Ocean Acidification International Coordination Centre

IAEA OA-ICC

UNIVERSITY OF GOTHENBURG

KUNGL. VETENSKAPS-AKADEMIEN

THE ROYAL SWEDISH ACADEMY OF SCIENCES

Basic training course on ocean acidification

EVT1804704

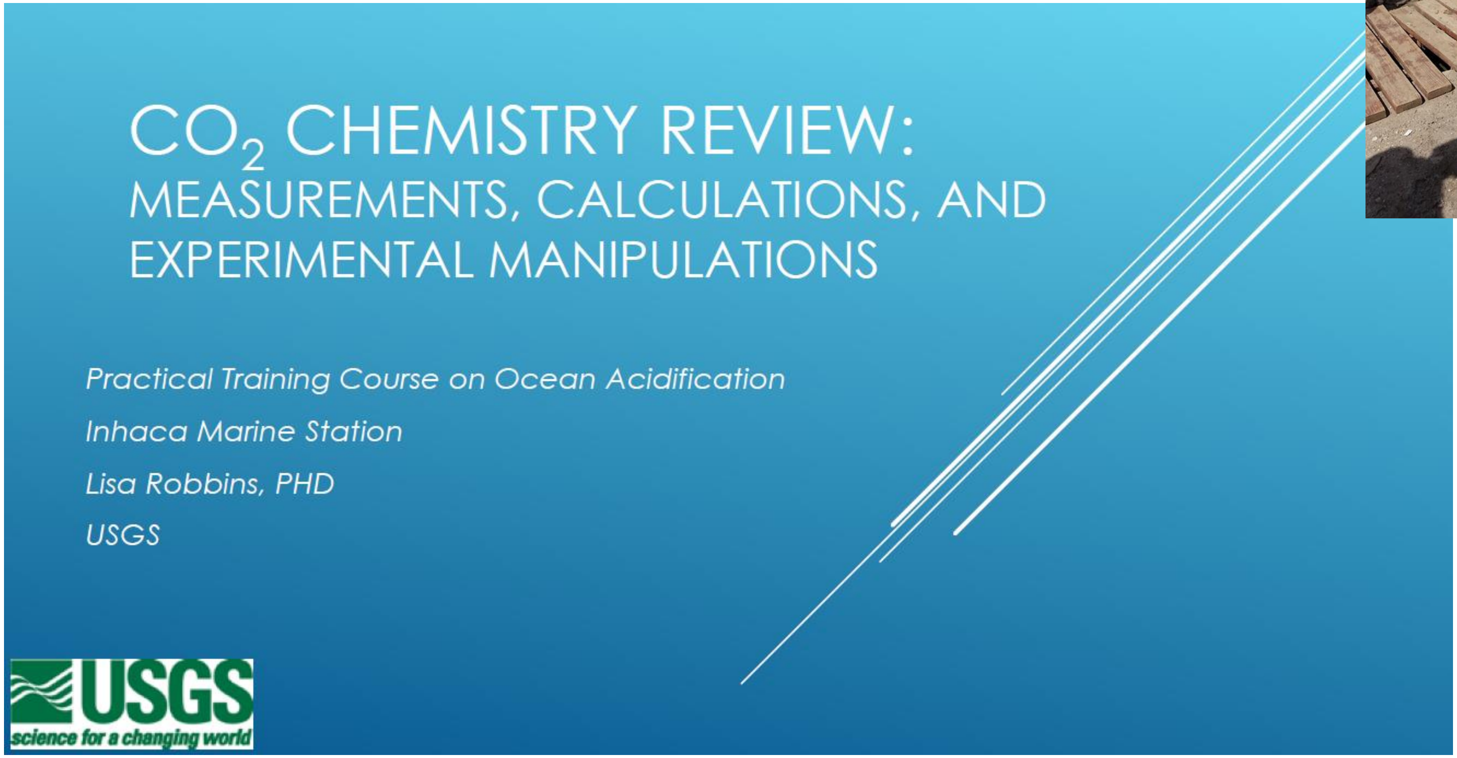
14-19 March 2022

(by a biologist !)

Seawater carbonate chemistry

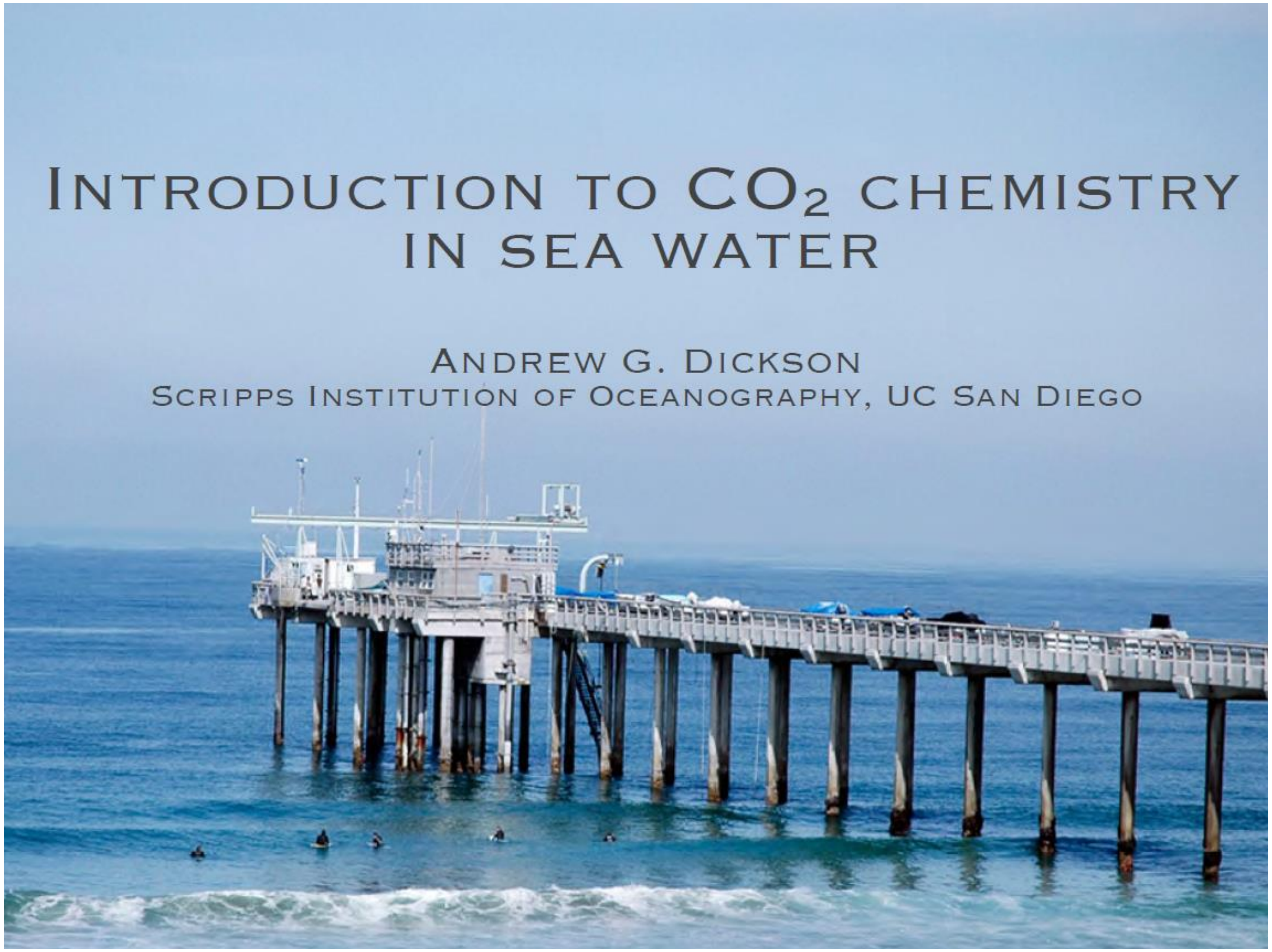
The real carbonate chemists

Dr. Lisa Robbins

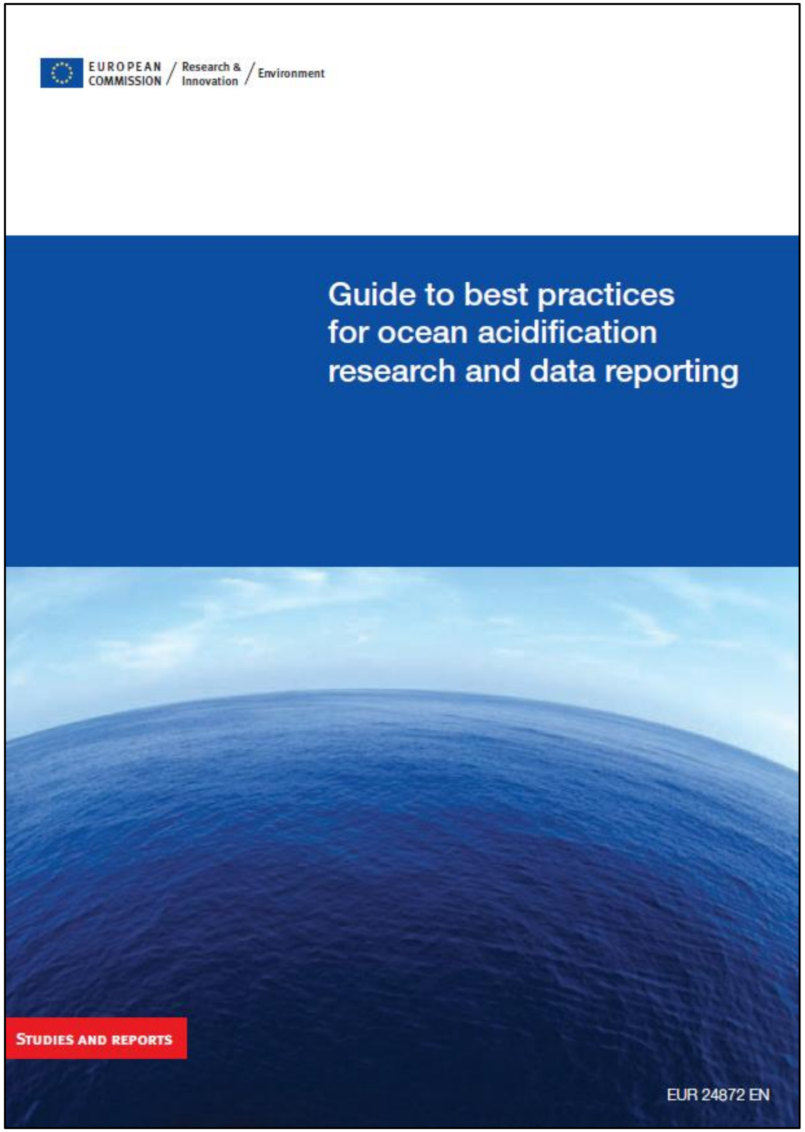


The real carbonate chemists

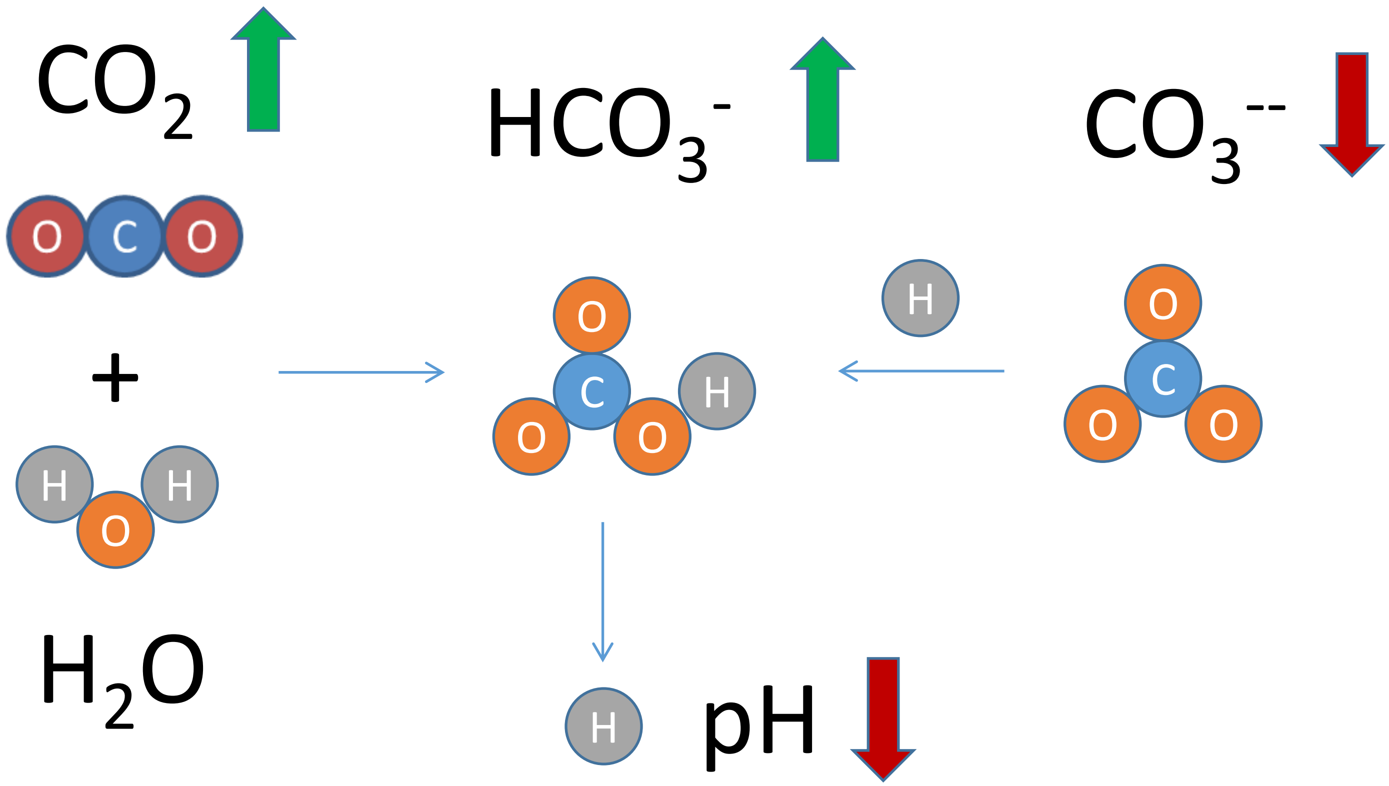
Dr. Andrew Dickson



The reference (but…)



Ocean acidification in a nutshell



Not so complicated?

To characterize the carbonate system we need to measure or calculate:

Parameter	Marine chemistry Notation	Unit
pH[(1)]	Total scale	-
Partial pressure of CO_2	$p(CO_2)$ (pCO_2, Pco_2, $p(CO_2)$)	µatm
CO_2 solubility	K_0	mol kg^{-1} atm^{-1}
Dissolved inorganic carbon or total CO_2	DIC (C_T, $\sum CO_2$, Tco_2)	mol kg^{-1}
Bicarbonate concentration	$[HCO_3^-]$	mol kg^{-1}
Carbonate concentration	$[CO_3^{2-}]$	mol kg^{-1}
Ammonium concentration	$[NH_4^+]$	mol kg^{-1}
Total alkalinity	A_T (TA, AT, ALK)	mol kg^{-1}
Saturation state	Ω	–

We can measure :

- pH
- DIC
- Alkalinity
- *p*CO_2

You also need Temp, salinity, and pressure

USE 2 TO CHARACTERIZE THE SYSTEM
BUT MUST USE EQUILIBRIUM
CONSTANTS FOR THE CALCULATIONS

Which one to measure?

	Advantages	Disadvantages
C_T	T, p independent Unambiguous interpretation of changes	Needs care with sample handling No autonomous system available
pH	Autonomous systems available Master variable?	Function of T, p Needs care with sample handling Interpretation problems
$p(CO_2)$	Autonomous systems available	Function of T, p Changes not easy to interpret
A_T	T, p independent Often possible to interpret changes	No autonomous system available Harder to interpret in some systems

1. Dissolved Inorganic Carbon (DIC)

1. Acidify a known amount of sample
2. Extract the CO_2
3. Measure the amount of CO_2

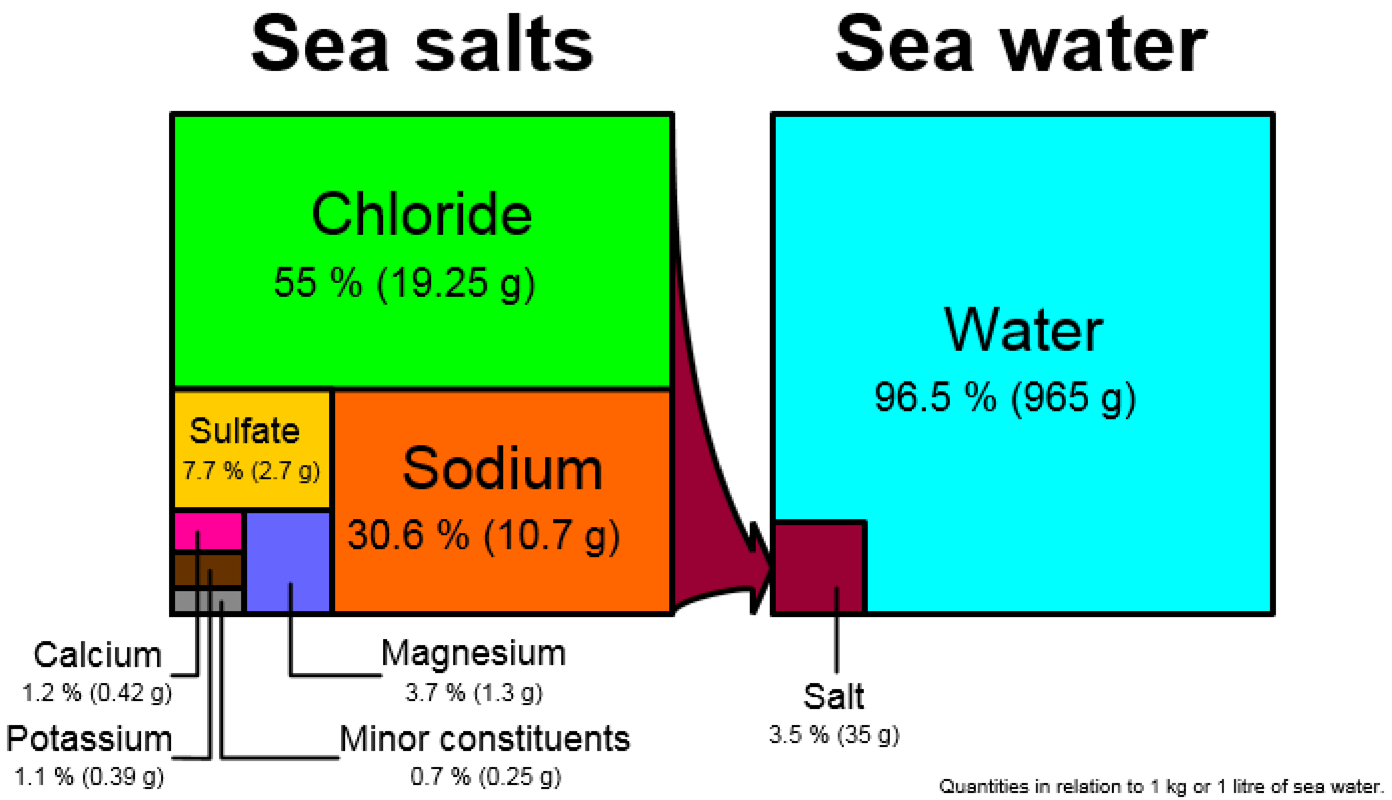
	Advantages	Disadvantages
IR system	Cheaper system Faster sample throughput Less waste disposal Less *start-up* time Smaller sample ?	Lower reproducibility Calibration not v. stable Limited collaborative testing as yet
Coulometry system	Higher reproducibility Stable calibration Well tested in many labs	Slower sample throughput Proprietary coulometer solution (hazardous) Significant *start-up* time needed

2. pH (Total Hydrogen ions concentration)

	Equipment Cost	Ease of use	Uncertainty in best labs
Electrometric pH cell	Relatively cheap (need *T* control)	Simple to use, needs regular recalibration*	0.02 limited availability of RMs
Using indicator & spectrophotometer	Mid-range k$ 10–25	Can be automated	< 0.01 limited availability of pure mCP

* The Honeywell DuraFET® seems to have a significantly more stable calibration than a conventional pH cell.

Well… seawater is…



ACID-BASE SPECIES COMPRISE A SUBSET OF THE "MINOR CONSTITUENTS" PRESENT IN SEAWATER

CO_2

OH^-

HCO_3^-

HF

CO_3^{2-}

H^+

H_2O

$B(OH)_3$

NH_4^+

$SiO(OH)_3^-$

H_3PO_4

$B(OH)_4$

PO_4^{3-}

organic acids

$H_2PO_4^-$

$Si(OH)_4$

NH_3

HPO_4^{2-}

organic bases

other acid/base species

2. pH (Total Hydrogen ions concentration)

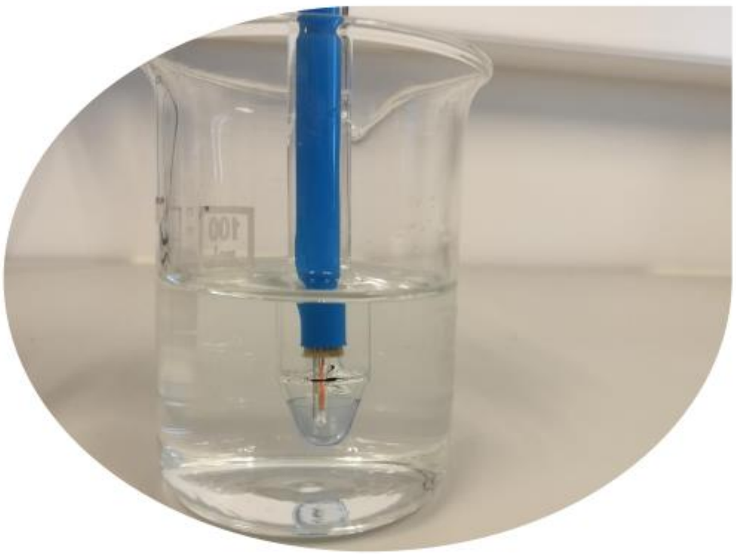
Important to use the right scale

Total scale

NBS / NIST scale

How to measure pH_T in biological experiments

TRIS buffer preparation, pH probe calibration, sampling and calculations



Sanja Grđan, University of Dubrovnik

Sam Dupont, University of Gothenburg

How to adjust the set pH value on your pH computer?

Sam Dupont (sam.dupont@gu.se)

Every time you are measuring pH in your aquarium system, it is important to ensure that your set value is still correct. For long-term experiments, it is common to have a drift in the reading of the glass electrode and to maintain an accurate seawater pH it is key to correct the **set value** on your computer.

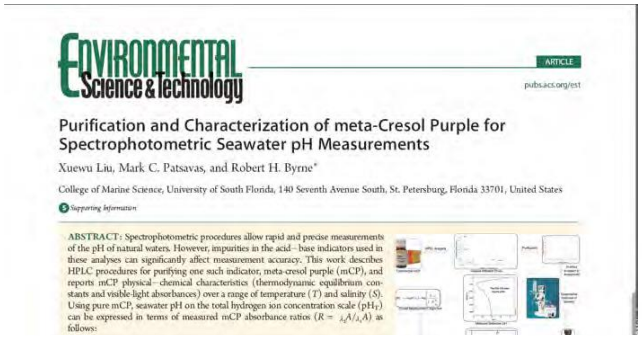
Here is the procedure to follow (see the xls sheet **pHset adjustments.xls**)

1. Before starting your experiment, you need to define:

- The **pH_T of the control** (e.g. 8.1)

2. pH (Total Hydrogen ions concentration)

Danger of using impure dyes



Environmental Science & Technology — ARTICLE — pubs.acs.org/est

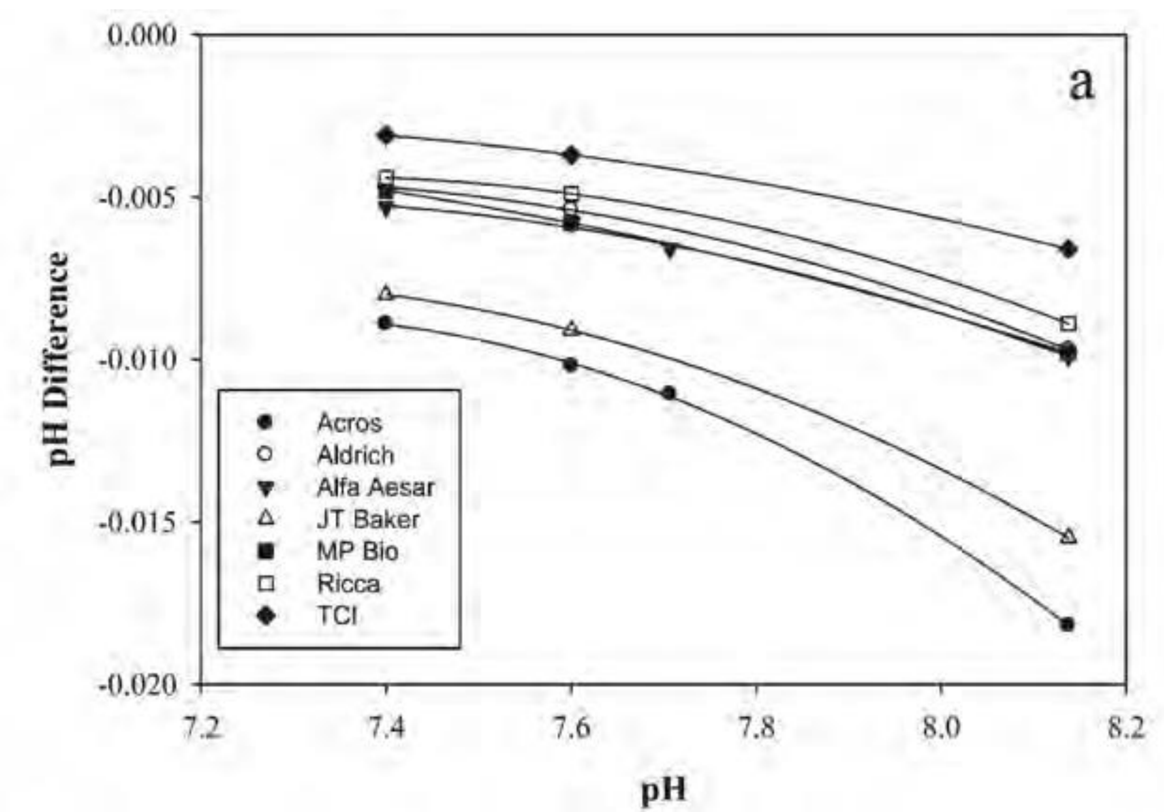
Purification and Characterization of meta-Cresol Purple for Spectrophotometric Seawater pH Measurements

Xuewu Liu, Mark C. Patsavas, and Robert H. Byrne*

College of Marine Science, University of South Florida, 140 Seventh Avenue South, St. Petersburg, Florida 33701, United States

Supporting Information

ABSTRACT: Spectrophotometric procedures allow rapid and precise measurements of the pH of natural waters. However, impurities in the acid–base indicators used in these analyses can significantly affect measurement accuracy. This work describes HPLC procedures for purifying one such indicator, meta-cresol purple (mCP), and reports mCP physical–chemical characteristics (thermodynamic equilibrium constants and visible-light absorbances) over a range of temperature (T) and salinity (S). Using pure mCP, seawater pH on the total hydrogen ion concentration scale (pH_T) can be expressed in terms of measured mCP absorbance ratios ($R = {}_{\lambda_2}A/{}_{\lambda_1}A$) as follows:



3. pCO_2

Species concentration, $[CO_2]$

A. Gas phase equilibration

- Measure $x(CO_2)$ in the gas phase using NDIR
- Measure $x(CO_2)$ in the gas phase using GC

B. Membrane equilibration (with gas or external solution)

- Measure $x(CO_2)$ in the gas phase using NDIR
- Measure pH in external solution (*see pH section*)

	Equipment Cost	Advantages / Disadvantages	Uncertainty*
infra-red analyzer	\$30,000 – \$60,000	Quality depends mostly on design of equilibrator	With careful calibration < 0.5%
pH-based analyzer	~\$25,000	Awkward to calibrate Membrane can foul	Can be 1–2%

* These values are for commercial systems when working well.

4. Total alkalinity

Acidimetric titration

- Closed-cell
- Open-cell

	Equipment Cost	Advantages / Disadvantages	Uncertainty*
Closed cell	~$30,000	Uses cell to measure *V* Problems with back-pressure	~2-4 μmol kg^{-1}
Open cell	$15,000 to $30,000	Can be very precise Easier to diagnose faults	~1–4 μmol kg^{-1}

* These values are for commercial systems when working well.

New simpler and cheaper technology

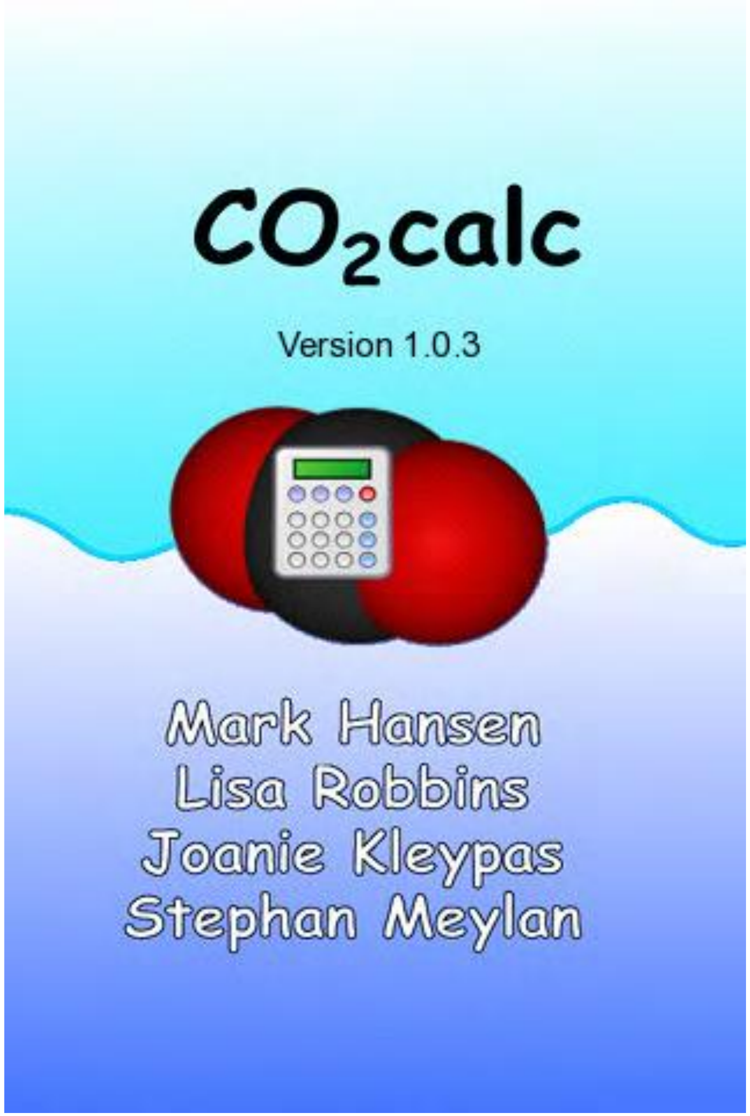
Ocean Acidification
International
Coordination Centre
OA-ICC

IAEA INT/7/019

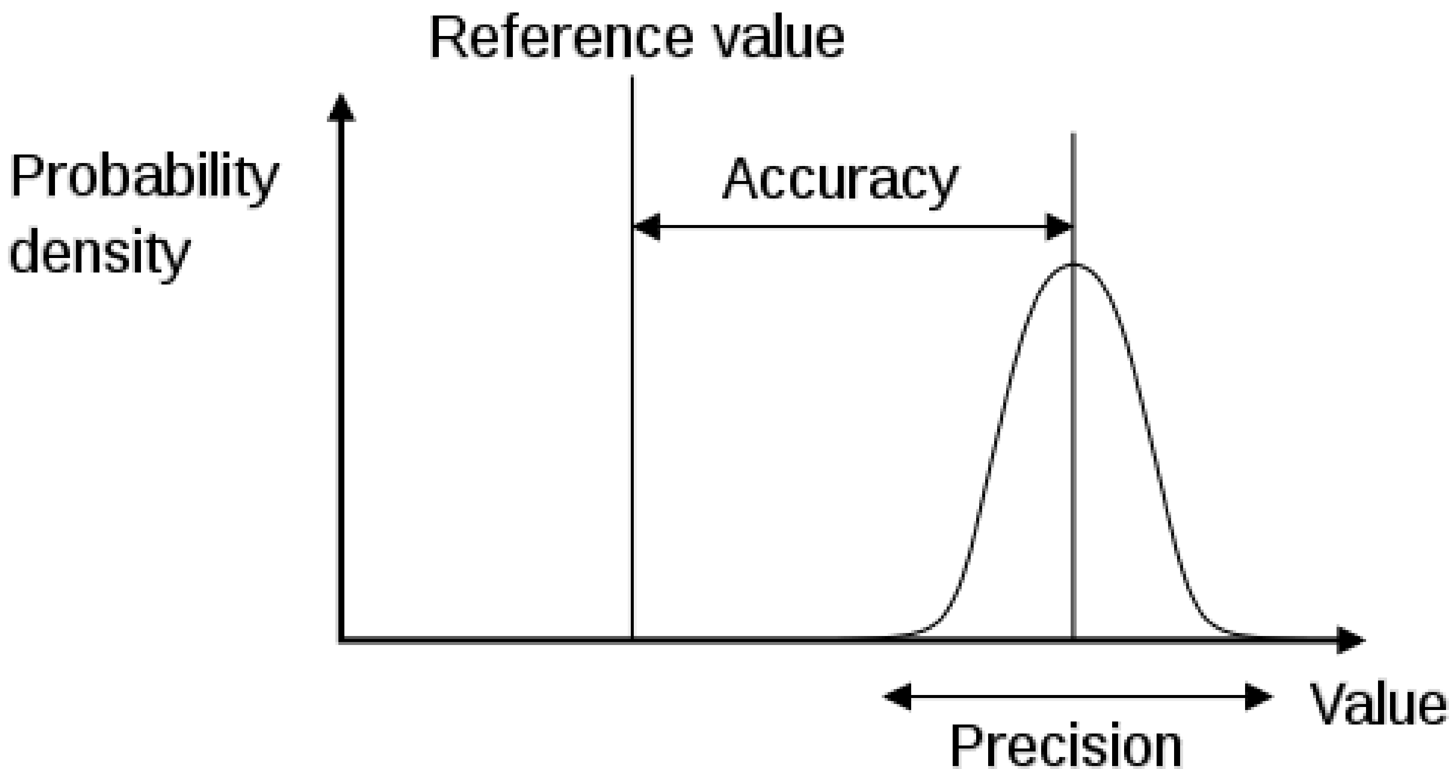
Supporting a global ocean acidification observing network - toward increased involvement of developing states

- New technology
- kits

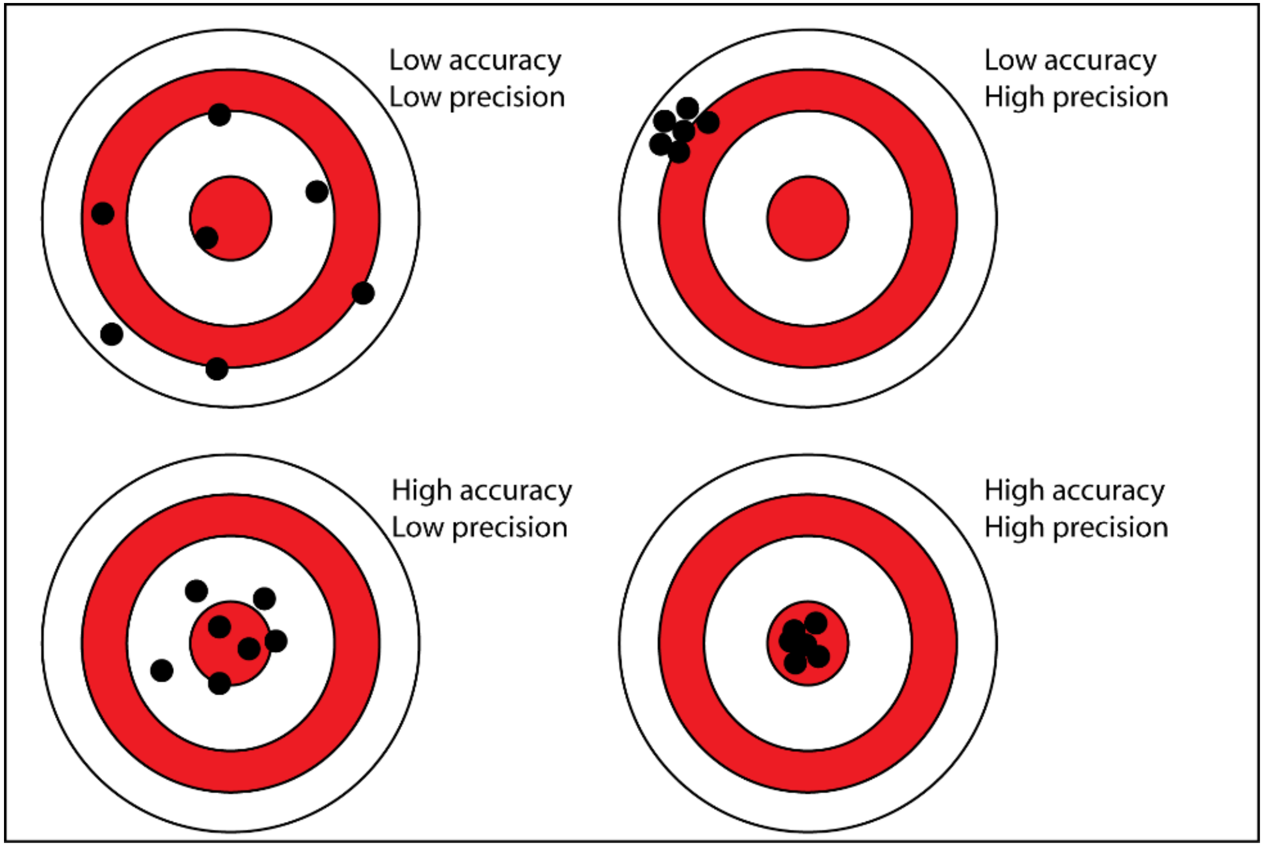
Calculations



Accuracy & Precision



Accuracy & Precision



Precision

	State-of-the-art laboratory	State-of-the-art at-sea lab (suitable RMs)	Other laboratories (suitable RMs)	Laboratories not using RMs
C_T	1.0 µmol kg^{-1}	2 µmol kg^{-1}	4–10 µmol kg^{-1}	?
pH	0.010 (0.003 ?)	0.010 (0.003 ?)	0.01–0.05	?
$p(CO_2)$ IR-based	1.0 µatm	2 µatm	5–10 µatm	?
A_T	1.2 µmol kg^{-1}	2 µmol kg^{-1}	4–10 µmol kg^{-1}	?

† Based on measuring surface oceanic CO_2 levels

Accuracy

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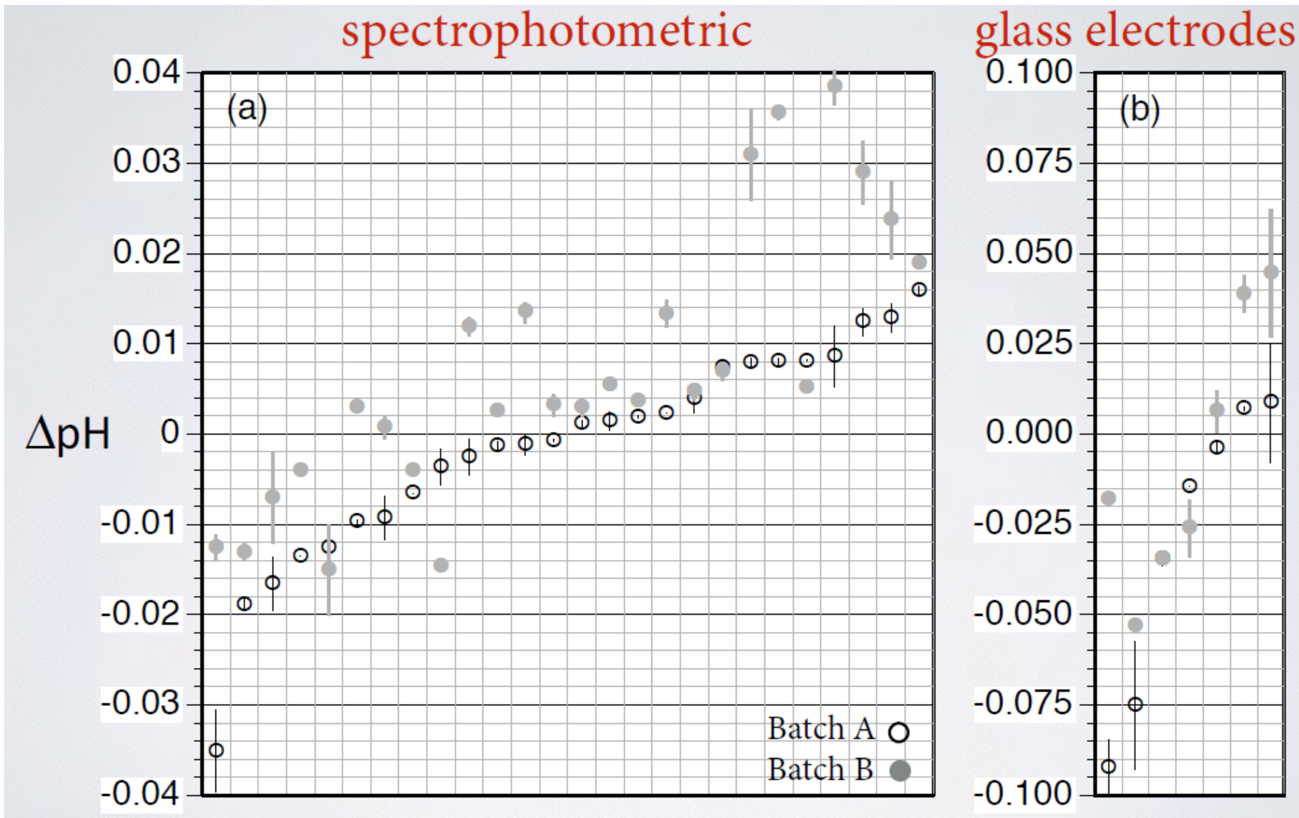
An inter-laboratory comparison assessing the quality of seawater carbon dioxide measurements

Emily E. Bockmon *, Andrew G. Dickson

Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, USA



Key to have reference material

What 2 parameters to use?

Analytical measurement	Desired accuracy†	Uncertainty††	Availability
Total dissolved inorganic carbon	± 1 μmol kg^{-1}	± 1 μmol kg^{-1}	Since 1991[a]
Total alkalinity	± 1 μmol kg^{-1}	± 1 μmol kg^{-1}	Since 1996[b]
pH	± 0.002	± 0.003	Since 2009[c]
Mole fraction of CO_2 in dry air	± 0.5 μmol/mol	± 0.1 μmol/mol	Since 1995[d]

Quality control requires at a minimum the following:

- Suitable and properly maintained equipment and facilities (trained technician)
- Well documented measurement procedures
- Regular and appropriate use of reference materials to evaluate measurement performance,
- Appropriate documentation of measurements and associated quality control information.

What 2 parameters to use?

Mathematically, all choices should be equivalent.

In practice that is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations resulting in uncertainties in the various calculated values.

In addition to uncertainties in the measured CO2 parameters, there are also uncertainties in the various equilibrium constants, and in the total concentrations of other acid-base systems such as boron, *etc.*
(Also, the expression used for alkalinity may be incomplete.)

What 2 parameters to use?

Pair of parameters	Relative uncertainty	Reference methods	State-of-the-art (using RMs)*	Other techniques (using RMs)
pH, A_T	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	2.6% 3.6%	2.9% 3.7%	6.1-8.7% 5.1-6.5%
pH, DIC	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	2.4% 4.1%	2.6% 4.2%	5.6-8.0% 5.7-7.3%
A_T, DIC	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	4.9% 0.6%	5.4% 1.7%	5.8-9.3% 2.2-5.5%
pH, p(CO_2)	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 5.3%	0.8% 5.7%	1.5-2.9% 10.6-15.0%
A_T, p(CO_2)	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 3.3%	0.8% 3.3%	1.5-2.9% 3.4-3.8%
DIC, p(CO_2)	$u_c([CO_2^*])/[CO_2^*]$ $u_c([CO_3^{2-}])/[CO_3^{2-}]$	0.6% 4.0%	0.8% 4.1%	1.5-2.9% 4.2-4.9%

APPENDIX

INDICATOR METHODOLOGY FOR 14.3.1

Indicator Description 14.3.1 – Average marine acidity (pH) measured at agreed suite of representative sampling stations.

Target

14.3: Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels.

pH on total scale
and/or pCO_2 [µatm or ppt], CT [µmol kg^{-1}],
AT [µmol kg^{-1}]

Computation methods

What to report

SOPs

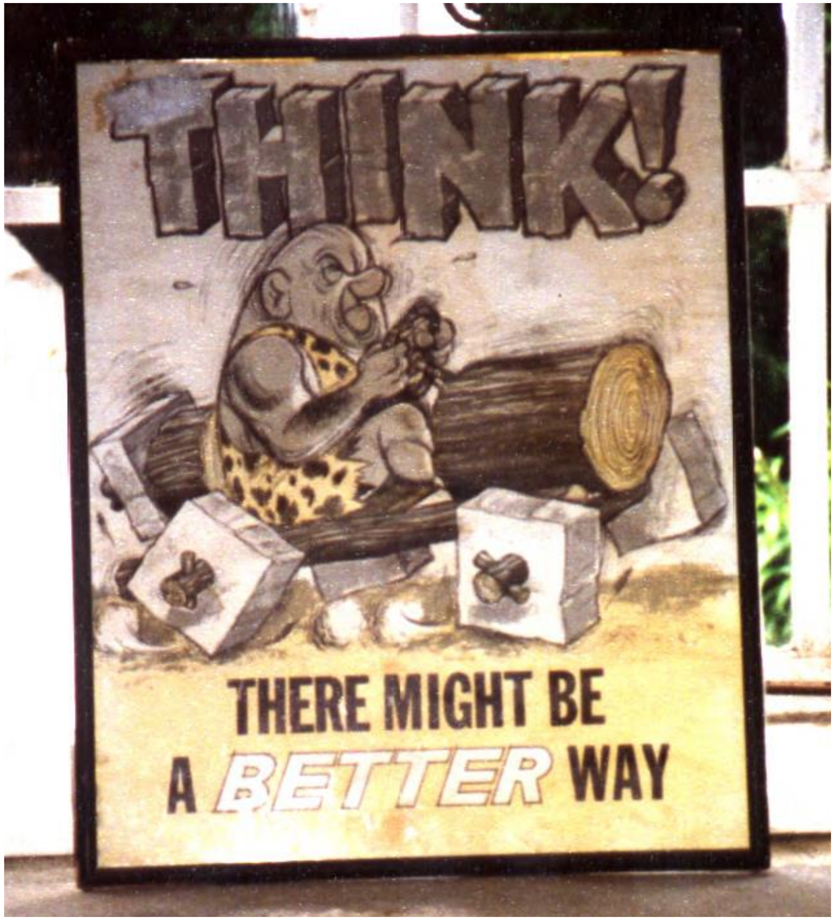
Standard Operating Procedures (SOP)

Table 2 provides links to existing SOPs for discrete, underway (ships of opportunity), and autonomous sensors.

Table 2. *List of standard operating procedures to measure different parameters of the carbonate system (procedures marked with * are able to attain climate quality).*

	Discrete	Underway	Fixed autonomous sensors
pH	Spectrophotometric * Potentiometric	Spectrophotometric ISFET	Spectrophotometric ISFET
CT	IR detection Coulometry *	-	-
AT	Potentiometric titration (open and closed cell; open recommended) *	-	-
pCO_2	-	Equilibration, headspace * Membrane-based	Equilibration * Membrane-based
Temperature	Sensor measurements	Sensor measurements	Sensor measurements
Salinity	Sensor measurements	Sensor measurements	Sensor measurements

How good is good enough?



Chemistry is time consumming

Chemistry is expensive
(time / money)

-> Design a sampling design that fits the purpose: time resolution / accuracy / precision

Table 1 Seawater carbonate chemistry parameters presented as mean ± SD. Seawater pH on the total scale (pH_T), temperature (T; °C) and total alkalinity (TA; mmol kg^{-1}) were used to calculate CO_2 partial pressure (pCO_2; μatm) as well as aragonite and calcite saturation states (respectively Ωa and Ωc), for a salinity of 31.9

Measured			Calculated		
pH_T	T (°C)	TA (mmol kg^{-1})	pCO_2 (μatm)	Ωa	Ωc
8.00 ± 0.03	9.38 ± 0.05	2.5 ± 0.5	498 ± 102	1.89 ± 0.42	2.99 ± 0.67
8.00 ± 0.05	9.25 ± 0.13	2.5 ± 0.5	491 ± 102	1.88 ± 0.48	2.97 ± 0.75
7.99 ± 0.04	9.27 ± 0.06	2.4 ± 0.5	484 ± 144	1.72 ± 0.31	2.73 ± 0.48
7.99 ± 0.06	9.27 ± 0.12	2.3 ± 0.5	474 ± 176	1.62 ± 0.32	2.56 ± 0.51
7.99 ± 0.05	9.68 ± 0.17	2.6 ± 0.5	531 ± 136	1.94 ± 0.44	3.07 ± 0.69
7.99 ± 0.05	9.23 ± 0.10	2.48 ± 0.5	516 ± 142	1.79 ± 0.43	2.84 ± 0.68
7.83 ± 0.02	9.13 ± 0.10	2.5 ± 0.7	768 ± 225	1.31 ± 0.36	2.08 ± 0.57
7.78 ± 0.17	9.18 ± 0.05	2.4 ± 0.5	854 ± 213	1.22 ± 0.51	1.93 ± 0.80
7.74 ± 0.04	9.43 ± 0.10	2.5 ± 0.6	968 ± 277	1.09 ± 0.25	1.73 ± 0.39
7.71 ± 0.14	9.30 ± 0.12	2.42 ± 0.3	1053 ± 396	0.99 ± 0.16	1.56 ± 0.25
7.67 ± 0.11	9.38 ± 0.10	2.6 ± 0.6	1161 ± 145	1.02 ± 0.48	1.62 ± 0.76
7.64 ± 0.01	9.15 ± 0.13	2.5 ± 0.6	1241 ± 302	0.86 ± 0.19	1.36 ± 0.30
7.62 ± 0.05	9.25 ± 0.06	2.5 ± 0.4	1272 ± 90	0.86 ± 0.23	1.35 ± 0.36
7.59 ± 0.02	9.40 ± 0.08	2.5 ± 0.6	1353 ± 260	0.79 ± 0.21	1.24 ± 0.33
7.44 ± 0.03	9.50 ± 0.10	2.3 ± 0.4	1867 ± 269	0.53 ± 0.11	0.83 ± 0.18
7.42 ± 0.03	9.25 ± 0.13	2.5 ± 0.6	2069 ± 405	0.55 ± 0.15	0.87 ± 0.24
7.34 ± 0.17	9.18 ± 0.17	2.5 ± 0.7	2475 ± 312	0.52 ± 0.36	0.83 ± 0.56
7.34 ± 0.10	9.23 ± 0.13	2.4 ± 0.5	2477 ± 600	0.45 ± 0.18	0.72 ± 0.29
7.25 ± 0.03	9.23 ± 0.10	2.5 ± 0.5	3018 ± 560	0.36 ± 0.08	0.58 ± 0.13
7.24 ± 0.06	9.48 ± 0.05	2.5 ± 0.5	3164 ± 490	0.37 ± 0.10	0.58 ± 0.16
7.19 ± 0.05	9.25 ± 0.13	2.5 ± 0.4	3613 ± 888	0.32 ± 0.06	0.51 ± 0.10
7.11 ± 0.04	9.30 ± 0.12	2.4 ± 0.4	4066 ± 942	0.25 ± 0.04	0.40 ± 0.06
7.01 ± 0.67	9.68 ± 0.13	2.4 ± 0.4	11 324 ± 15 426	0.47 ± 0.68	0.74 ± 1.08
6.98 ± 0.04	9.38 ± 0.05	2.3 ± 0.4	5493 ± 965	0.18 ± 0.04	0.29 ± 0.06
6.50 ± 0.03	9.48 ± 0.15	2.4 ± 0.5	17 136 ± 2246	0.06 ± 0.02	0.10 ± 0.03
6.45 ± 0.06	9.33 ± 0.10	2.3 ± 0.4	18 061 ± 2557	0.05 ± 0.02	0.09 ± 0.02
6.44 ± 0.04	9.28 ± 0.05	2.4 ± 0.6	19 928 ± 6030	0.06 ± 0.01	0.09 ± 0.02

Objective ?

"*Climate*"

Defined as data of quality sufficient to assess long term trends with a defined level of confidence

With respect to ocean acidification, this is to support detection of the long-term anthropogenically-driven changes in hydrographic conditions and carbon chemistry over multi-decadal timescales

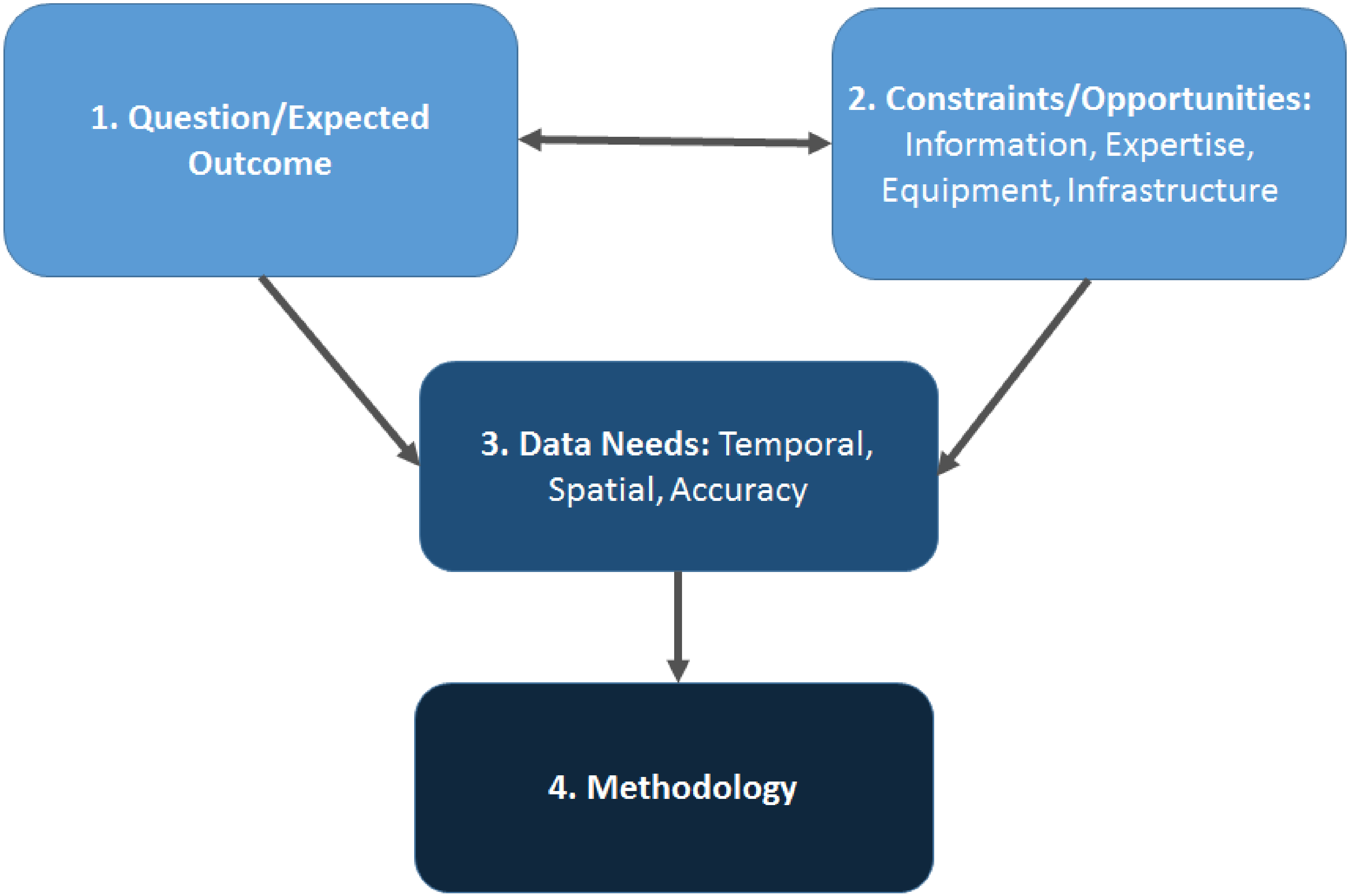
"*Weather*"

Defined as data of sufficient and defined quality used to identify relative spatial patterns and short-term variation

With respect to ocean acidification, this is to support mechanistic interpretation of the ecosystem response to and impact on local, immediate ocean acidification dynamics

My primary focus will be here

Sampling strategy



Conclusions

- ✓ Think about your question (climate vs weather, monitoring vs experimentation)
- ✓ Design your sampling accordingly
- ✓ Select your parameters based on needs, expertise
- ✓ Use these tools to think/design biological experiments