Approaches/challenges to monitoring carbonate chemistry of coral reef ecosystems

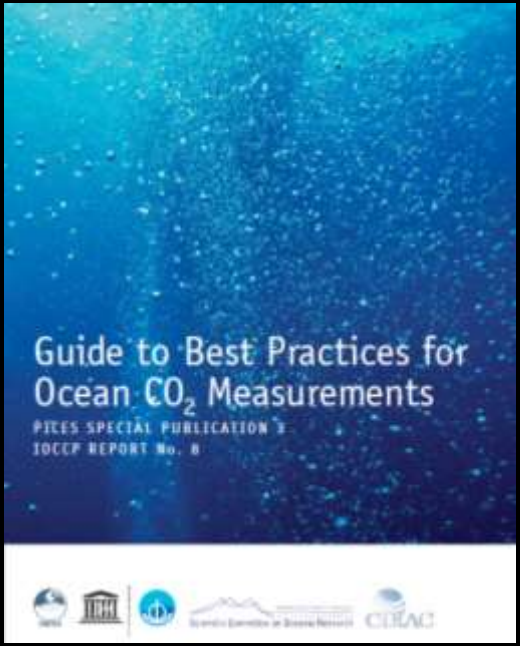
Adrienne Sutton | Dwight Gledhill | NOAA

WESTPAC Workshop on Research and Monitoring of the Ecological Impacts of Ocean Acidification on Coral Reef Ecosystems | 20 January 2015

Approaches to monitoring carbonate chemistry

Discrete sampling (ship-based, laboratory)

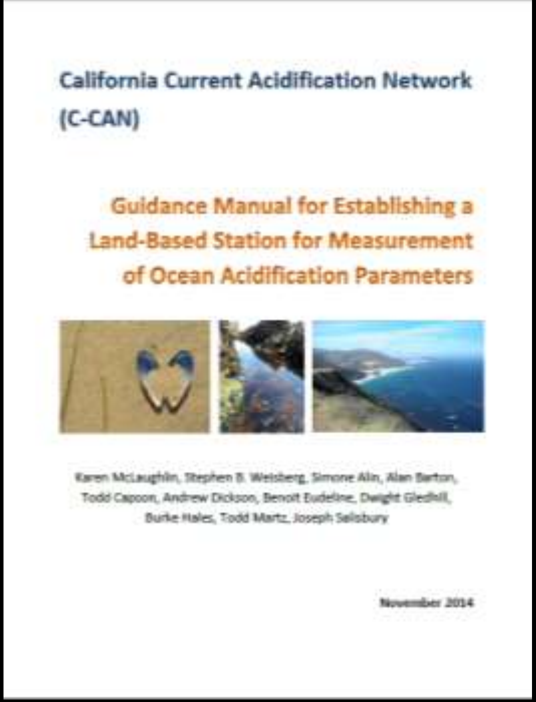
Autonomous sensors (flow-through or fixed-location)



Guide to Best Practices for Ocean CO_2 Measurements

PICES SPECIAL PUBLICATION 3

IOCCP REPORT No. 8



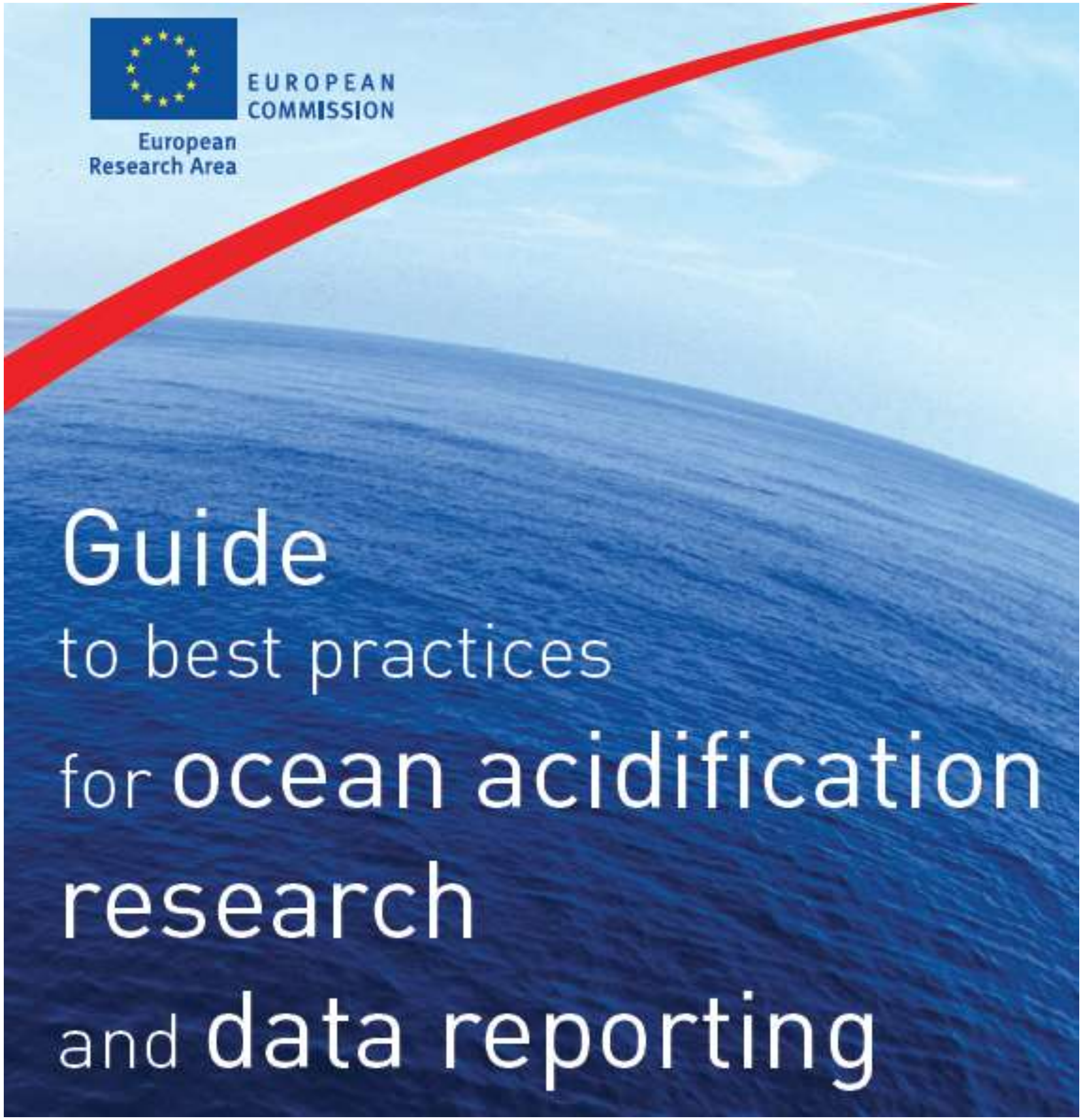
California Current Acidification Network (C-CAN)

Guidance Manual for Establishing a Land-Based Station for Measurement of Ocean Acidification Parameters

Karen McLaughlin, Stephen B. Weisberg, Simone Alin, Alan Barton, Todd Capoon, Andrew Dickson, Benoit Eudeline, Dwight Gledhill, Burke Hales, Todd Martz, Joseph Salisbury

November 2014

Guide
to best practices
for ocean acidification
research
and data reporting



EUROPEAN
COMMISSION

European
Research Area

Guide to best practices for ocean acidification research and data reporting

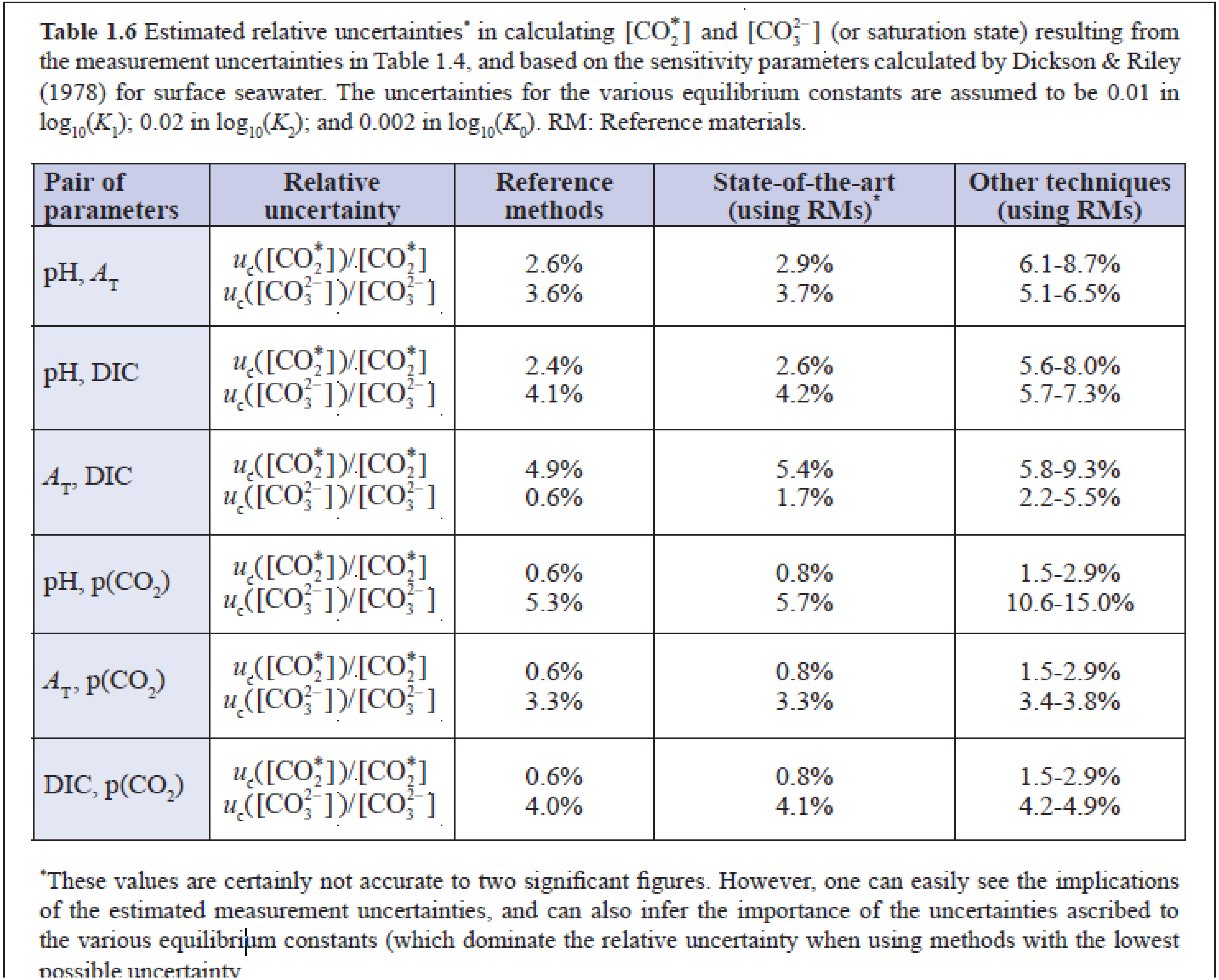


Table 1.6 Estimated relative uncertainties* in calculating $[\mathrm{CO}_2^*]$ and $[\mathrm{CO}_3^{2-}]$ (or saturation state) resulting from the measurement uncertainties in Table 1.4, and based on the sensitivity parameters calculated by Dickson & Riley (1978) for surface seawater. The uncertainties for the various equilibrium constants are assumed to be 0.01 in $\log_{10}(K_1)$; 0.02 in $\log_{10}(K_2)$; and 0.002 in $\log_{10}(K_0)$. RM: Reference materials.

Pair of parameters	Relative uncertainty	Reference methods	State-of-the-art (using RMs)*	Other techniques (using RMs)
pH, A_T	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	2.6% 3.6%	2.9% 3.7%	6.1-8.7% 5.1-6.5%
pH, DIC	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	2.4% 4.1%	2.6% 4.2%	5.6-8.0% 5.7-7.3%
A_T, DIC	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	4.9% 0.6%	5.4% 1.7%	5.8-9.3% 2.2-5.5%
pH, $p(\mathrm{CO}_2)$	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	0.6% 5.3%	0.8% 5.7%	1.5-2.9% 10.6-15.0%
A_T, $p(\mathrm{CO}_2)$	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	0.6% 3.3%	0.8% 3.3%	1.5-2.9% 3.4-3.8%
DIC, $p(\mathrm{CO}_2)$	$u_c([\mathrm{CO}_2^*])/[\mathrm{CO}_2^*]$ $u_c([\mathrm{CO}_3^{2-}])/[\mathrm{CO}_3^{2-}]$	0.6% 4.0%	0.8% 4.1%	1.5-2.9% 4.2-4.9%

*These values are certainly not accurate to two significant figures. However, one can easily see the implications of the estimated measurement uncertainties, and can also infer the importance of the uncertainties ascribed to the various equilibrium constants (which dominate the relative uncertainty when using methods with the lowest possible uncertainty

At present there are four parameters that can be reliably measured for the seawater carbon dioxide system (*AT, DIC, pH, p(CO2)), and one of these, pH, has multiple possible definitions which in turn can result in* multiple values for acid-dissociation constants (Dickson, 1984).

Handbook of methods for the analysis of the various parameters of the carbon dioxide system in seawater (DOE, 1994) and of the more recent Guide to best practices for ocean CO2 measurements (Dickson et al., 2007) and recommends use of the so-called total hydrogen ion concentration scale to define pH in
seawater media.

At this time, the analytical methods described in the *Guide to best practices for ocean CO2 measurements*
(Dickson *et al., 2007) are presently the best understood and have the lowest uncertainty.*

For studies on natural seawater, my recommendation would be to measure *AT and DIC (as samples for these can be preserved easily* and the measurements made with low uncertainty).

Key Recommendations:

1. writing appropriate Standard Operating Procedures for the techniques in use;
2. interlaboratory comparison exercises to assess the various figures of merit for each technique (trueness and precision);
3. regular use of certified reference materials to assist in the quality control;
4. regular laboratory performance testing using blind samples.

Challenges to using autonomous sensors

pCO_2/pH pair

Depth

Accuracy

Biofouling

Shipping/customs issues for factory recalibrations

Recommendations for autonomous sensors

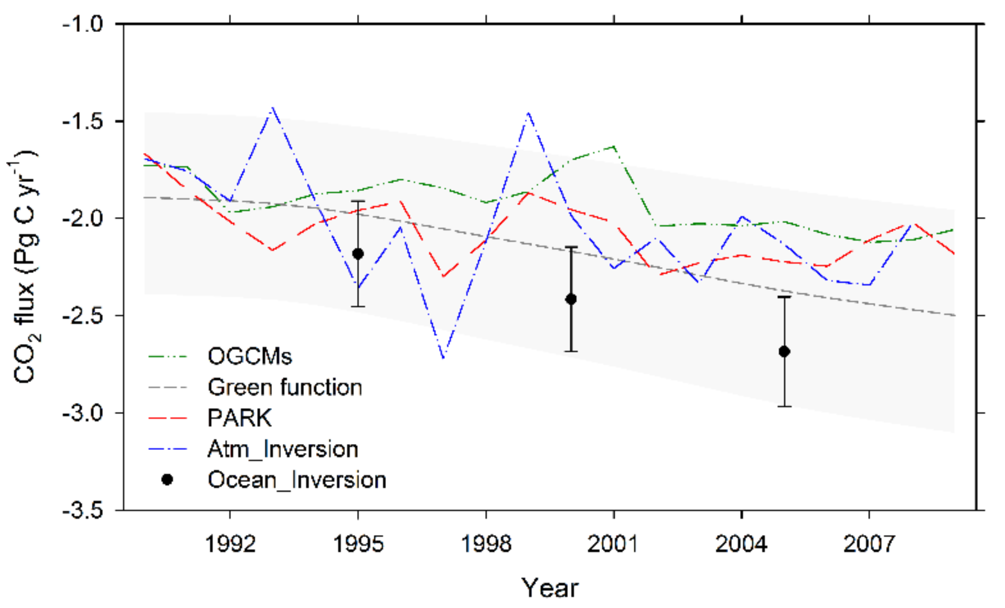
Choose a sensor that can answer your research questions

Is the ocean sink keeping pace with atmospheric CO_2 increases?

Current estimates of anthropogenic CO_2 ocean uptake range from 2.0 – 2.5 Pg C yr^{-1}

ocean is keeping pace with atm. CO_2 increases

ocean is NOT keeping pace with atm. CO_2 increases



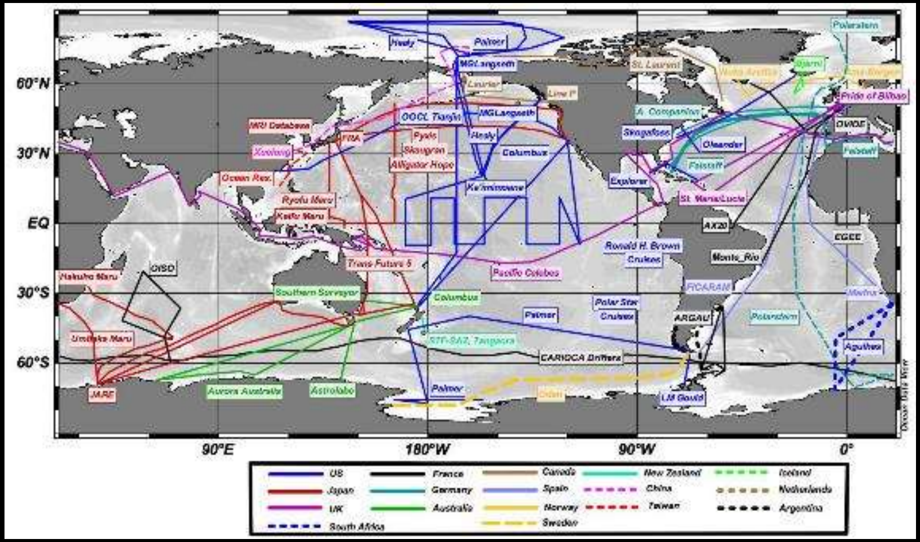
Wanninkhof et al. 2013, Biogeosciences, RECCAP

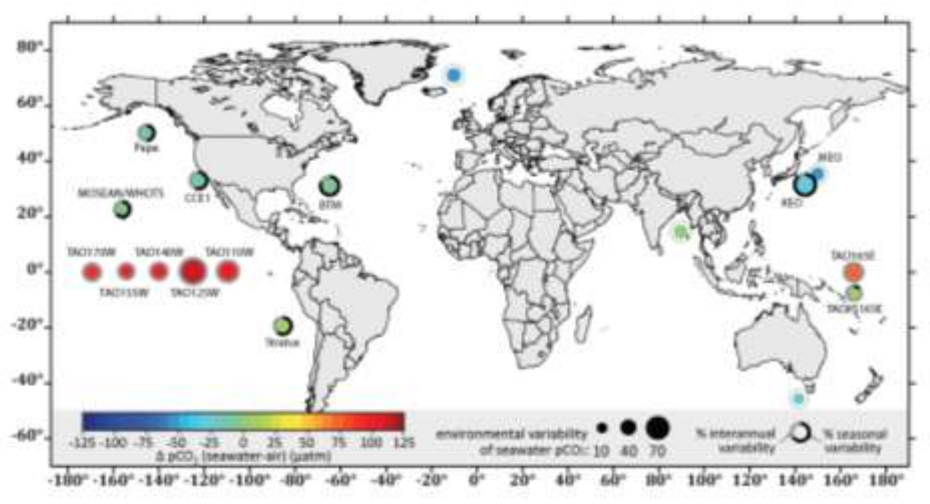
1) surface ocean CO_2 flux
2) decadal changes in inventories of anthropogenic carbon

Recommendations for autonomous sensors

Choose a sensor that can answer your research questions

pCO_2 sensor
uncertainty < 2 µatm

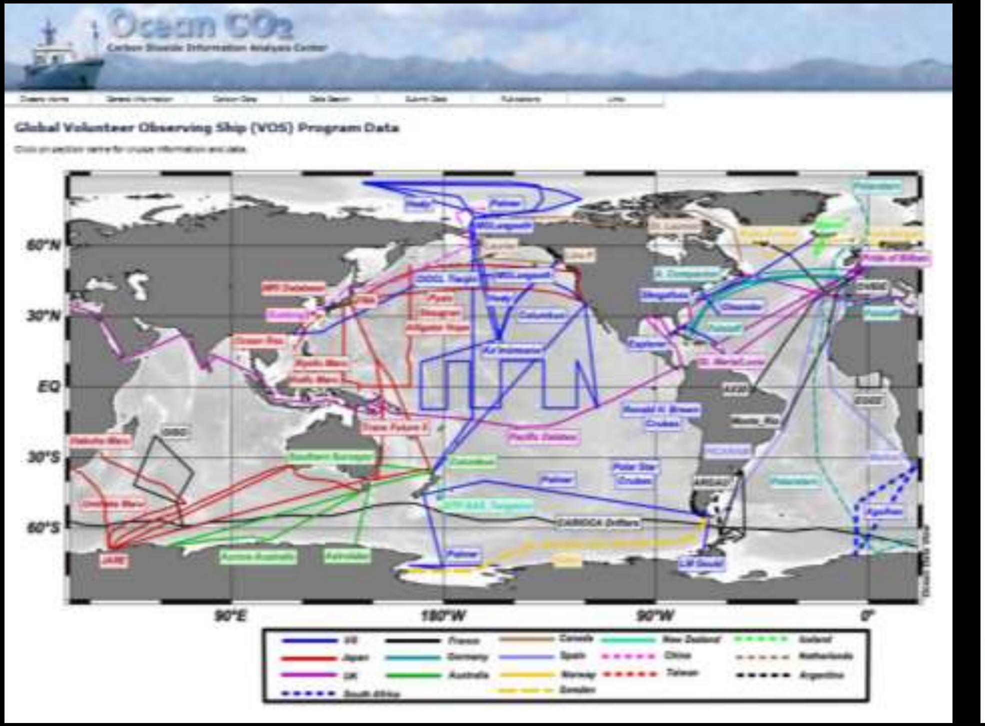




Recommendations for autonomous sensors

Choose a sensor that can answer your research questions

Collaborate with existing observational programs



Global Volunteer Observing Ship (VOS) Program Data

The Global Ocean Acidification Observing Network (GOA-ON) is a collaborative international approach to document the status and progress of ocean acidification in open-ocean, coastal and estuarine environments, to understand the drivers and impacts of ocean acidification on marine ecosystems, and to provide spatially and temporally resolved biogeochemical data necessary to optimize modeling for ocean acidification.

Approach and Goals

Detailed information about the GOA-ON background, design, implementation, and data strategy can be found here:

Interactive Map of Ocean Acidification Platforms

Building on the existing global oceanic carbon observatory network of repeat hydrographic surveys, time-series stations, floats and glider observations, and volunteer observing ships, the interactive map below offers the best information available on the current inventory of global OA observing platforms. This is a strong foundation of observations of the carbonate chemistry needed to understand chemical changes resulting from ocean acidification.

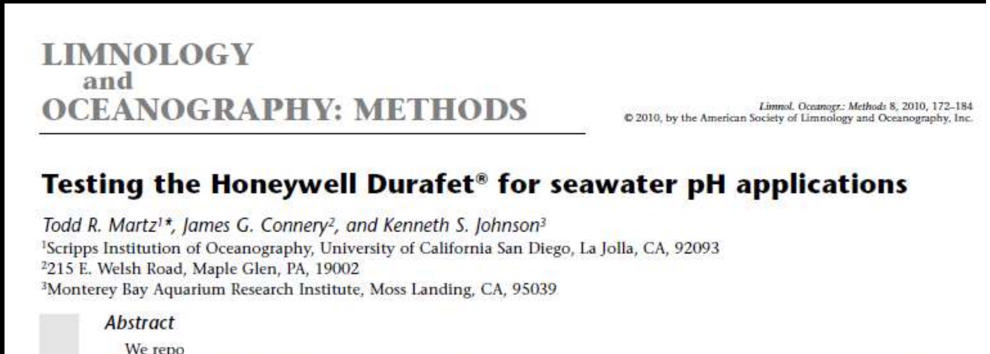
An International Effort

Recommendations for autonomous sensors

Choose a sensor that can answer your research questions

Collaborate with existing observational programs

Seek information about sensor uncertainty in the literature



LIMNOLOGY
and
OCEANOGRAPHY: METHODS

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Testing the Honeywell Durafet® for seawater pH applications

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Abstract

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PAPER

Alliance for Coastal Technologies: Advancing Moored pCO_2 Instruments in Coastal Waters

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ABSTRACT

The Alliance for Coastal Technologies (ACT) has been established to support innovation and to provide the information required to select the most appropriate tools for studying and monitoring coastal and ocean environments. ACT is a con-

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www.earth-syst-sci-data.net/6/353/2014/
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Earth System Science Data

A high-frequency atmospheric and seawater pCO_2 data set from 14 open-ocean sites using a moored autonomous system

Available online at www.sciencedirect.com
ScienceDirect

ELSEVIER

Marine Chemistry 109 (2008) 18–28

MARINE CHEMISTRY

www.elsevier.com/locate/marchem

A sensor for in situ indicator-based measurements of seawater pH

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Abstract

Indicator-based spectrophotometric pH methods are now proven and commonly used for analysis of ocean samples; however, no autonomous system for long-term in situ applications has been developed based on this method. We describe herein an

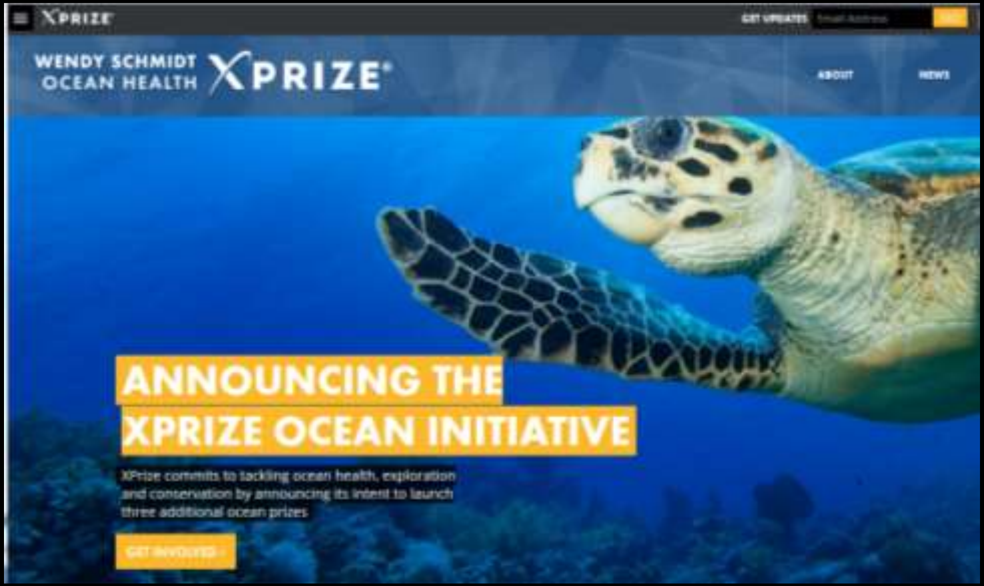
Recommendations for autonomous sensors

Choose a sensor that can answer your research questions

Collaborate with existing observational programs

Seek information about sensor uncertainty in the literature

Anticipate future technologies



ANNOUNCING THE
XPRIZE OCEAN INITIATIVE

XPrize commits to tackling ocean health, exploration and conservation by announcing its intent to launch three additional ocean prizes