Measuring carbon dioxide parameters for ocean acidification observing systems: how good is good enough?

Andrew G. Dickson
Scripps Institution of Oceanography, UC San Diego

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THINK!
THERE MIGHT BE
A BETTER WAY

Faster, better, cheaper

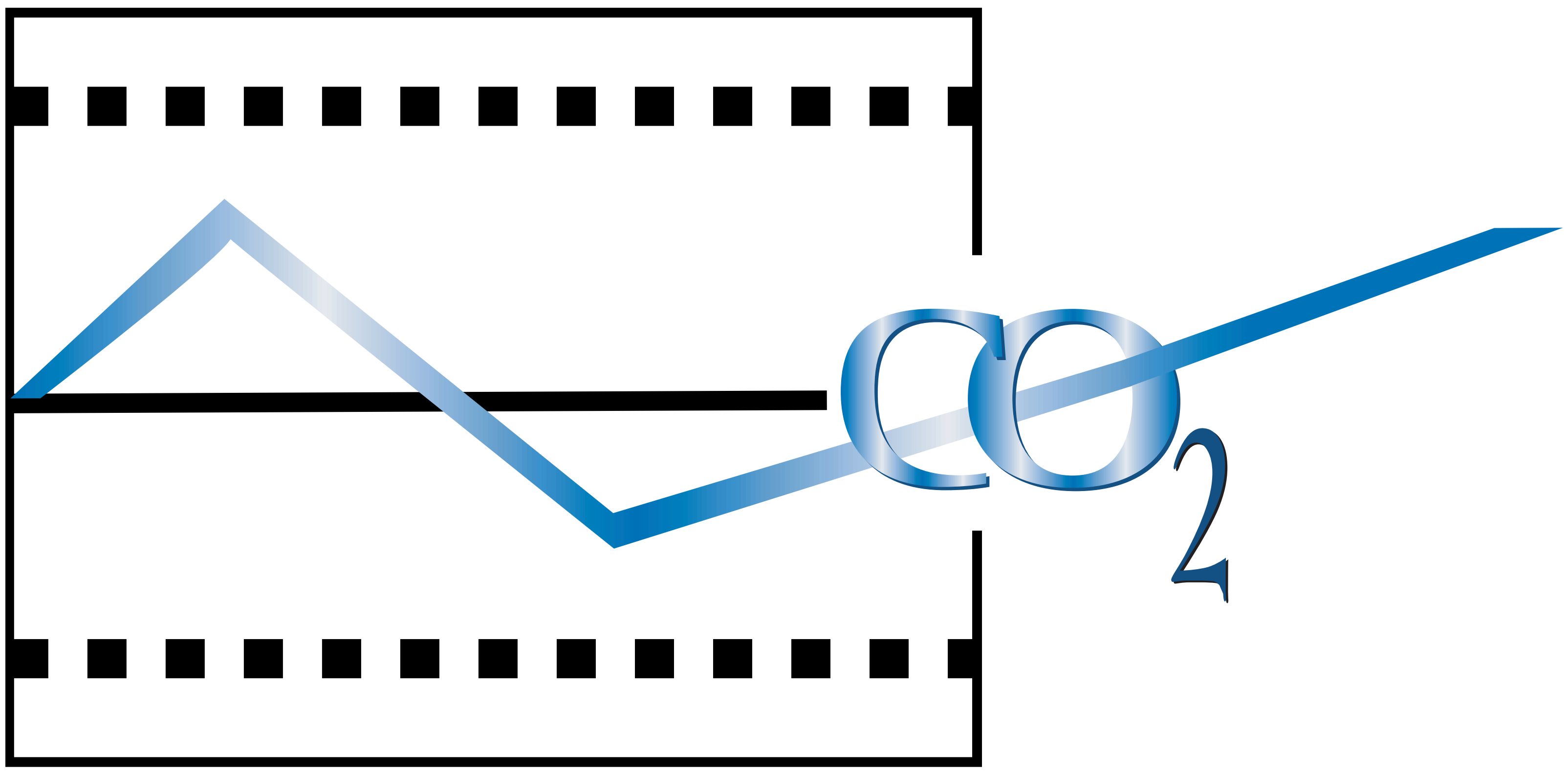
In 1992, NASA Administrator Daniel Goldin began the agency's "Faster, Better, Cheaper" initiative.

The popular consensus on "Faster, Better, Cheaper" is often expressed in the supposedly self-evident saying: "faster, better, cheaper — pick two."

Is this necessarily true for seawater carbonate system measurements?

We clearly understand the meanings of "faster" and "cheaper", but how should we define "better"?

Desire for high-quality measurements



What is quality?

Quality is fitness for purpose.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Fitness for purpose therefore refers to the magnitude of the uncertainty associated with a measurement in relation to the needs of the application area.

Has implications for the level of resources needed!

When assessing "better", uncertainty is not the only measure!

You should consider:

1. Overall uncertainty required
2. Cost of measurement(s)
    a. Cost of equipment (purchase / maintenance)
    b. Cost of training
    c. Cost of analysis (time & materials)
3. Convenience of measurement
    a. Availability of equipment (purchase / maintenance)
    b. Sample size required
    c. Time until results are available
4. Cost of making a wrong measurement.

These procedures are aimed at scientists making open ocean measurements

Note too that most of these methods are at least 20 years old!

http://cdiac.ornl.gov/oceans/Handbook_2007.html

For open-ocean measurements

You should consider:

1. Overall uncertainty required — As good as possible!
2. Cost of measurement(s) — Money no object?
   a. Cost of equipment (purchase / maintenance)
   b. Cost of training
   c. Cost of analysis (time & materials)
3. Convenience of measurement — Would be nice!
   a. Availability of equipment (purchase / maintenance)
   b. Sample size required
   c. Time until results are available
4. Cost of making a wrong measurement. — Perceived as high!

For ocean acidification measurements

You should consider:

1. Overall uncertainty required — Still needs thought
2. Cost of measurement(s) — Be nice it it were cheap!
   a. Cost of equipment (purchase / maintenance)
   b. Cost of training
   c. Cost of analysis (time & materials)
3. Convenience of measurement — Please!!
   a. Availability of equipment (purchase / maintenance)
   b. Sample size required
   c. Time until results are available
4. Cost of making a wrong measurement. — Needs thought

Key Questions to Ask About any Analytical Method

Key Questions

1. What is the overall uncertainty of the measured value?
2. Does it provide the quality I need?
3. What does the method cost to use?
4. How does the method work?
5. Can I maintain the system?
6. How is it calibrated?
7. How does one achieve effective QA/QC?

What Measurement quality do I need?

Toward a Global Ocean Acidification Observing Network

Consensus of an international workshop held at the University of Washington
Seattle, WA, USA 26-28 June 2012
Sponsored by: NOAA, IOCCP, GOOS, IOOS, and UW
JA Newton, RA Feely, EB Jewett, D Gledhill

GOA-ON

Global Ocean Acidification Observing Network

3rd GOA-ON Science Workshop

May 8-10, 2016

CSIRO Marine Laboratories

Hobart, Tasmania, Australia

http://www.goa-on.org/

GOA-ON

Global Ocean Acidification Observing Network

Global Ocean Acidification Observing Network:

Requirements and Governance Plan

First Edition

September 2014

J.A. Newton, R.A. Feely, E.B. Jewett, P. Williamson, J. Mathis

IOOS Integrated Ocean Observing System

NOAA

IAEA

Ocean Acidification International Coordination Centre OA-ICC

UNESCO United Nations Educational, Scientific and Cultural Organization

Intergovernmental Oceanographic Commission

GOOS The Global Ocean Observing System

International Ocean Carbon Coordination Project IOCCP

UK Ocean Acidification Research Programme

Blue Planet Oceans and Society

http://www.goa-on.org

http://www.goa-on.org

A Global Ocean Acidification Observing Network

Goal 1: Provide an understanding of global ocean acidification conditions

Goal 2: Provide an understanding of ecosystem response to ocean acidification

Goal 3: Provide data necessary to optimize modeling for ocean acidification

Goal 1, Level 1 Measurements for Oceans and Coasts

temperature,
salinity,
oxygen,
carbonate system

My primary focus will be here

Data quality levels for the global ocean acidification observing network

"***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

Valid Analytical Measurement (VAM) Principles

1. Analytical measurements should be made to satisfy an agreed requirement.
2. Analytical measurements should be made using methods and equipment which have been tested to ensure they are fit for purpose.
3. Staff making analytical measurements should be both qualified and competent to undertake the task.
4. There should be a regular independent assessment of the technical performance of a laboratory.
5. Analytical measurements made in one location should be consistent with those elsewhere.
6. Organisations making analytical measurements should have well defined quality control and quality assurance procedures.

valid analytical measurement

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Valid Analytical Measurement (VAM) Principles

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Each of these requires that we specify a measurement uncertainty associated with each parameter that is being "observed".

4. There should be a regular independent assessment of the technical performance of a laboratory.

5. Analytical measurements made in one location should be consistent with those elsewhere.

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Measurement uncertainty

A non-negative parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

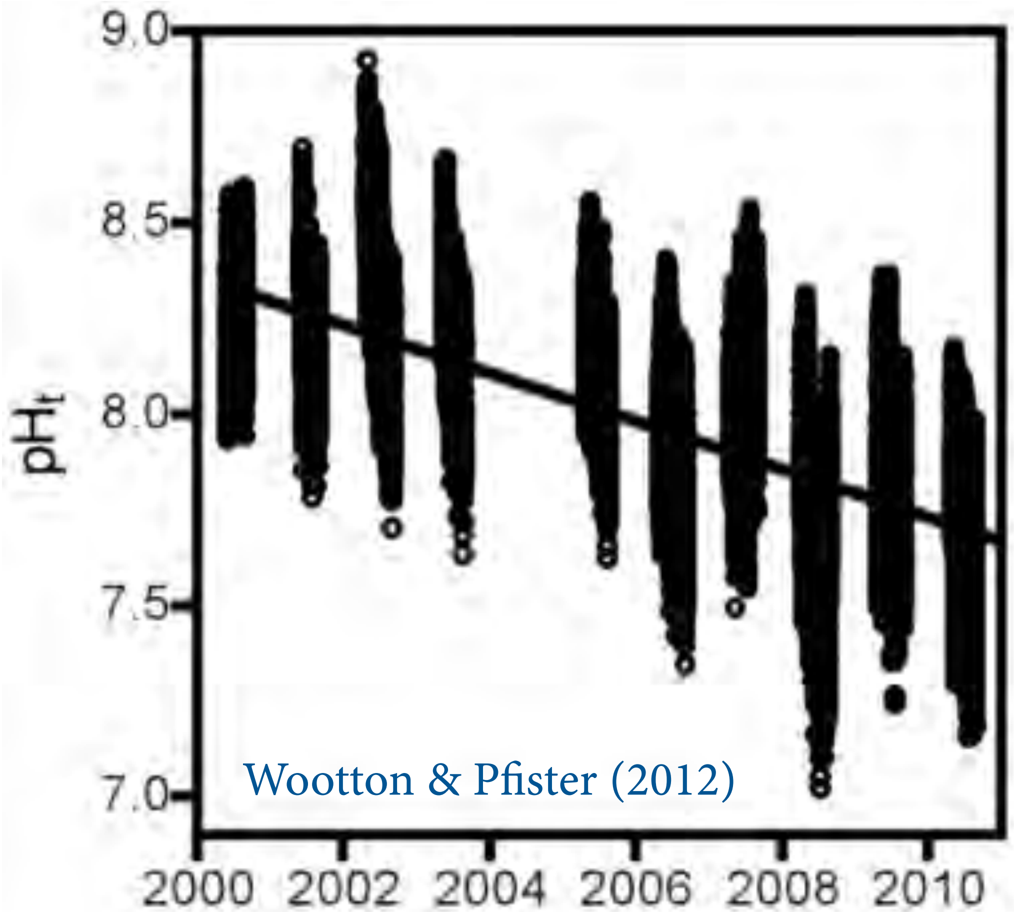
NOTE 1: This parameter is usually expressed as the half-width of an interval having a stated coverage probability.

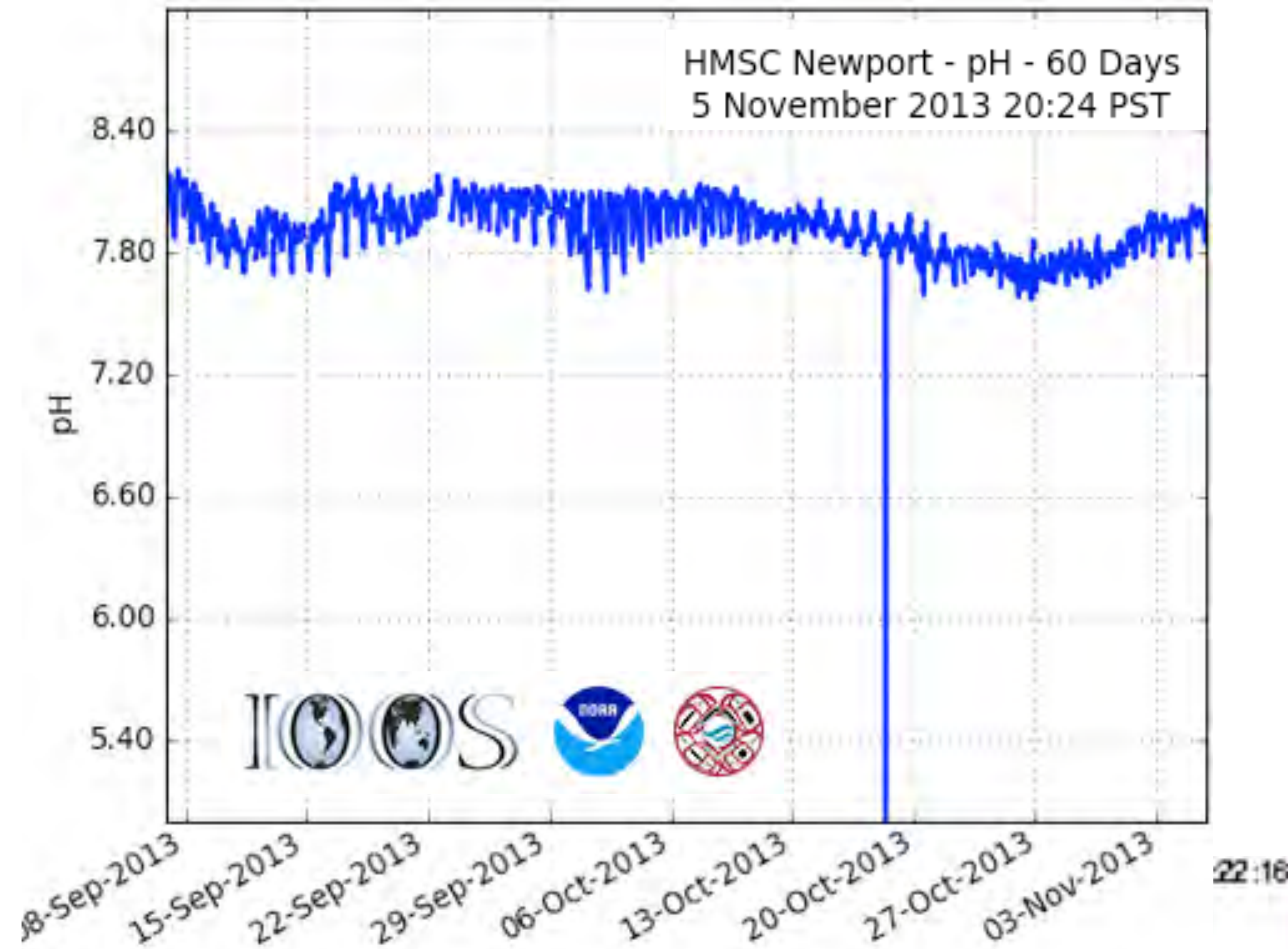
I believe that 95% confidence would be a useful level

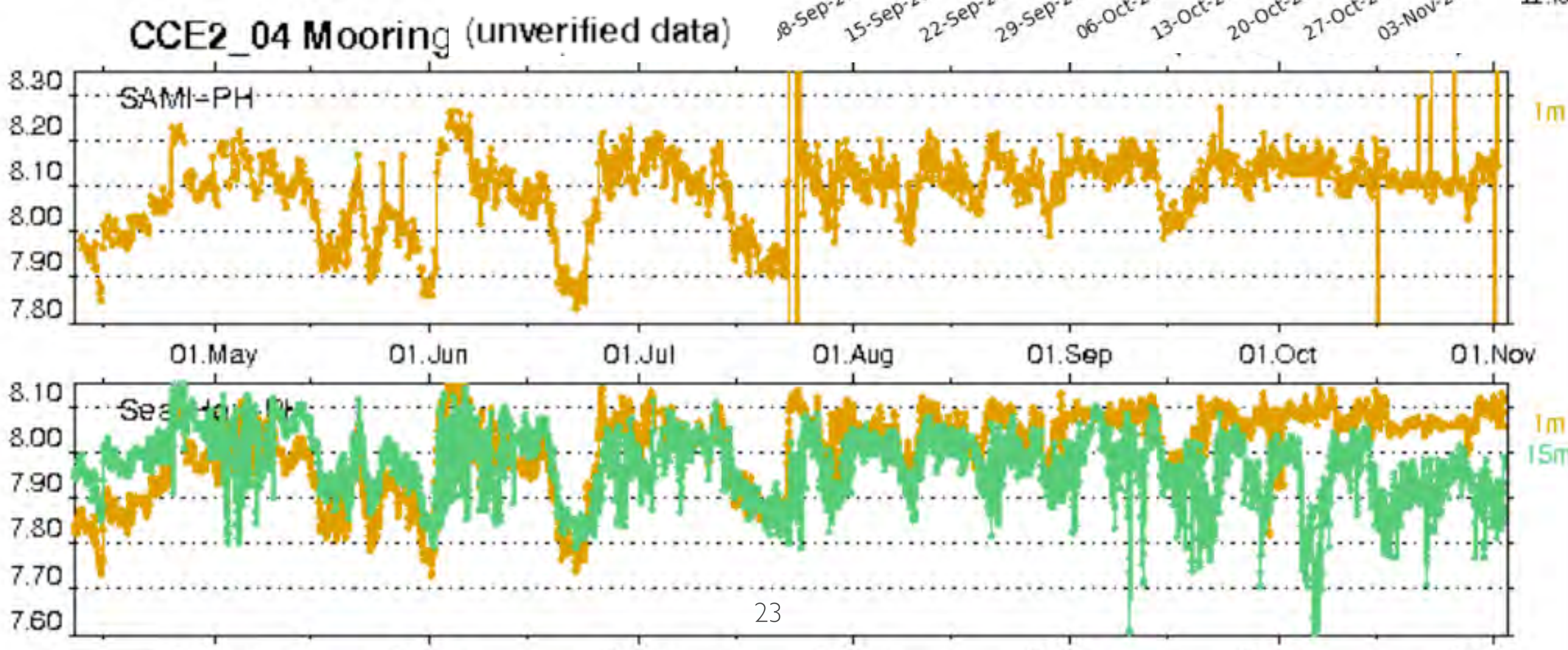
NOTE 2: Measurement uncertainty includes components arising from systematic effects, such as components associated with corrections and the assigned quantity values of measurement standards, as well as the definitional uncertainty. Sometimes estimated systematic effects are not corrected for but, instead, associated measurement uncertainty components are incorporated.

Note, measurement uncertainty is **not** the same as precision!

Let's look at some coastal pH data


9.0
8.5
8.0
7.5
7.0
pH_t
2000 2002 2004 2006 2008 2010
Wootton & Pfister (2012)


HMSC Newport - pH - 60 Days
5 November 2013 20:24 PST
8.40
7.80
7.20
6.60
6.00
5.40
pH
8-Sep-2013 15-Sep-2013 22-Sep-2013 29-Sep-2013 06-Oct-2013 13-Oct-2013 20-Oct-2013 27-Oct-2013 03-Nov-2013
22:16


CCE2_04 Mooring (unverified data)
SAMI-PH
8.30
8.20
8.10
8.00
7.90
7.80
1m
01.May 01.Jun 01.Jul 01.Aug 01.Sep 01.Oct 01.Nov
8.10
8.00
7.90
7.80
7.70
7.60
1m
15m

But, pH alone is not enough information!

An unambiguous description of the carbonate system in seawater requires significantly more information:

- The relevant equilibrium constants – $f(S, T, p)$
- At least **two** carbonate system measurements – pH, $p(CO_2)$, C_T, (A_T)
- If A_T is one of the two, also need information about non-CO_2 acid-base systems that are present (*e.g.* total concentrations, equilibrium constants)

An added complication is that it is therefore not possible to identify a single CO_2-related factor that is responsible for biological responses to ocean acidification.

Cautions!

Although we talk about ocean acidification, for organisms it is the actual composition of the surrounding seawater that matters, not (necessarily) how it came to be that way.

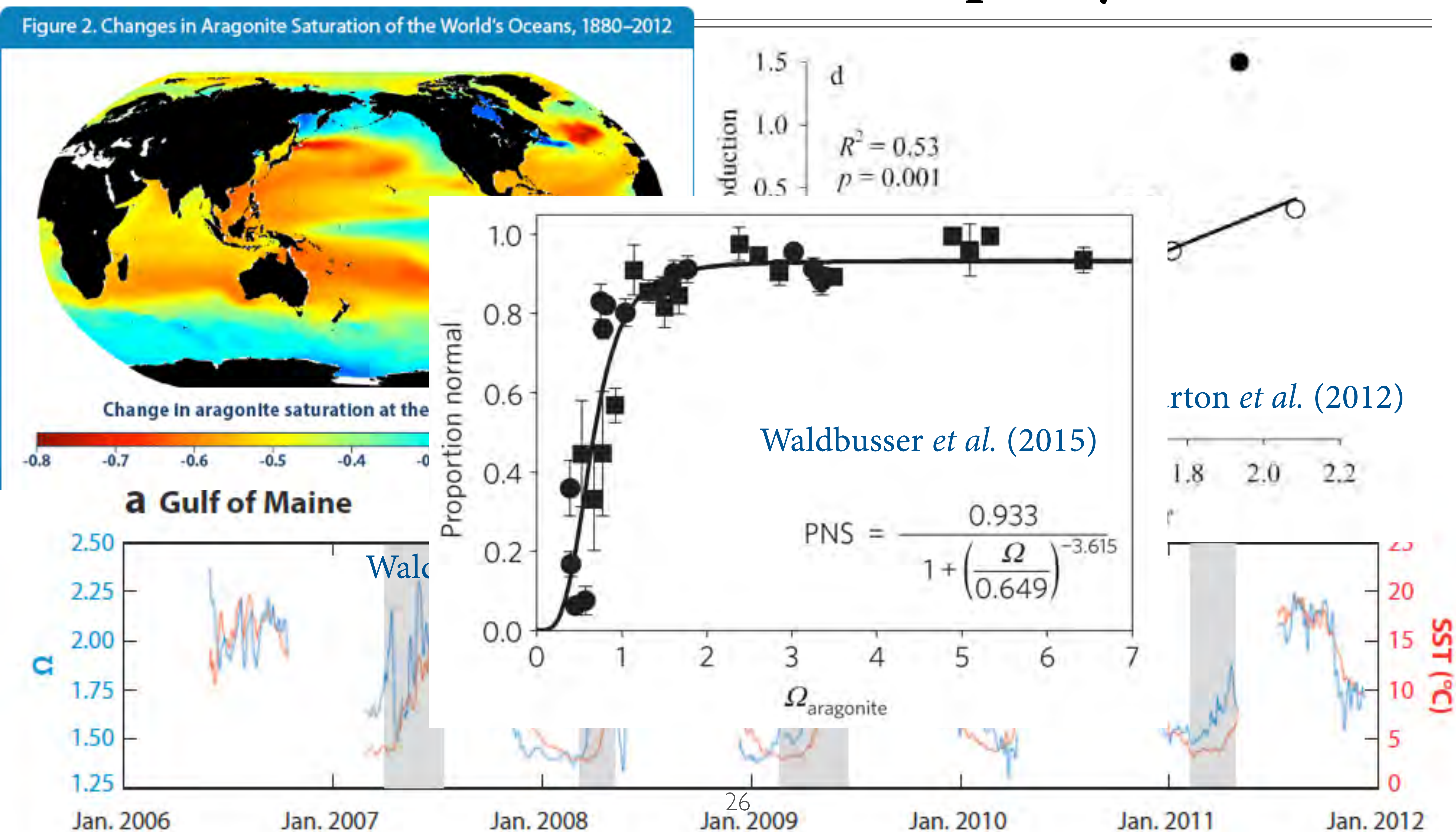
The CO_2 system in the natural environment varies on a variety of time-scales due (largely) to the effects of biological activity.

As the CO_2 system has 2 degrees of freedom, it is essential that you measure at least two CO_2-related parameters to be able to characterize a coastal seawater unambiguously.

Also you cannot design perfect single-factor experiments to study organismal responses to changes in the CO_2 system in coastal environments.

$$\Omega(arag) = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}(arag)}$$

A common approach is to use aragonite saturation state as a suitable OA proxy



Defining ocean acidification requirements

C-CAN (California Current Acidification Network):

Recommendation 1: Measurements should facilitate determination of aragonite saturation state (Ω_{arag}) and a complete description of the carbonate system, including pH and $p(CO_2)$.

Recommendation 2: A ±0.2 maximum uncertainty in the aragonite saturation state (Ω) calculation is required to adequately link changes in ocean chemistry to changes in ecosystem function.

McGlaughlin *et al.* (2015)

Defining ocean acidification requirements

GOA-ON (Global Ocean Acidification Observing Network):

The weather objective requires the carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of 10%. This implies an uncertainty of approximately 0.02 in pH; of 10 μmol kg^{-1} in measurements of total alkalinity (TA) and total dissolved inorganic carbon (DIC); and a relative uncertainty of about 2.5% in the partial pressure of carbon dioxide: $p(CO_2)$. Such ~~precision~~ uncertainty should be achievable in competent laboratories, and is also achievable with the best autonomous sensors.

Newton *et al.* (2014)

Defining ocean acidification requirements

C-CAN (California Current Acidification Network):

> "A ±0.2 maximum uncertainty in the aragonite saturation state (Ω) calculation is required"

GOA-ON (Global Ocean Acidification Observing Network):

> "The weather objective requires the carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of 10%."

Note: these two statements are not the same!

What might it take to achieve such confidence levels in $[CO_3^{2-}]$ (Ω) ?

In principle, one can use any of a variety of combinations of measurable carbon system parameters to estimate $[CO_3^{2-}]$ (Ω)

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 CO_2 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.)

It is essential for us to choose a desired **target uncertainty** (95% confidence) for **each** of the measured and/or calculated parameters reported in coastal ocean acidification observations.

An example of uncertainty propagation

If the (relative) uncertainties **(95% confidence)** of measurement for the various carbon system parameters are:

$u(A_\mathrm{T})/A_\mathrm{T} = 0.5\%$ $\quad$ $u(A_\mathrm{T}) \sim 10\ \mu\mathrm{mol\ kg^{-1}}$

$u(C_\mathrm{T})/C_\mathrm{T} = 0.5\%$ $\quad$ $u(C_\mathrm{T}) \sim 10\ \mu\mathrm{mol\ kg^{-1}}$

$u(\mathrm{pH}) = 0.02$ $\quad$ $u[\mathrm{H^+}]/[\mathrm{H^+}] \sim 5\%$

$u(p(\mathrm{CO_2}))/p(\mathrm{CO_2}) = 3\%$ $\quad$ $u(p(\mathrm{CO_2})) \sim 12\ \mu\mathrm{atm}$ (at 400 μatm)

$u(\mathrm{p}K_0) = 0.004$

$u(\mathrm{p}K_1) = 0.015$

$u(\mathrm{p}K_2) = 0.030$

I believe these are reasonable uncertainty estimates (based on a recent inter-laboratory studies)

Note: cannot calculate better than you can measure

For a seawater sample with pH ~ 8.1 and Ω ~ 2.5, the calculated combined *relative* uncertainties, $u_c(x)/x$, are approximately
(values in red are are the relative uncertainties of the measured parameters)

pH* ([H+])	C_T	A_T	$p(CO_2)$	$[CO_3^{2-}]$
0.02 (5%)	0.5%	~1%	~6%	~8%
0.02 (5%)	~1%	0.5%	~6%	~8%
0.02 (5%)	~7%	~7%	3%	~13%
0.05 (11%)	0.5%	0.5%	~12%	~8%
0.02 (5%)	0.5%	~1%	3%	~7%

* uncertainty in pH (not relative uncertainty)

Includes estimates of errors on equilibrium constants

For a seawater sample with pH ~ 7.6 and Ω ~ 1.0, the calculated combined *relative* uncertainties, $u_c(x)/x$, are approximately
(values in red are are the relative uncertainties of the measured parameters)

pH* ([H^+])	C_T	A_T	$p(CO_2)$	[CO_3^{2-}]
0.02 (5%)	0.5%	~1%	~6%	~9%
0.02 (5%)	~1%	0.5%	~6%	~9%
0.02 (5%)	~7%	~7%	3%	~13%
0.06 (11%)	0.5%	0.5%	~14%	~15%
0.02 (5%)	0.5%	~1%	3%	~8%

* uncertainty in pH (not relative uncertainty)

Includes estimates of errors on equilibrium constants

Can we achieve these uncertainty goals?

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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

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ABSTRACT

Seawater CO_2 measurements are being made with increasing frequency as interest grows in the ocean's response to changing atmospheric CO_2 levels and to climate change. The ultimate usefulness of these measurements depends on the data quality and consistency. An inter-laboratory comparison was undertaken to help evaluate and understand the current reliability of seawater CO_2 measurements. Two seawater test samples of different CO_2 content were prepared according to the usual method for the creation of seawater reference materials in the Dickson Laboratory at Scripps Institution of Oceanography. These two test samples were distributed in duplicate to more than 60 laboratories around the world. The laboratories returned their measurement results for one or more of the following parameters: total alkalinity (A_T), total dissolved inorganic carbon (C_T), and pH, together with information about the methods used and the expected uncertainty of the measurements. The majority of laboratories reported A_T and C_T values for all their measurements that were within 10 μmol kg^{-1} of the assigned values (i.e. within $\pm 0.5\%$), however few achieved results within 2 μmol kg^{-1} (i.e. within $\pm 0.1\%$), especially for C_T. Results for the analysis of pH were quite scattered, with little suggestion of a consensus value. The high-CO_2 test sample produced results for both C_T and pH that suggested in many cases that CO_2 was lost during analysis of these parameters. This study thus documents the current quality of seawater CO_2 measurements in the various participating laboratories, and helps provide a better understanding of the likely magnitude of uncertainties in these measurements within the marine science community at the present time. Further improvements will necessarily hinge on adoption of an improved level of training in both measurement technique and of suitable quality control procedures for these measurements.

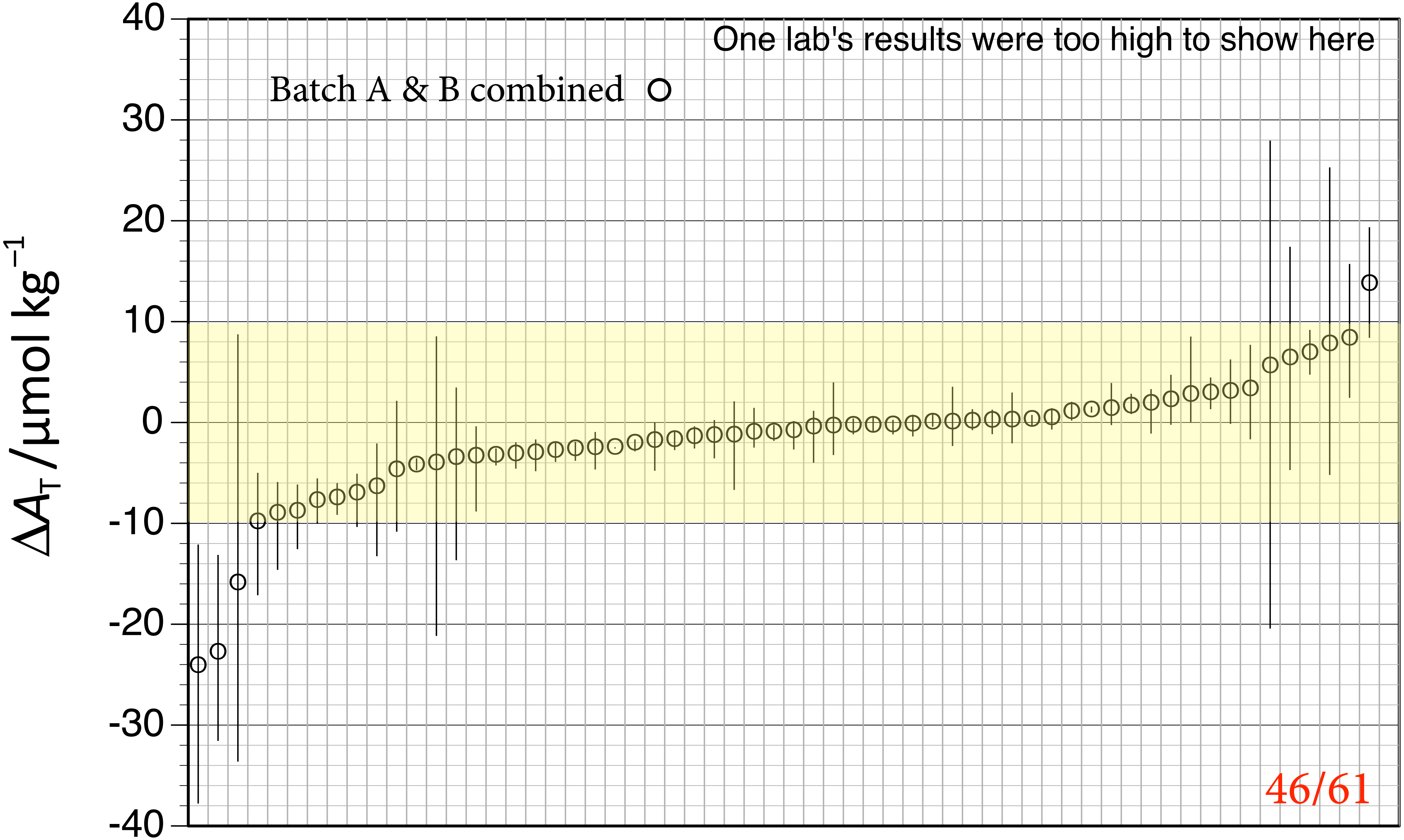
Recent inter-laboratory proficiency study

Assigned values for total alkalinity, total dissolved inorganic carbon, and pH (25 °C; total scale) for the two test samples. Values are expressed as *mean* ± *standard deviation* (*number of analyses*).

	Batch A	Batch B
Salinity	33.190	33.186
Total alkalinity	2215.08 ± 0.49 (24) µmol kg^{-1}	2216.26 ± 0.52 (18) µmol kg^{-1}
Total dissolved inorganic carbon	2015.72 ± 0.74 (9) µmol kg^{-1}	2141.94 ± 0.37 (6) µmol kg^{-1}
pH (25 °C; total scale)	7.8796 ± 0.0019 (18)	7.5541 ± 0.0020 (18)
	Normal RM	High-CO_2 RM

Bockmon & Dickson, 2015

Recent inter-laboratory proficiency study



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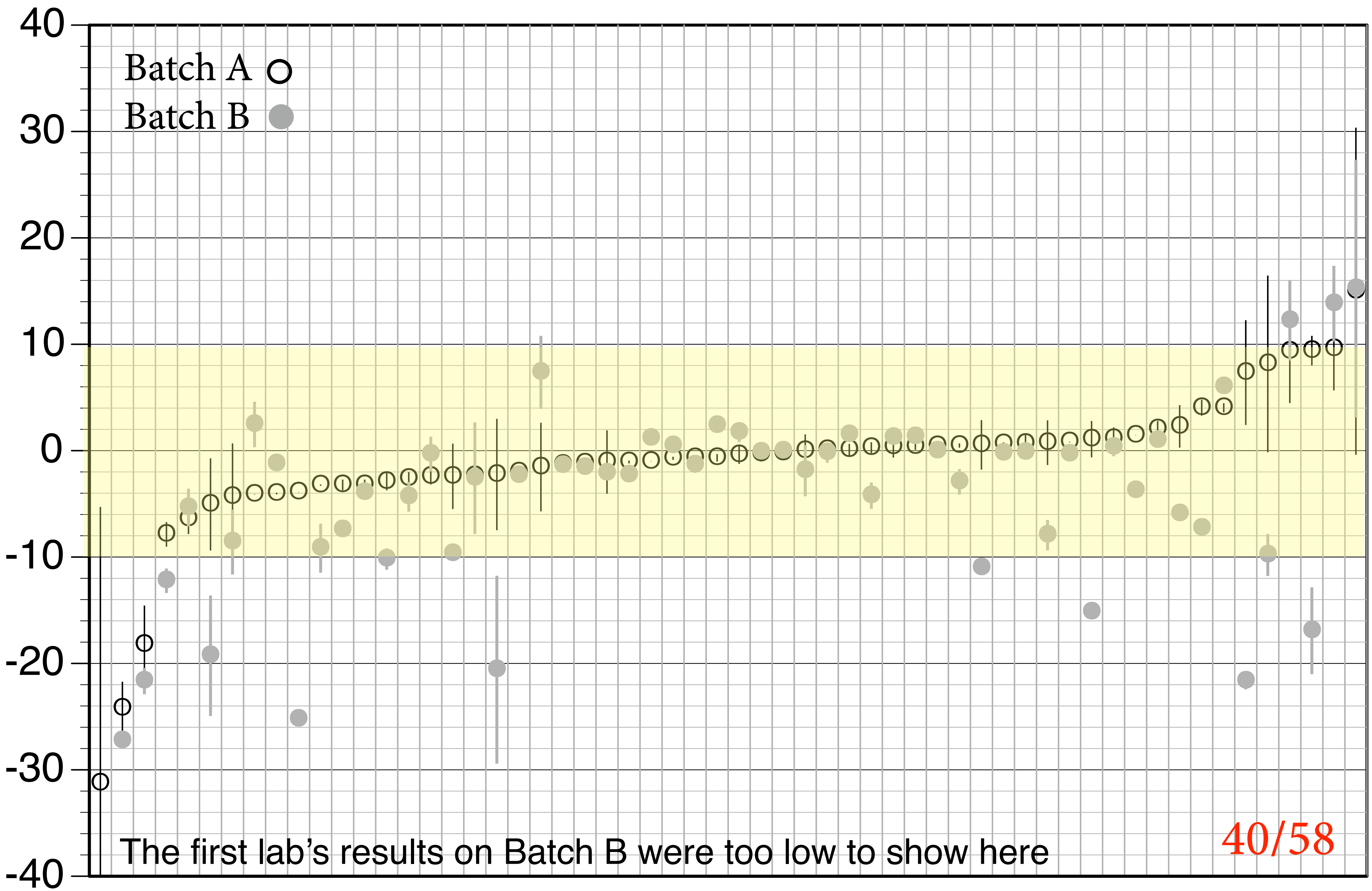

Bockmon & Dickson, 2015

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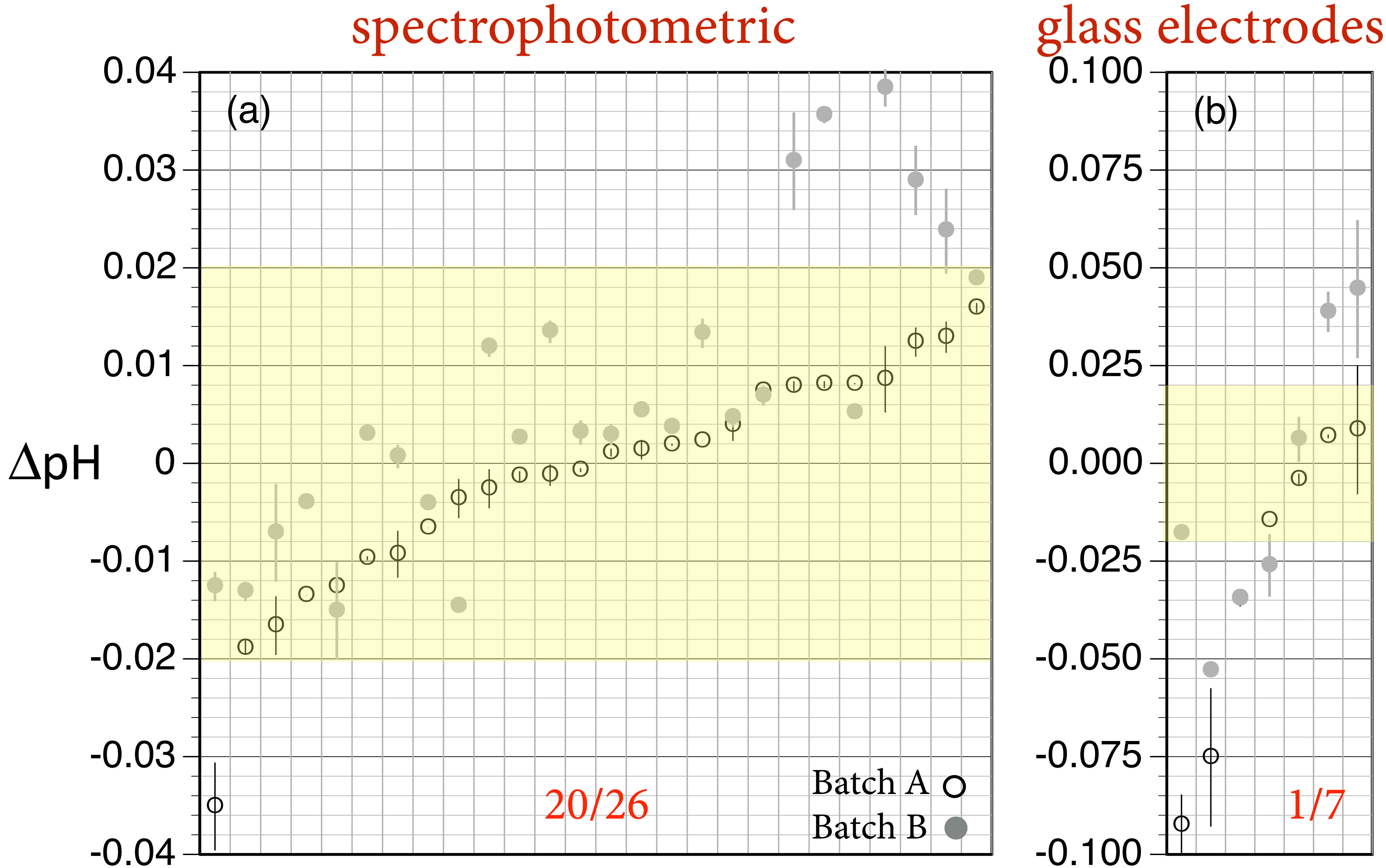

Bockmon & Dickson, 2015

So how good is “good enough”?

I don’t believe we have yet defined this as well as we need to. However, the “weather” criteria for GOA-ON provide a good starting place for a discussion.

Conclusions

We (the ocean acidification observing community) must agree on appropriate target measurement uncertainties for each of the individual "Level 1" parameters: *T*, *S*, $[O_2]$, CO_2-parameters. These will, almost certainly, be different for the different goals, but should be based on a balanced consideration of scientific ambition and technical achievability.

We also need to agree on how to assess the magnitude of such measurement uncertainties in a clear and defensible manner for each measuring approach to a particular parameter that will be used in an observing network.

We still have to develop quality control procedures for our proposed measurement systems that can assure us and our "customers" that any particular set of observations meets these target measurement uncertainties.


BATCH 114