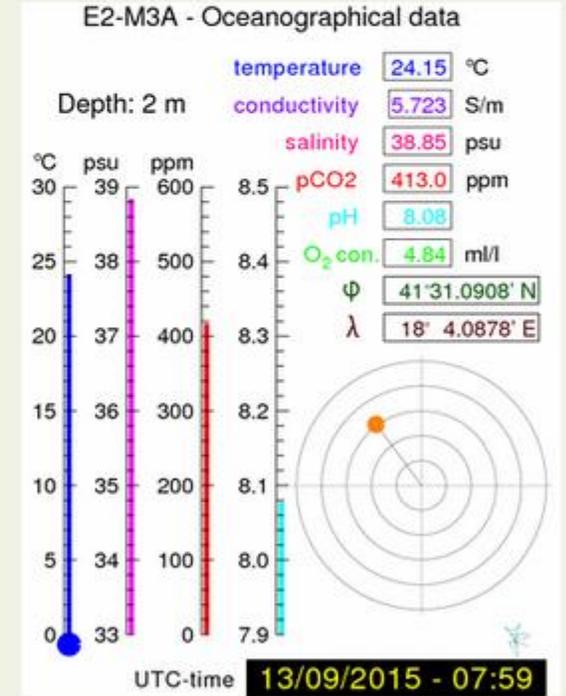
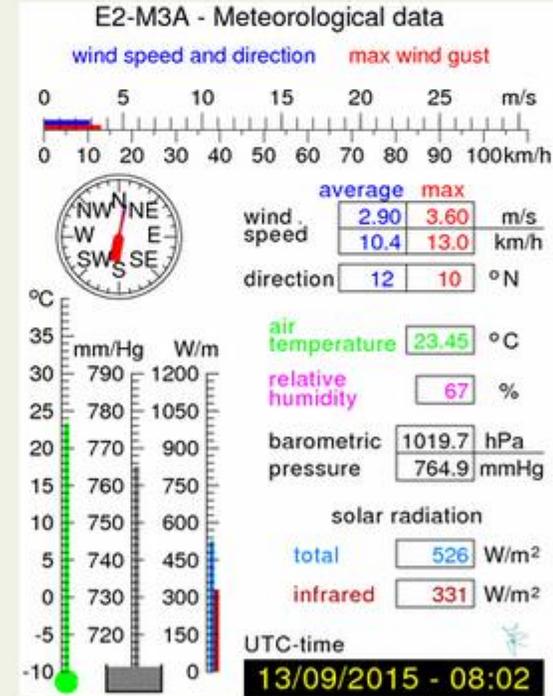
FixO3 sites



click for the Mediterranean FixO3 sites



Surface Buoy last measurements



Last 10 days diagrams



FixO3 is a FP7 Collaborative Project coordinated by the National Oceanography Centre, Southampton, UK



La ricerca italiana per il mare

For more information please contact: V. Cardin
Last update: February 19, 2015 -- Webmaster: R.lung
Thanks to the NOAA for the chart



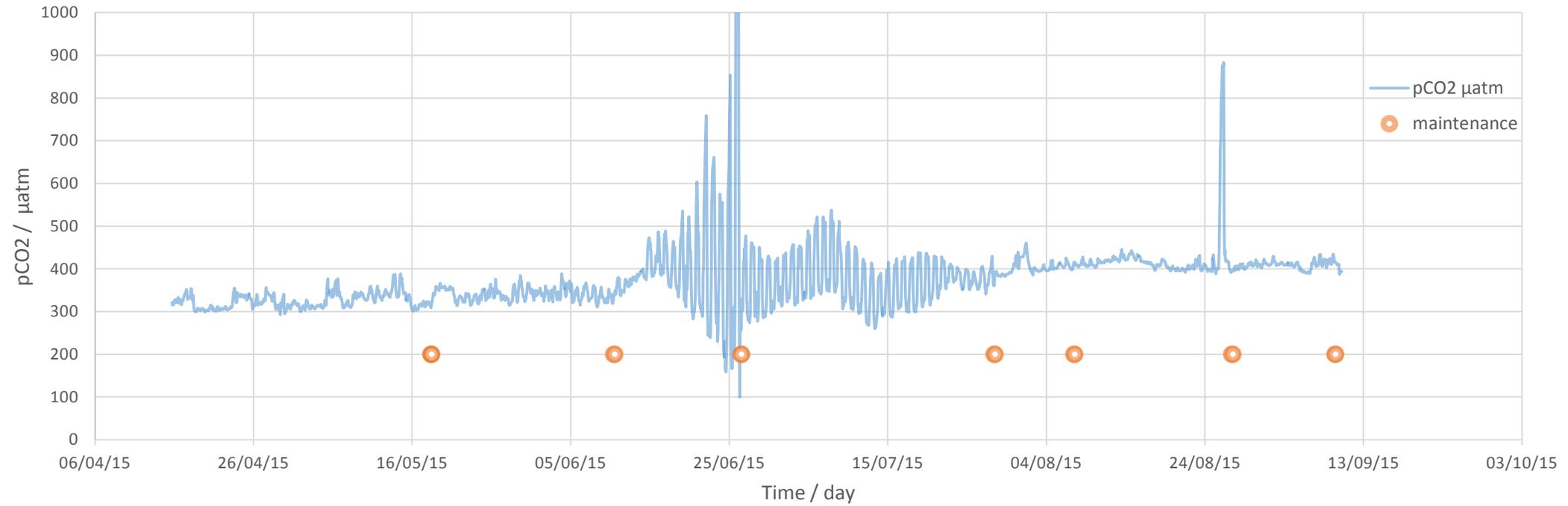
pCO₂ buoy data

DD/MM/YYYY	HH:mm:ss	ZeroAD (counts)	Current (counts)	XCO ₂ wet ppm	IRGAav T °C	pH ₂ O mbar	HumT °C	Press mbar	IRGA Det T °C	IRGA Sou T °C	pCO ₂ µatm	N	difx %
15/04/2015	15:59:05	44599	42066	324.95	39.9	13.117	18.32	1054	39.6	40.3	-99	0	-inf
15/04/2015	16:59:05	44599	42173	313.2	39.9	13.535	18.8	1040	39.5	40.3	321.47	1	4.247
15/04/2015	17:59:05	44599	42210	310.78	39.9	13.594	18.64	1031	39.6	40.3	316.22	2	0.016
15/04/2015	18:59:05	44599	42219	311.3	39.9	13.766	18.72	1025	39.6	40.4	314.91	3	0.004
15/04/2015	19:59:05	44599	42213	313.98	39.9	14.074	18.84	1022	39.6	40.3	316.69	4	-0.006
15/04/2015	20:59:04	44599	42216	314.03	39.9	14.137	18.8	1020	39.6	40.3	316.12	5	0.002
15/04/2015	21:59:05	44599	42215	315.12	39.9	14.311	18.88	1018	39.6	40.3	316.6	6	-0.002
15/04/2015	22:59:30	44654	42370	304.59	39.9	14.663	19.92	1002	39.6	40.3	-99	0	0.049
15/04/2015	23:59:04	44654	42219	327.85	39.9	14.536	19.12	1008	39.6	40.3	326.15	1	4.294
16/04/2015	00:59:04	44654	42222	325.81	39.9	14.411	18.88	1011	39.6	40.3	325.09	2	0.003
16/04/2015	01:59:04	44654	42241	322.31	39.9	14.2	18.76	1012	39.6	40.2	321.91	3	0.01
16/04/2015	02:59:05	44654	42204	328.03	39.9	14.248	18.6	1013	39.6	40.3	327.95	4	-0.019
16/04/2015	03:59:05	44654	42199	328.17	39.9	14.36	18.72	1015	39.6	40.3	328.74	5	-0.002
16/04/2015	04:59:05	44654	42229	323.52	39.9	14.248	18.6	1014	39.6	40.2	323.76	6	0.015
16/04/2015	05:59:05	44654	42203	327.79	39.9	14.307	18.56	1015	39.5	40.3	328.36	7	-0.014
16/04/2015	06:59:05	44654	42245	320.46	39.9	14.382	18.64	1015	39.6	40.3	321.01	8	0.022
16/04/2015	07:59:30	44657	42389	299.82	39.9	14.757	19.68	1007	39.6	40.3	-99	0	0.072
16/04/2015	08:59:05	44657	42249	321.77	39.9	14.495	18.76	1011	39.5	40.3	321.06	1	4.243
16/04/2015	09:59:04	44657	42238	322.51	39.9	14.631	18.8	1014	39.6	40.3	322.75	2	-0.005
16/04/2015	10:59:04	44657	42229	323.16	39.9	14.708	18.88	1016	39.6	40.3	324.04	3	-0.004
16/04/2015	11:59:04	44657	42171	331.45	39.9	15.174	19.36	1019	39.6	40.3	333.33	4	-0.029
16/04/2015	12:59:05	44657	42190	327.84	39.9	15.111	19.4	1020	39.6	40.3	330.02	5	0.01
16/04/2015	13:59:04	44657	42206	324.85	39.9	14.994	19.28	1020	39.5	40.3	327.01	6	0.009
16/04/2015	14:59:04	44657	42250	318.24	39.9	14.571	18.84	1019	39.5	40.4	320.05	7	0.021
16/04/2015	15:59:05	44657	42231	321.11	39.9	14.844	18.92	1019	39.6	40.3	322.93	8	-0.009
16/04/2015	16:59:30	44661	42377	299.91	39.9	15.203	19.92	1013	39.6	40.3	-99	0	0.072
16/04/2015	17:59:04	44661	42198	327.71	39.9	15.095	19.28	1018	39.5	40.3	329.25	1	4.326
16/04/2015	18:59:04	44661	42233	321.5	39.9	14.767	18.84	1019	39.6	40.3	323.32	2	0.018
16/04/2015	19:59:05	44661	42264	316.21	39.9	14.517	18.68	1019	39.6	40.4	318	3	0.016

Seawater pCO₂



surface seawater pCO₂ MAMBO buoy



Laboratory measurements of
the carbonate system:
pH and TA

CARBON DIOXIDE PARAMETERS IN SEA WATER

Total Dissolved Inorganic Carbon

$$C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad T, p \text{ independent}$$

UNITS: moles per kilogram of solution (usually $\mu\text{mol kg}^{-1}$)

Total Hydrogen Ion Concentration (pH)

$$\text{pH} = -\lg [\text{H}^+] \quad \text{or on the total scale} \quad \text{pH}_T = -\log ([\text{H}^+]_F + [\text{HSO}_4^-]) \quad T, p \text{ dependent}$$

UNITS: pH is dimensionless

But, total hydrogen ion concentration is in moles per kilogram of solution

Partial Pressure of CO_2

(in air that is in equilibrium with the water sample)

$$p(\text{CO}_2) = x(\text{CO}_2) p = [\text{CO}_2] / K_0 \quad T, p \text{ dependent}$$

UNITS: pressure units (usually μatm)

Total Alkalinity

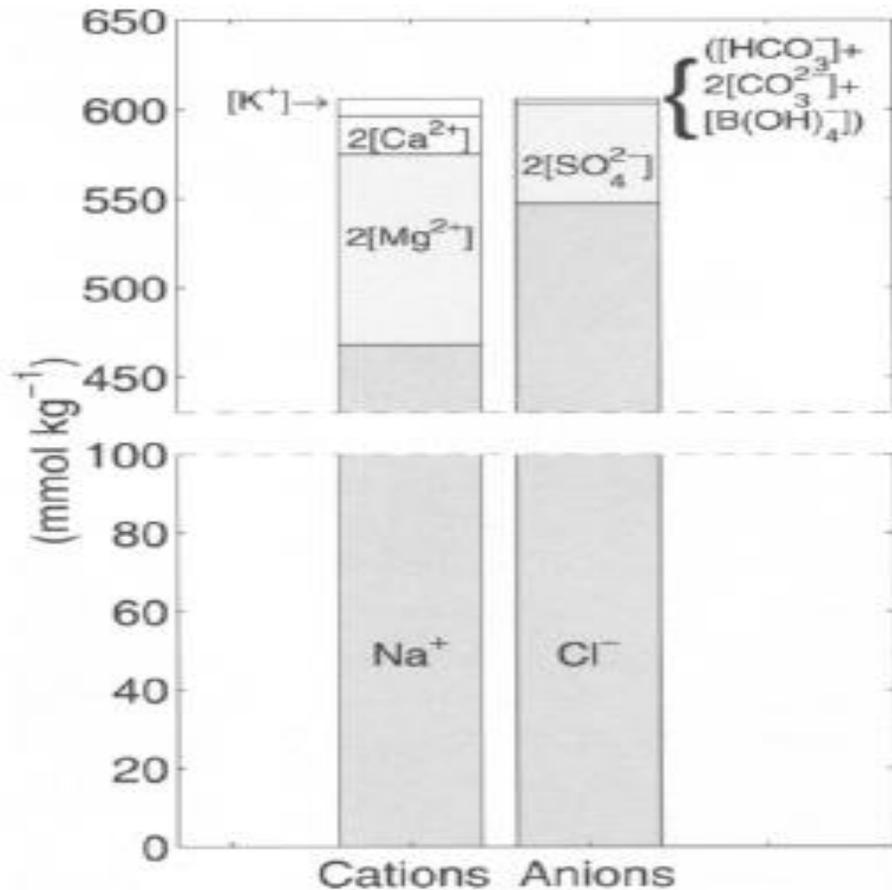
$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+] \quad T, p \text{ independent}$$

UNITS: moles per kilogram of solution (usually $\mu\text{mol kg}^{-1}$)

Table 1.3 Methods for the measurement of parameters of the carbon dioxide system in seawater (also see notes below).

Total dissolved inorganic carbon <ul style="list-style-type: none">A. Acidification / vacuum extraction / manometric determinationB. Acidification / gas stripping / coulometric determinationC. Acidification / gas stripping / infrared detectionD. Closed-cell acidimetric titration
Total alkalinity <ul style="list-style-type: none">E. Closed-cell acidimetric titrationF. Open-cell acidimetric titrationG. Other titration systems
pH <ul style="list-style-type: none">H. Electrometric determination with standard Tris bufferI. Spectrophotometric determination using <i>m</i>-cresol purple
$x'(\text{CO}_2) / p(\text{CO}_2)$ <ul style="list-style-type: none">J. Direct infrared determination of $x'(\text{CO}_2)$

Total alkalinity



$([Na^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [K^+])$ over negative charge $([Cl^-] + 2[SO_4^{2-}])$ is compensated by $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$, where the latter sum represents the most important contribution to TA.

Figure 1.2.15: Charge balance of the major ions in seawater (cf. Broecker and Peng, 1998). The small excess charge of the conservative cations over anions is mainly balanced by $[HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-]$.

The total charge concentration of the conservative cations yields 605.0 mmol kg⁻¹, while the total charge concentration of the conservative anions yields 602.8 mmol kg⁻¹.

The small charge imbalance of 2.2 mmol kg⁻¹ is equal to the total alkalinity in seawater

(strictly, this is only correct when phosphate, ammonia and bisulfate ion are neglected).

A more exact definition (Dickson, 1981) of total alkalinity is the quantity of hydrogen ion required to neutralize bases formed from weak acids with $pK_a > 4.5$. Our determination of total alkalinity employs the potentiometric titration of a seawater sample with hydrochloric acid.

Certified Reference Materials

Table 1.5 Availability of reference materials for the quality control of carbon dioxide measurements in seawater.
RM: Reference materials.

Analytical measurement	Desired accuracy [†]	Uncertainty ^{††}	Availability
Total dissolved inorganic carbon	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	Since 1991 [Ⓐ]
Total alkalinity	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	Since 1996 [Ⓑ]
pH	± 0.002	± 0.003	Since 2009 [Ⓒ]
Mole fraction of CO ₂ in dry air	$\pm 0.5 \mu\text{mol/mol}$	$\pm 0.1 \mu\text{mol/mol}$	Since 1995 [Ⓓ]

[†]These values are based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO₂ content of seawater that allow the increases due to the burning of fossil fuels to be observed.

^{††}Estimated standard uncertainties for the reference materials described here.

[Ⓐ]Sterilised natural seawater, certified using a definitive method based on acidification, vacuum extraction, and manometric determination of the CO₂ released. Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

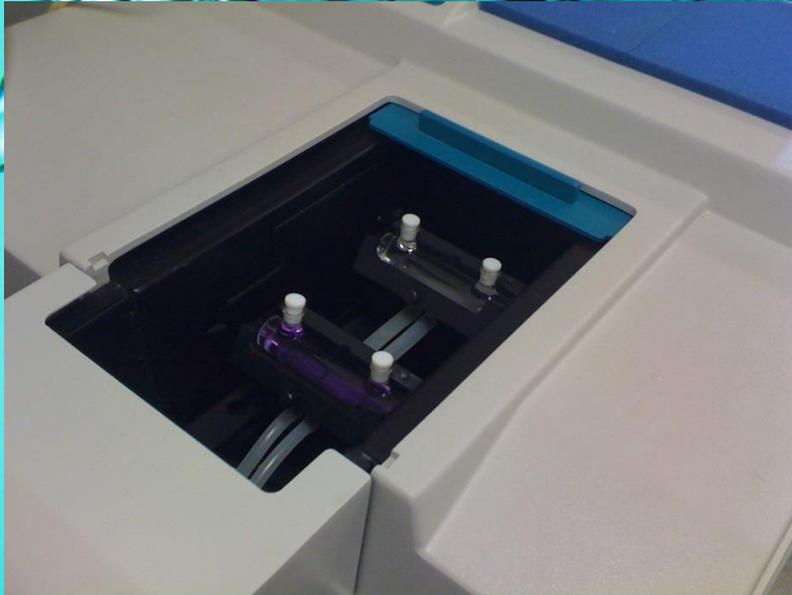
[Ⓑ]Certified using a definitive method based on an open-cell acidimetric titration technique (Dickson *et al.*, 2003). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

[Ⓒ]Standard buffer solutions based on Tris in synthetic seawater (Nemzer & Dickson, 2005). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

[Ⓓ]Cylinders of air certified by non-dispersive infrared spectrometry. Available from NOAA/ESRL, Boulder, CO (<http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>). However, gas mixtures certified to a lesser accuracy can be obtained from a variety of manufacturers.

Spectrophotometric pH measurement

- seawater sampled directly in the spectrophotometric cells avoiding CO₂ exchanges with the atmosphere
- measurements performed immediately after sampling
- thermostatted cells at 25,0 during measurements
- indicator: *m*-cresol violet



Methods – pH spectrophotometric measurements using *m*-cresol purple

The standard operative procedure was followed (SOP 6b., Dickson et al ., 2007)

- The measurements have been carried out in a double beam Varian Cary 100 spectrophotometer with thermostated (25.0° C) cylindrical cell holders.
- Duplicate spectrophotometric measurements were performed on each sample adding a double amount (30 µL) of indicator (pH ~8.0) in order to corrected for effect of the addition of the indicator

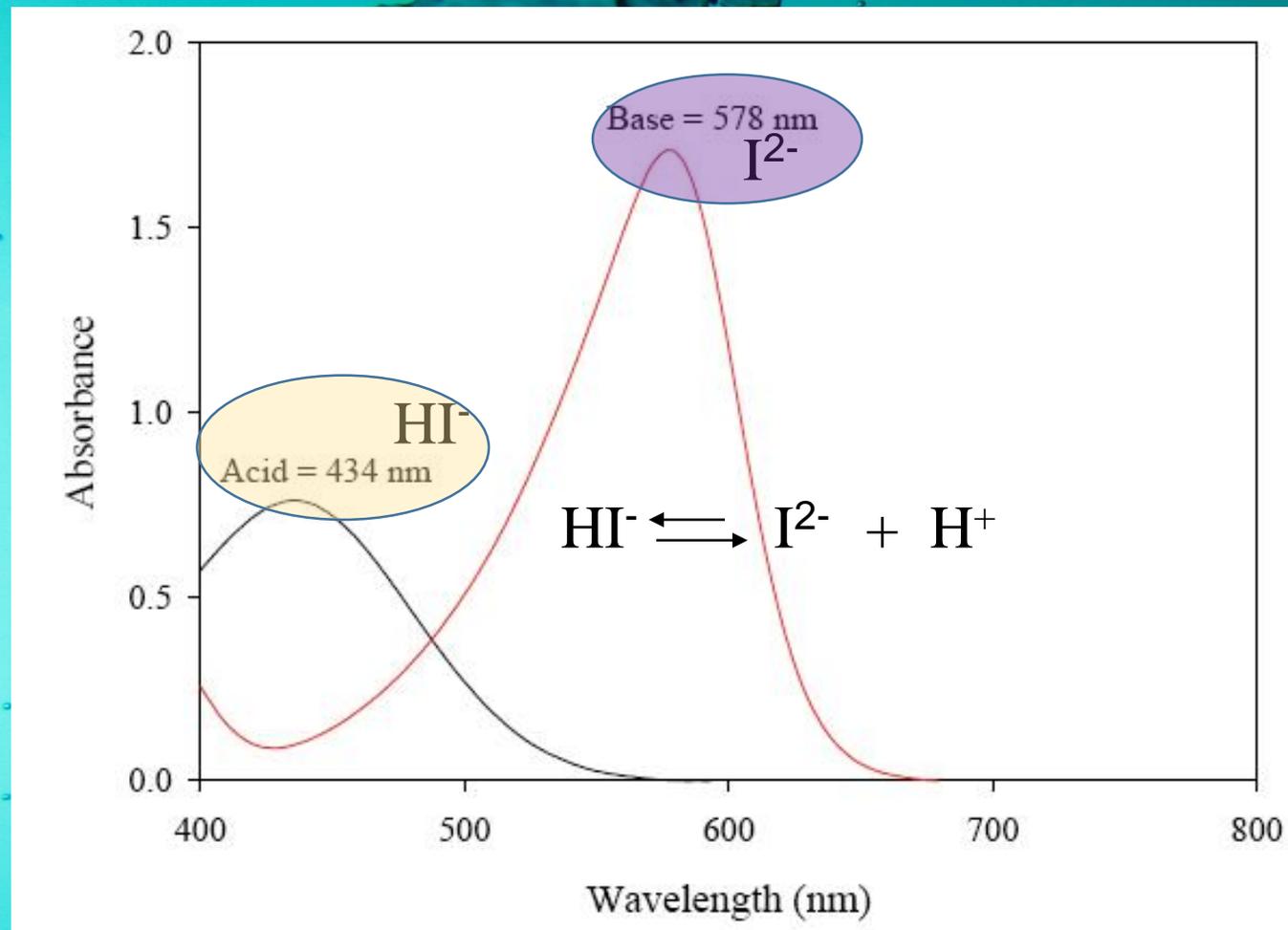
The results were expressed on the pH_T scale, the in situ pH can be calculated on the basis of the in situ temperature and salinity, according to the algorithm of Millero (2007).



The accuracy of measurements was eastimated from periodic determinations of newly opened CRM Batch 107, deriving the pH_T from the certified measurements of DIC ad A_T , by the CO2SYS software (Lewis and Wallace, 1998) using the dissociation constants for carbonic acids reported by Millero et al. (2006) , the dissociation constant for bisulfate ion of Dickson (1990).

Accuracy	Reproducibility
≤ 0.005	± 0.001

Spectrophotometric pH measurement

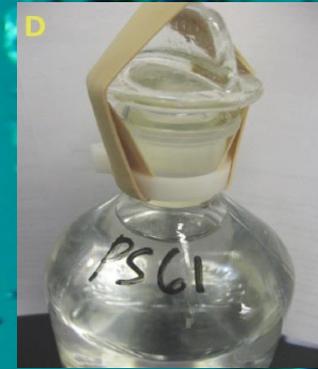
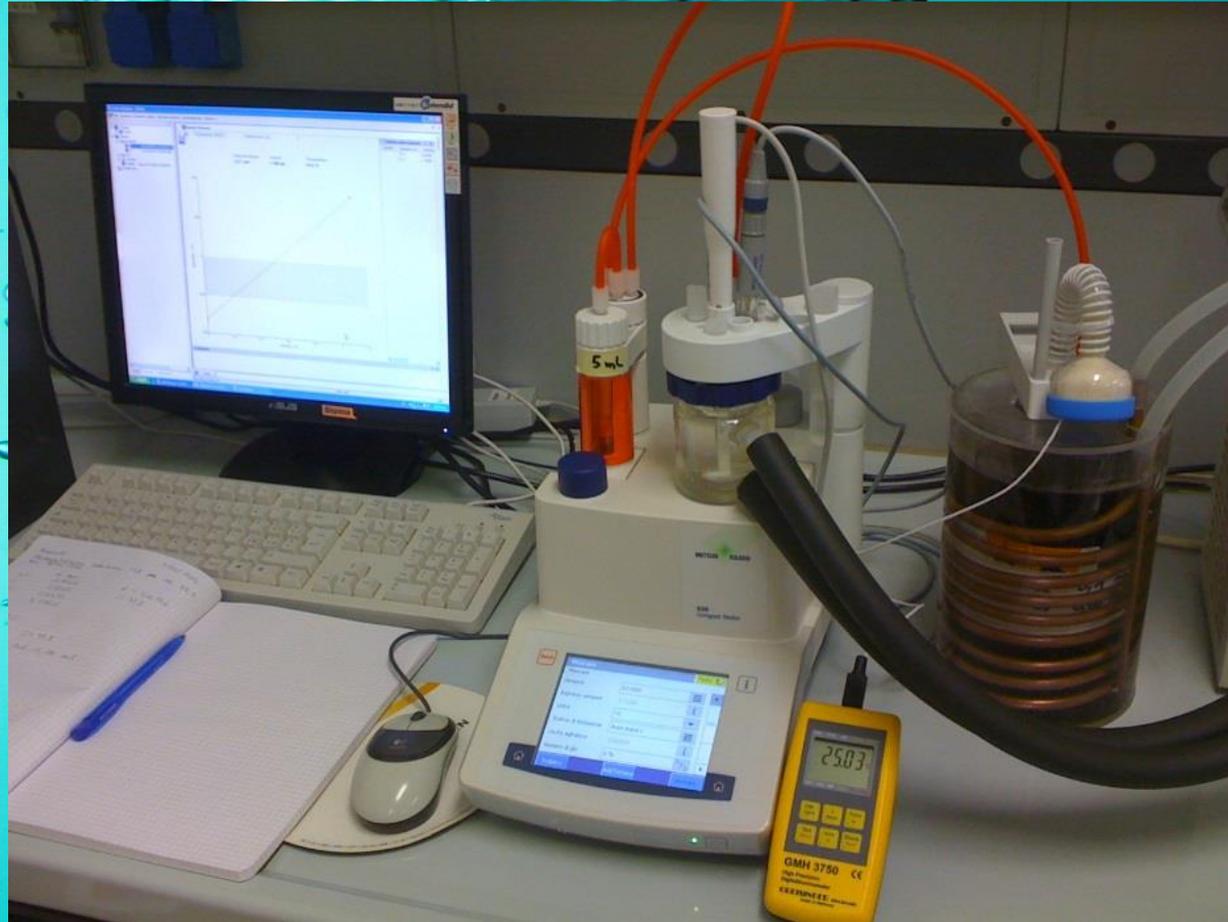


$$\text{pH} = -\lg K(\text{HI}^-) \left(\frac{\epsilon_1(\text{I}^{2-})}{\epsilon_2(\text{HI}^-)} \right) + \lg \left(\frac{A_1 / A_2 - \epsilon_1(\text{HI}^-) / \epsilon_2(\text{HI}^-)}{1 - (A_1 / A) \epsilon_2(\text{I}^{2-}) / \epsilon_1(\text{I}^{2-})} \right)$$

(Dikson et al., 2007)

Total alkalinity determination

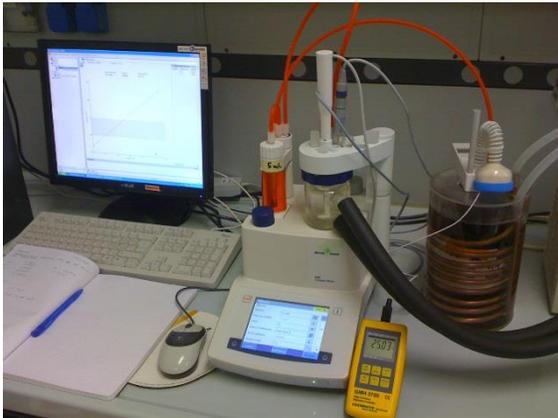
- Potentiometric titration with HCl in open cell



Total alkalinity (AT) - open cell potentiometric titration

The standard operative procedure was followed (SOP 3b., Dickson et al ., 2007)

- The coastal seawater samples are filtered in order to remove the particulate carbonates which is mainly due to the discharge of local rivers and resuspension of bottom sediments, 200 μL of HgCl_2 saturated are added to 500 mL sample
- The 0.1 M HCl titration solution was prepared in NaCl medium matching the ionic strength of the samples, standardized against Na_2CO_3 .



Periodic controls on the accuracy have been carried out on certified reference material CRM Batch 107 supplied by University of California, San Diego USA.

Accuracy	Reproducibility
$\leq 2 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$

To estimate AT from titration data, a computer program, based on a non-linear least squares evaluation of the data, was adapted from

Dickson et al. 2007

Dickson A.G., Sabine C. L., Christian J.R. SOP 3b (2007) - Determination of total alkalinity in seawater using an open-cell titration, ver. 3.01 2008. In: Dickson, A.G., Sabine, C.L., Christian, J.R. (eds.) 2007. Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 p.

pCO₂ calculations from At and pHT

Different computer programs are available for the calculation of the carbonate system base on the thermodynamic equilibria

Provide built in data for the various equilibrium constants and for total concentrations such as boron that are proportional to salinity.

Allow calculation of CO₂ (acid-base)speciation; typically from two (or more) analytical parameters, as well as salinity, temperature & pressure.

We will use

CO₂SYs Excel ver 2.1 (2012)

Table 1. Carbonate system software packages.

Package	Language	Version	Reference
CO ₂ SYs ^a	QBasic	1.05	Lewis and Wallace (1998)
CO ₂ SYs ^b	Excel	24	Pelletier et al. (2007)
CO ₂ SYs ^a	Excel	2.1	Pierrot et al. (2006)
CO ₂ SYs ^a	MATLAB	1.1	van Heuven et al. (2011)
CO ₂ calc ^c	Visual Basic	1.3.0	Robbins et al. (2010)
csys ^d	MATLAB	04–2014	Zeebe and Wolf-Gladrow (2001)
ODV ^e	C++	4.5.0	Schlitzer (2002)
mocsy ^f	Fortran 95	2.0	Orr and Epitalon (2015)
seacarb ^g	R	3.0.6	Gattuso et al. (2015)
swco ₂ ^h	Excel	2	Hunter (2007); Mosley et al. (2010)
swco ₂ ^h	Visual Basic	2	Hunter (2007)

^a <http://cdiac.ornl.gov/oceans/co2rprt.html>

^b <http://www.ecy.wa.gov/programs/eap/models.html>

^c <http://pubs.usgs.gov/of/2010/1280/>

^d <http://www.soest.hawaii.edu>

^e <http://odv.awi.de/>

^f <http://ocmip5.ipsl.jussieu.fr/mocsy>

^g <http://cran.r-project.org/package=seacarb>

^h http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

Input:

- - Salinity, Temperature and Pressure (or depth) (input conditions). If left empty, the Pressure is assumed zero in the calculations.
- - Total Si (optional) and Total Phosphate (optional). If left empty the total Si and Total P concentrations are assumed zero in the calculations.
- - Two (2) known CO₂ parameters (TA, TCO₂ , pH, pCO₂ or fCO₂)
- Temperature and Pressure (or depth) at which the parameters wish to be calculated (output conditions)

Scales and constants

K1 and K2 for carbonic acid*

KB for boric acid*

Kw for water

KSO4 for bisulphate ion*

KF for hydrogen fluoride

KP1, KP2, KP3 for phosphoric acid

Ksi for silicic acid

Solubility products Ksp(calcite), Ksp (aragonite) and K0
(CO2 in seawater)

* Requires operator choice

Choosing equilibrium constants

The important constraint is that the pH and the pKs are on the same scale.

Through comparisons with field data it is presently considered that these are the best:

- Lueker et al (Mehrbach *et al.* (1973) fitted to total hydrogen ion scale valid for S: 19 - 43 and T : 2 - 35 C,
- Mehrbach 1973 refitted by Dickson and Millero, 1987
- Cai and Wang (1998) suitable for estuarine waters
- Millero et al (2006) suitable for extreme T and S (0-50)
- Millero (2010), applicable over wider ranges of S(1–50) and T (0–50 C).
- the sulphate constant from Dickson (1990)
- the parameterization of borate from Uppström (1974)

Output (for both “input” and “output” conditions):

- - The other three (3) CO₂ parameters.
 - - Contributions to the alkalinity.
 - - Carbonate speciation.
 - - Degree of saturation for calcite and for aragonite.
 - - Revelle Factor
-
- The last four (4) are referred to as “Auxiliary Data” in the macro.

How to Run the Macro

1. Open the file in Excel...

- a. Remember to enable macros.
- b. If Excel doesn't give you the choice, go to "Tools Macros Security..." and select "medium". Close the file and re-open it.

2. In Sheet "INFO":

You can select which section of the program you want information on by selecting the appropriate option from the left column. The information will be listed in the text box in the middle of the page.

3. In Sheet "INPUT":

- a. Select the set of CO₂ constants you want to use for the calculations
- b. Select the KHSO₄
- c. Select the pH scale of your data.
- d. Select the Total Boron formulation to use.

pCO₂ calculation from A_T and pH_T 25°C

- CO2SYS

Outputs

CO2Sys_v2.1_Acidit_luglio [modalità compatibilità] - Excel

FILE HOME INSERISCI LAYOUT DI PAGINA FORMULE DATI REVISIONE VISUALIZZA Foxit PDF

Comic Sans MS 12

Testo a capo

Generale

Formattazione condizionale Formatta come tabella Stili cella

Inserisci Elimina Formato

Ordina e filtra Trova e seleziona

Salinity

	AI	AM	AN	AO	AP	AQ	AR	AS	AT	AU	AV	AW	AX	AY	AZ	BA	BB	BI	BD	BE
1																				
2	RESULTS (Output Conditions)																			
3	t(oC) out	P (dbars) out	pH out	fCO2 out (µatm)	pCO2 out (µatm)	HCO3 out (µmol/kgSW)	CO3 out (µmol/kgSW)	CO2 out (µmol/kgSW)	B Alk out (µmol/kgSW)	OH out (µmol/kgSW)	P Alk out (µmol/kgSW)	Si Alk out (µmol/kgSW)	Revelle out	ΩCa out	ΩAr out	xCO2 out (dry at 1 atm) (ppm)		SubFlag		
4	27.264	0.0	8.081	424.7	426.0	2034.9	292.3	11.3	110.2	9.0	0.0	0.0	9.103	7.00	4.65	441.5				
5	23.737	10.0	8.060	441.7	443.1	2060.0	258.3	12.8	105.0	6.5	0.0	0.0	9.545	6.06	3.99	456.0				
6	22.490	20.0	8.068	433.2	434.6	2076.4	255.5	12.9	104.9	5.9	0.0	0.0	9.627	5.96	3.92	446.3				
7	15.870	30.0	8.079	418.4	419.9	2139.8	211.5	15.0	92.2	3.2	0.1	0.1	10.645	4.92	3.17	427.3				
8	28.362	0.0	8.095	408.9	410.2	2006.7	306.2	10.7	113.6	10.2	0.0	0.0	8.894	7.37	4.92	426.1				
9	24.328	10.0	8.045	455.4	456.9	2050.8	256.2	12.9	104.9	6.6	0.0	0.0	9.530	5.99	3.96	470.7				
10	20.432	20.0	8.068	430.0	431.4	2081.9	237.4	13.5	100.2	4.9	0.1	0.1	9.940	5.53	3.61	441.7				
11	12.610	35.0	8.070	429.4	431.0	2198.9	188.2	17.0	83.8	2.3	0.1	0.2	11.429	4.37	2.80	437.2				
12	29.337	0.0	8.109	394.8	396.0	1983.7	314.9	10.1	113.3	11.2	0.0	0.0	8.798	7.68	5.13	412.3				
13	23.055	10.0	8.084	415.5	416.8	2049.7	259.7	12.3	104.9	6.3	0.0	0.0	9.540	6.13	4.03	428.5				
14	18.277	20.0	8.067	434.2	435.7	2127.5	223.8	14.5	95.4	4.0	0.0	0.1	10.340	5.21	3.38	444.7				
15	12.410	35.0	8.046	461.7	463.5	2237.3	179.5	18.5	79.5	2.1	0.0	0.3	11.823	4.17	2.67	470.0				
16	29.008	0.0	8.101	403.1	404.3	1995.6	311.1	10.4	113.3	10.8	0.0	0.0	8.843	7.54	5.04	420.7				
17	21.693	10.0	8.105	392.0	393.3	2046.9	260.8	12.0	106.8	5.9	0.1	0.0	9.510	6.13	4.01	403.4				
18	16.873	20.0	8.097	398.8	400.2	2110.8	225.0	13.9	97.0	3.7	0.1	0.1	10.279	5.24	3.39	407.8				
19	13.057	30.0	7.993	536.0	538.0	2290.8	166.8	21.0	72.9	2.0	0.2	0.3	12.429	3.88	2.49	545.9				

PRONTO

Acknowledgements

- **Mark Barry**, Pro-Oceanus Systems, Bridgewater, NS, Canada
- **Paolo Mansutti**, OGS Trieste, Italy
- **Enrico Vinzi**, Marine Protected Area of Miramare, Trieste, Italy
- **Riccardo lungwirth**, OGS Trieste, Italy

Acid.it (Science for mitigation and adaptation policy of ecological and socio economical impacts of Acidification in italian seas) and RITMARE Programs supported by Ministero dell'Istruzione, dell'Università e della Ricerca

FIXO3 FP7 EU Project

Thank you for
your attention

