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

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2nd international workshop

Global Ocean Acidification Observing Network

St Andrews, UK: 24-26 July 2013

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

OceanObs'09

Ocean information for society:
sustaining the benefits,
realizing the potential

21-25 September 2009, Venice, Italy

GOA-ON

Global Ocean Acidification Observing Network

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

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

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.

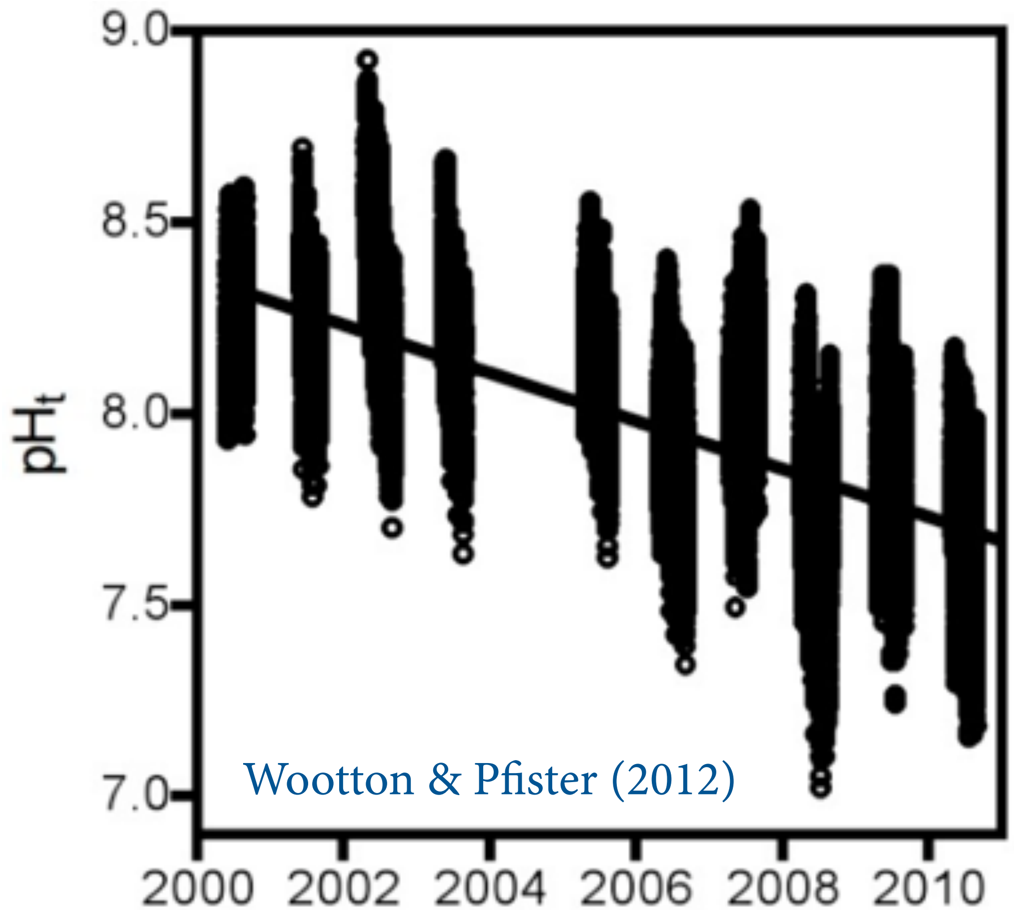
NOTE 1: This parameter is usually expressed as the half-width of an interval having a stated coverage probability.

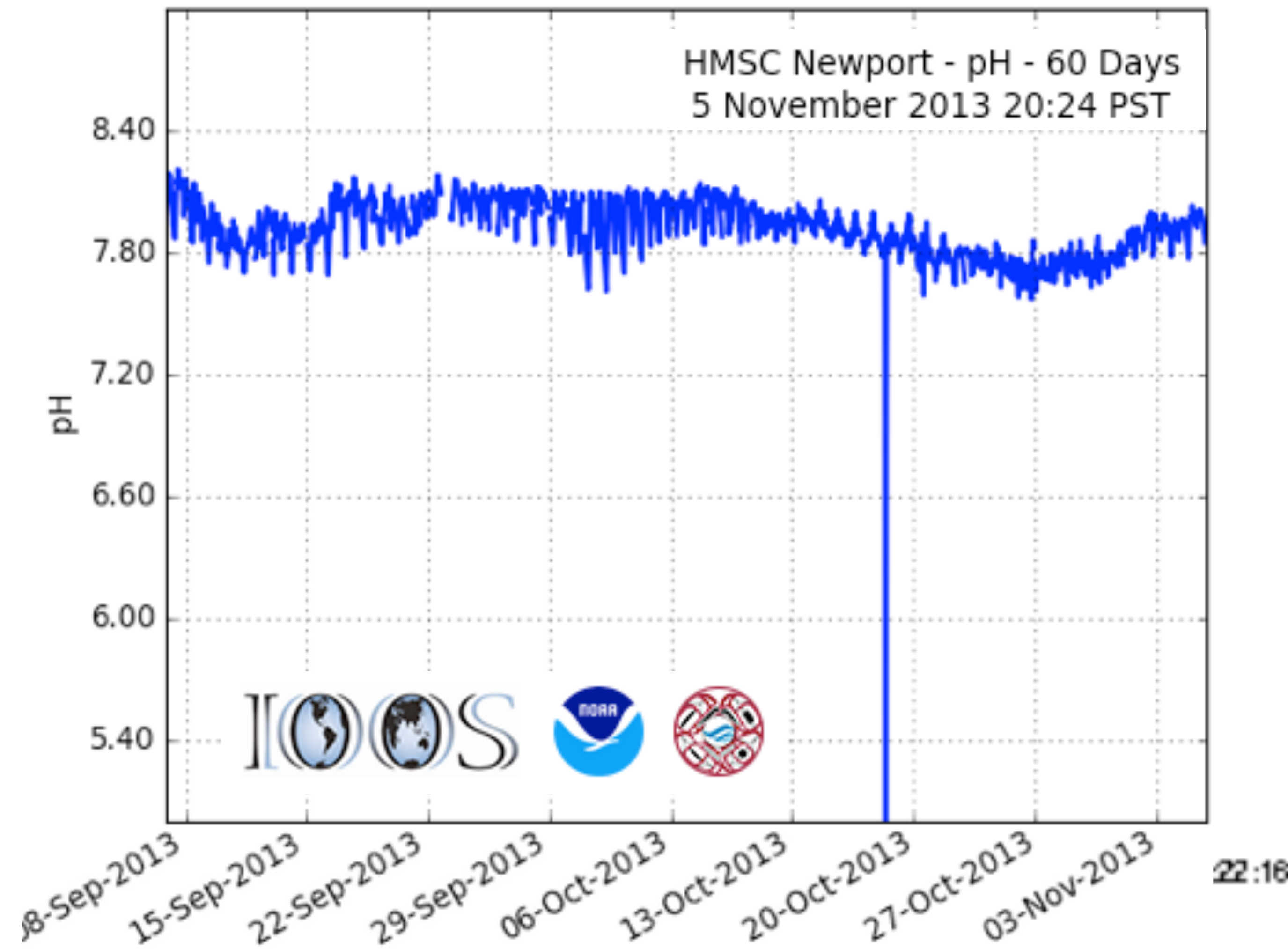
I propose that we choose 95% confidence for this

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


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


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


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

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.

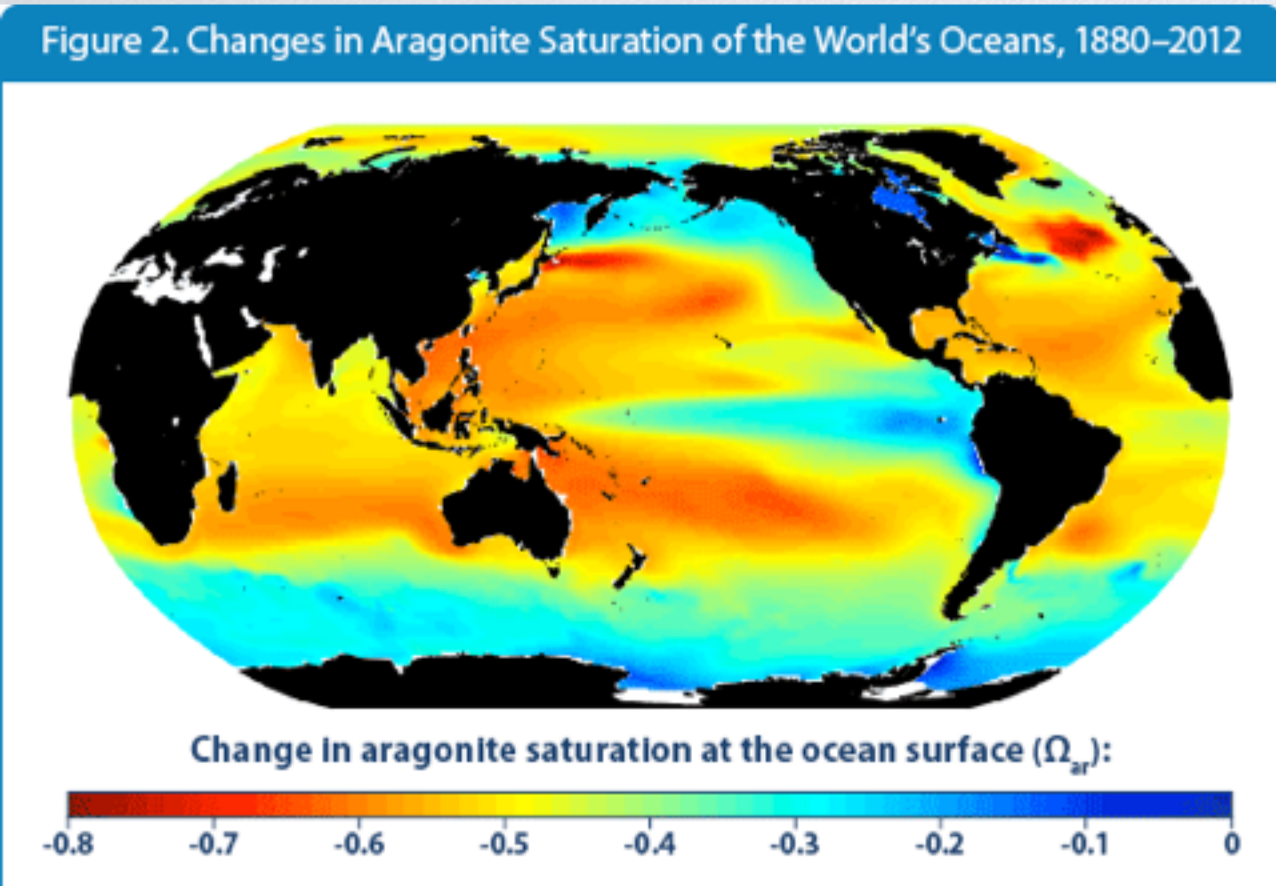
The CO_2 system in the natural environment varies on a variety of time-scales due (largely) to the effects of biological activity.

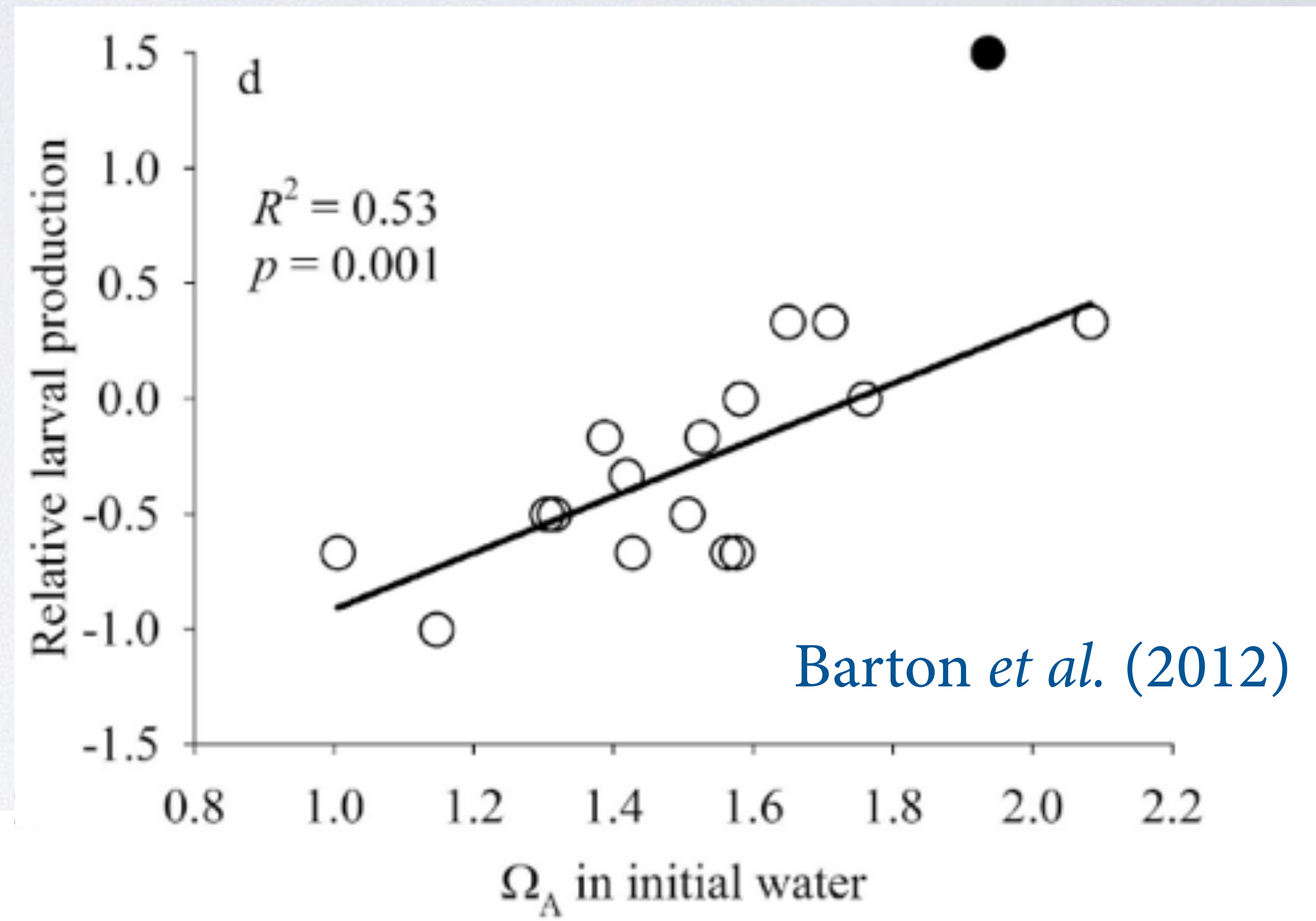
As the CO_2 system has 2 degrees of freedom, it is essential that you measure at least two CO_2-related parameters to be able to characterize a coastal seawater unambiguously.

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

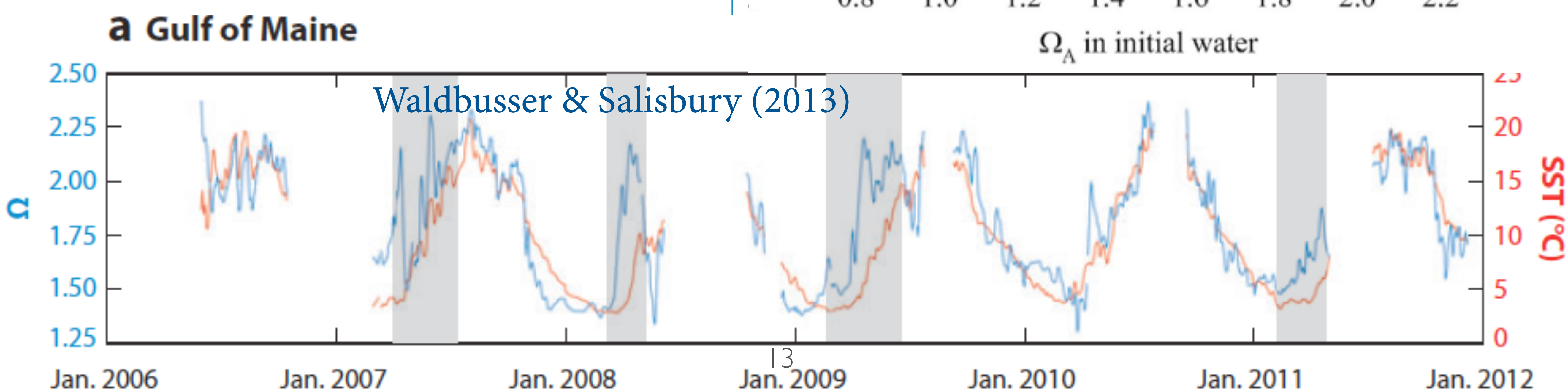
$$\Omega(arag) = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}(arag)}$$

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





Barton *et al.* (2012)



Waldbusser & Salisbury (2013)

Defining ocean acidification requirements

C-CAN (California Current Acidification Network):

“Measurements are required that enable the saturation state of seawater with respect to aragonite to be determined with an uncertainty of ±0.2, and that also enable a complete description of the seawater CO_2 system – including $p(CO_2)$ and pH.”

The Seattle Workshop Report (Global Ocean Acidification Network):

“The **weather** objective requires ±10% measurement resolution of Ω .”

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> "The **weather** objective requires ±10% measurement resolution of Ω ."

Let's assume that these statements can be taken to imply 95% confidence.

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:

$u(A_T)/A_T = 0.5\%$	$u(A_T) \sim 10\ \mu mol\ kg^{-1}$
$u(C_T)/C_T = 0.5\%$	$u(C_T) \sim 10\ \mu mol\ kg^{-1}$
$u(pH) = 0.02$	$u[H^+]/[H^+] \sim 5\%$
$u(p(CO_2))/p(CO_2) = 3\%$	$u(p(CO_2)) \sim 12\ \mu atm$ (at 400 μatm)

$u(pK_0) = 0.004$

$u(pK_1) = 0.015$

$u(pK_2) = 0.030$

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

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 the measured parameters)

pH*	C_T	A_T	$p(CO_2)$	$[CO_3^{2-}]$
0.02	0.5%	~1%	~6%	~8%
0.02	~7%	~7%	3%	~13%
0.045	0.5%	0.5%	~12%	~8%
0.019	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 the measured parameters)

pH*	C_T	A_T	$p(CO_2)$	$[CO_3^{2-}]$
0.02	0.5%	~1%	~6%	~9%
0.02	~7%	~7%	3%	~13%
0.058	0.5%	0.5%	~14%	~15%
0.02	0.5%	~1%	3%	~8%

* uncertainty in pH (not relative uncertainty)

Includes estimates of errors on equilibrium constants

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 then 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.

Quality control of seawater CO_2 measurements

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

valid analytical measurement

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

Chapter 3

Quality assurance

1. Introduction

This chapter is intended to indicate some general principles of analytical quality assurance appropriate to the measurement of oceanic CO_2 parameters. Specific applications of analytical quality control are detailed as part of the individual standard operating procedures (Chapter 4).

What is meant by quality assurance?

A quality assurance program consists of two separate related activities, quality control and quality assessment:

Quality control — The overall system of activities whose purpose is to control the quality of a measurement so that it meets the needs of users. The aim is to ensure that data generated are of known accuracy to some stated, quantitative degree of probability, and thus provides quality that is satisfactory, dependable, and economic.

Quality assessment — The overall system of activities whose purpose is to provide assurance that quality control is being done effectively. It provides a continuing evaluation of the quality of the analyses and of the performance of the analytical system.

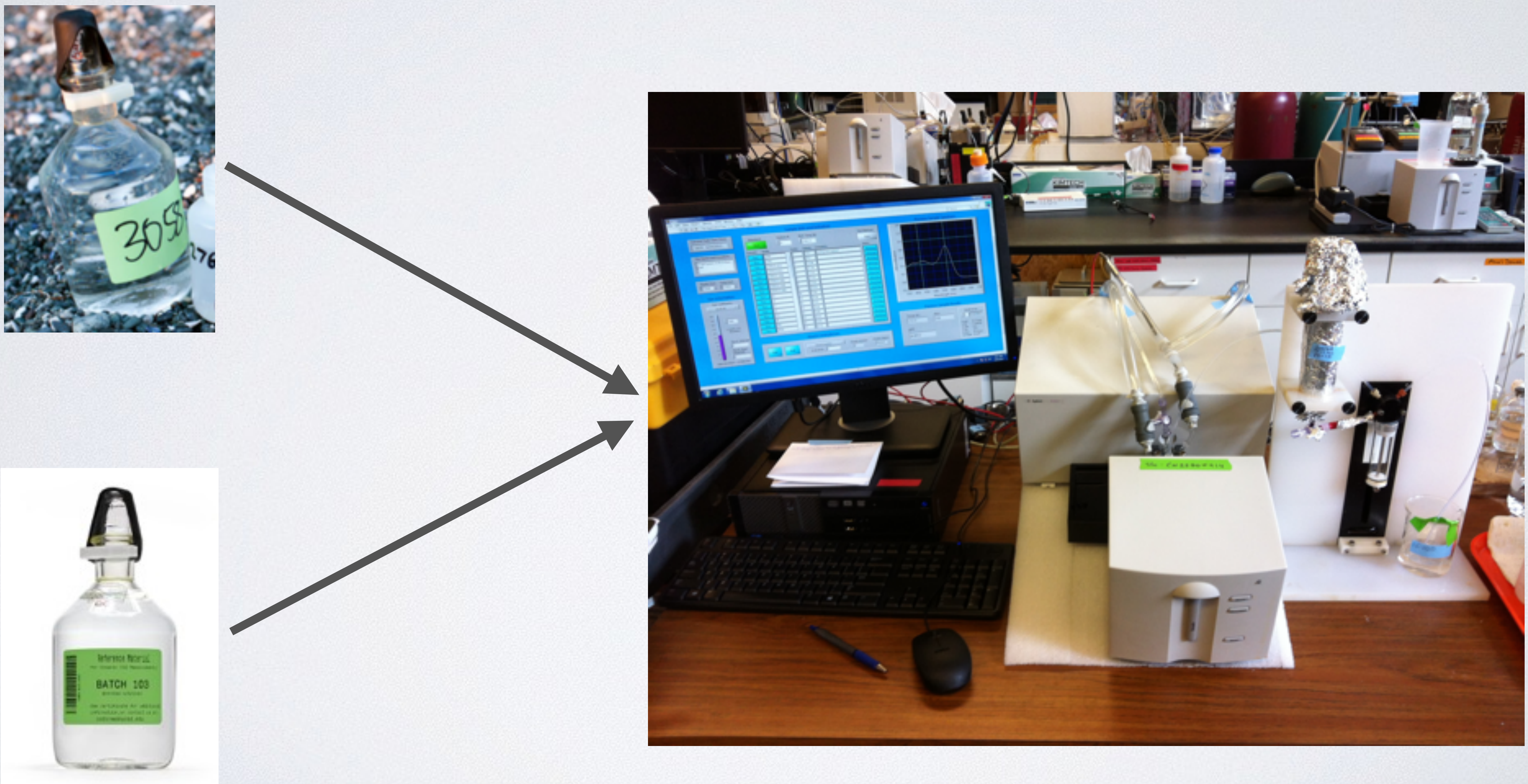
Need to consider the whole process

From the water

into the sample container,

to the analysis laboratory.

Not just the chemical analysis



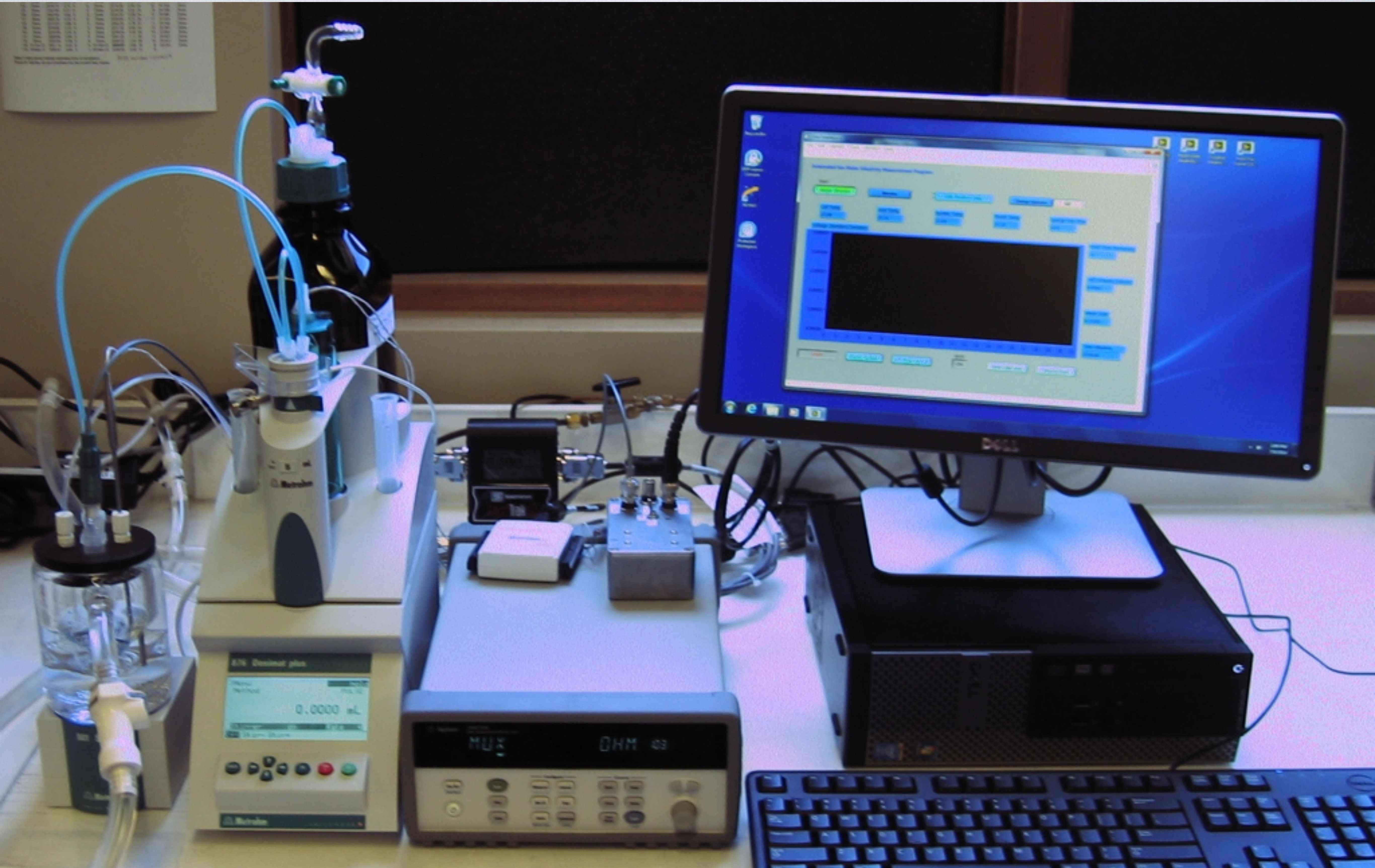
Quality control of sampling Process

- Need a documented, tested, sampling procedure
- Need suitable sampling containers
- Need to have a sampling process that is suitable for the site
- Must take replicate samples How many?
- Must document sampling: Who? Where? When? Why?
- Must inspect on arrival in laboratory

Laboratory quality control

- Need a laboratory quality control plan in place to ensure that the measurements performed achieve the desired uncertainty
- Need to use a documented, tested, analytical procedure that will provide results of appropriate quality
- Analytical staff need training both in the chosen analytical procedures and also in the maintenance of the equipment
- Need to confirm calibrations regularly
- Need a continuous assessment of laboratory performance to demonstrate that the day-to-day measurements do indeed achieve the necessary uncertainty.

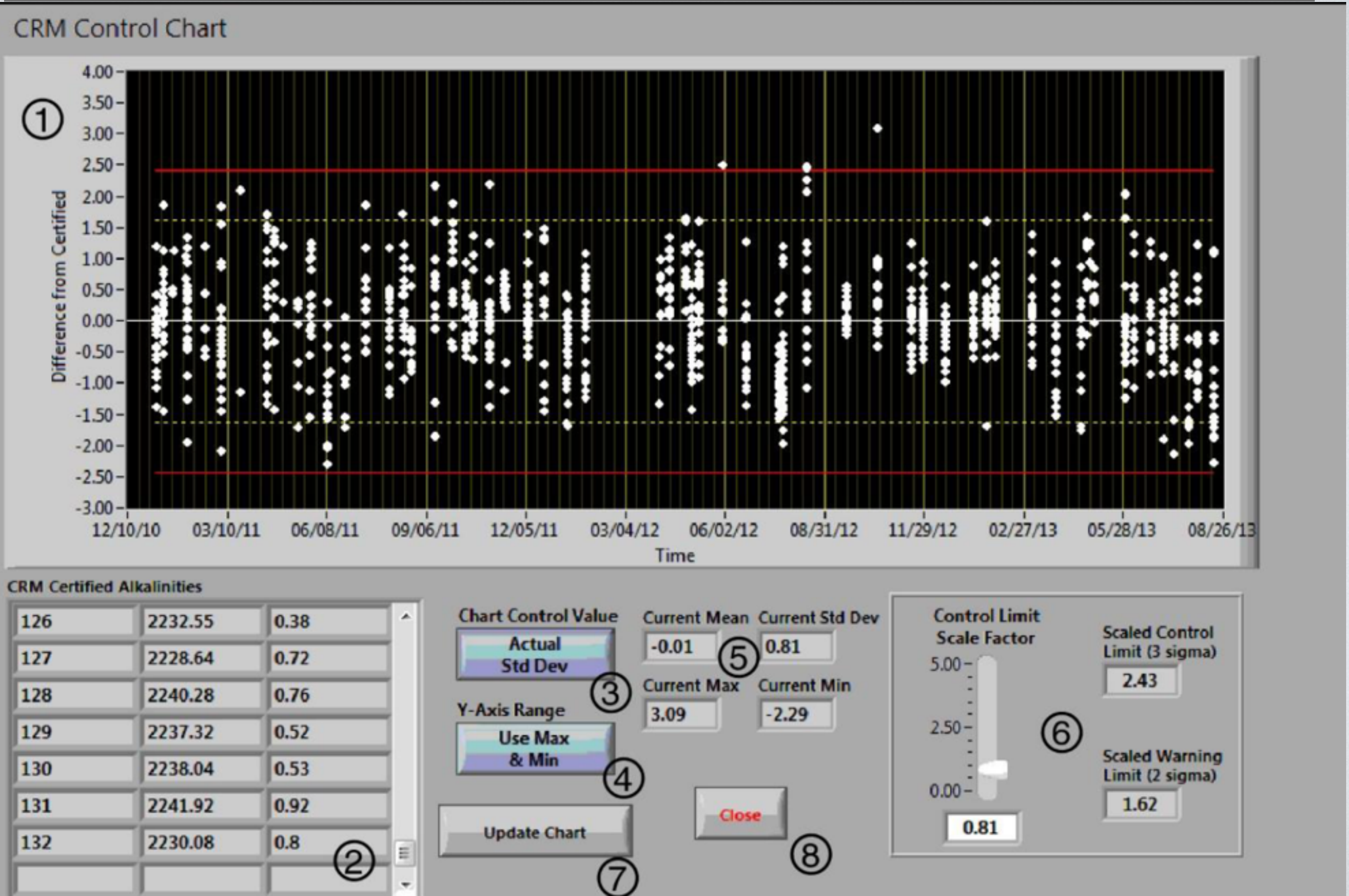
Example (Total alkalinity)



Check list for quality control

- Method / operator
  - Suitable equipment
  - Documented method
  - Trained operator
- Calibration checks
  - Titration acid
  - Temperature probes
  - Burette
  - Voltmeter
- Measurements on reference materials

ALKALINITY SYSTEM CONTROL CHART



Quality assessment techniques

Internal techniques

- Repetitive measurements
- Internal test samples
- Control charts
- Interchange of operators
- Interchange of equipment
- Audits

External techniques

- Collaborative tests
- Exchange of samples
- External reference materials
- Certified reference materials
- Audits

Current status of seawater reference materials

Analytical measurement	Uncertainty	Availability
Total dissolved inorganic carbon	1.0 µmol kg^{-1}	Since 1991
Total alkalinity	1.2 µmol kg^{-1}	Since 1996
pH (total hydrogen ion)	0.01	Since 2012
$p(CO_2)$	–	–

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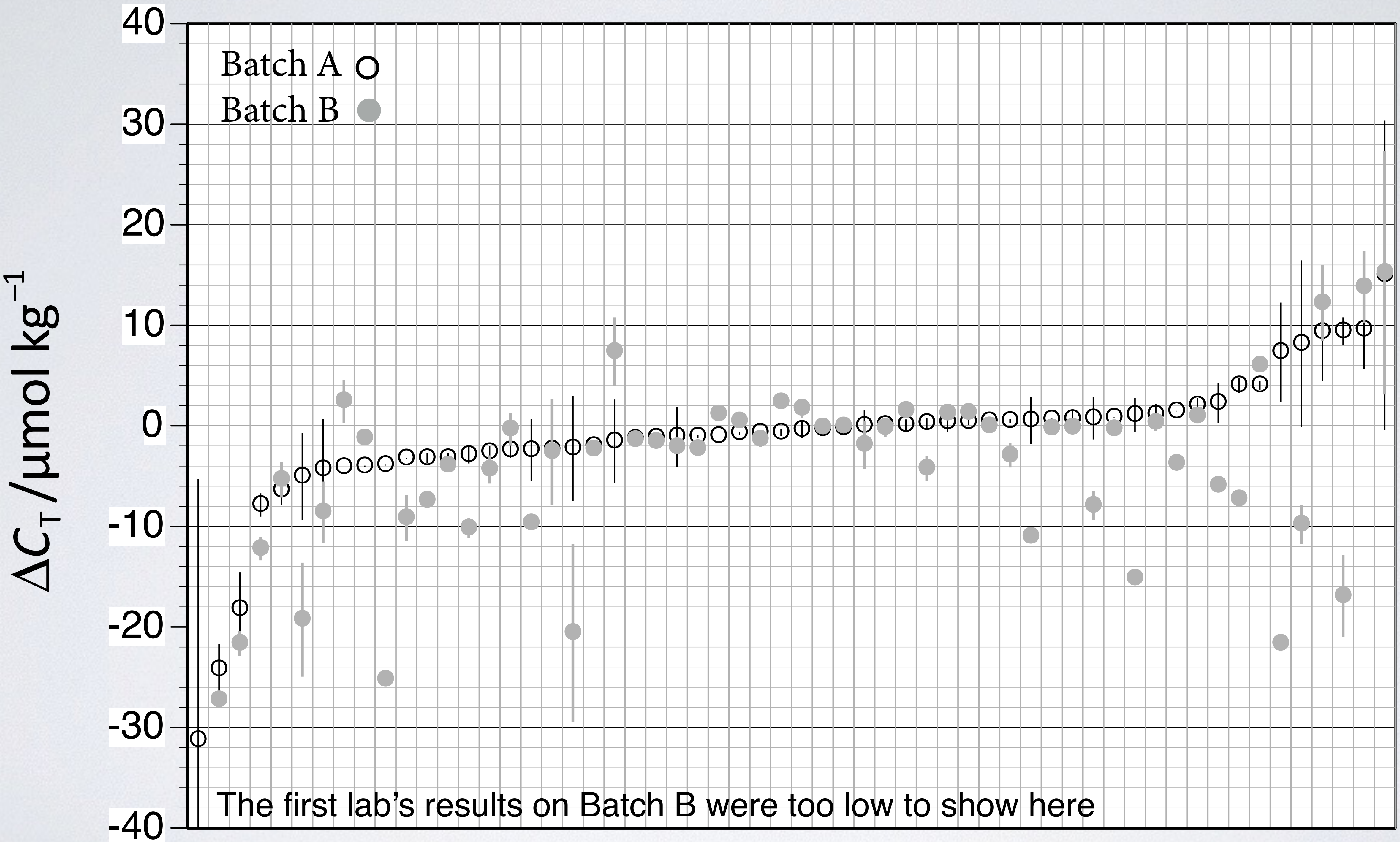
Recent inter-laboratory proficiency study



Bockmon & Dickson, 2015


I DON'T BELIEVE IN