

**Response to EPA Notice of Call for Public Comment on 303(d)
Program and Ocean Acidification from the Ocean Carbon and
Biogeochemistry (OCB) Program**

May 21, 2010

We are pleased that the EPA is considering ocean acidification as it addresses protection of both marine and fresh water. The scientific community has focused primarily on the atmosphere-ocean linkage in ocean acidification. Technically, ocean acidification is the pH decrease of the Earth's oceans due to the uptake of atmospheric carbon dioxide, but we are aware that there are also many other local factors that contribute to alterations in seawater pH (Doney et al., 2007; Doney et al., 2009a and 2009b; Feely, Alin, et al., in press).

As we address your questions on this issue, we have concentrated on two themes: (1) the global-scale ocean acidification due to rising atmospheric CO₂ concentrations, and (2) the impact on marine organisms. We have not addressed ocean acidification due to other sources, either from other atmospheric compounds (e.g., Doney et al., 2007) or other point-source pollutants that affect marine carbonate chemistry. However, we hope that the information in this response provides context on the changing baseline of seawater carbonate chemistry relevant to possible regulation of both carbon dioxide emissions and other sources of pollution that can either exacerbate or ameliorate the shift in carbonate chemistry of waters from their natural state.

The following comments are compiled from the U.S. Ocean Carbon and Biogeochemistry (OCB) community of scientists (see <http://www.us-ocb.org/>). The goal of the Ocean Carbon and Biogeochemistry Program is to help coordinate and facilitate U.S. marine biogeochemistry and related ecological research working in conjunction with relevant federal science agencies (e.g., NSF, NASA and NOAA). The OCB is a community of scientists, primarily at academic and research institutions. Much of the information in this document is drawn from the OCB Response to EPA Notice of Data Availability in 2009 (OCB, 2009), which itself is a summary of several key reviews (Box 1) on the state of ocean acidification research findings, but this document also includes updates from the recent scientific literature.

It should be noted that major recommendations in these reviews (Box 1) are to improve and increase monitoring of ocean acidification, including in the coastal zone, and to increase research on its impacts on marine organisms and ecosystems. These efforts will significantly aid development of appropriate criteria regarding acidification by EPA.

We have addressed the EPA questions in the order that they were proposed in the Request for Public Comment. Items in **Blue** are original questions posed by EPA.

Box 1: Recent key review documents

National Research Council (2010) Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean, Ocean Studies Board Division on Earth and Life Studies, National Research Council. http://www.nap.edu/catalog.php?record_id=12904

Dickson AG, Sabine CL, Christian JR (Eds) (2007) Guide to best practices for ocean CO₂ measurements, PICES Special Publication, 3, 191 pp., 2007. (and pH references within) http://cdiac.ornl.gov/oceans/Handbook_2007.html

Box 1 (continued): Recent key review documents

Doney, S.C., W.M. Balch, V.J. Fabry, and R.A. Feely (2009a): [Ocean acidification: A critical emerging problem for the ocean sciences](#). *Oceanography*, 22(4), 18–27.

Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009b) Ocean acidification: the other CO₂ problem. *Ann Rev Mar Sci* 1:169-192

Fabry VJ, Langdon C, Balch WM, Dickson AG, Feely RA, Hales B, Hutchins DA, Kleypas JA, Sabine CL (2009) Present and future impacts of ocean acidification on marine ecosystems and biogeochemical cycles, Report of the Ocean Carbon and Biogeochemistry Scoping Workshop on Ocean Acidification Research (UCSD, Scripps Institution of Oceanography; 9–11 October 2007).

Feely, R.A., S.C. Doney, and S.R. Cooley (2009): [Ocean acidification: Present conditions and future changes in a high-CO₂ world](#). *Oceanography*, 22(4), 36–47.

Feely, R.A., V.J. Fabry, A. Dickson, J.-P. Gattuso, J. Bijma, U. Riebesell, S. Doney, C. Turley, T. Saino, K. Lee, K. Anthony, and J. Kleypas (2010): An international observational network for ocean acidification. In *Proceedings of the “OceanObs ’09: Sustained Ocean Observations and Information for Society” Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306. [In press].

Kleypas JA, Feely RA, Fabry VJ, Langdon C, Sabine CL, Robbins LL (2006b) Impacts of ocean acidification on coral reefs and other marine calcifiers: A guide for future research. Report of a workshop held 18-20 April, 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey, 88 pp.

OCB Subcommittee on Ocean Acidification (2009) Ocean Acidification – Recommended Strategy for a U.S. National Research Program, Ocean Carbon and Biogeochemistry Program, 14 pp.

Riebesell, U., Fabry, V., Hansson, L., Gattuso, J.-P. (eds.) 2010. Guide to best practices in ocean acidification research and data reporting. Office for Official Publications of the European Communities, Luxembourg, 264 pp. <http://www.epoca-project.eu/index.php/Home/Guide-to-OA-Research/>

1. What considerations should EPA take into account when deciding how to address the listing of waters as threatened or impaired for ocean acidification under the 303(d) program?

Main points:

- The “baseline” of ocean chemistry is changing due to increases in atmospheric CO₂ concentration, which is driving more CO₂ into surface waters and thus causing a shift in the carbonate system in seawater including a decrease in pH. Present-day conditions already reflect substantial anthropogenic perturbations from pre-industrial conditions.
- Ocean acidification typically refers to the global (non point source) contribution of CO₂ from the atmosphere. However, other non-point sources (e.g. acid rain) and point-source pollutants can also affect acidification of both fresh and marine waters at regional to local scales.
- Ocean acidification represents a suite of changes in the carbonate system in seawater, and each change can have both direct and indirect effects on marine life.

- The responses of marine life to ocean acidification are compounded by other concurrent impacts such as global warming, eutrophication, and hypoxia.

The release of carbon dioxide (CO₂) from industrial and agricultural activities since the Industrial Revolution has increased atmospheric CO₂ concentrations from a stable baseline of approximately 280 parts per million (ppm) to the present level of 387 ppm. The atmospheric concentration of CO₂ is now higher than experienced on Earth for at least the last 800,000 years, and its level and emissions are expected to accelerate as human societies worldwide become increasingly industrialized. During the transition to today's industrialized world, the ocean has absorbed more than 450 billion tons of carbon dioxide from the atmosphere, equaling nearly one-third of anthropogenic carbon emissions. This absorption has benefited humankind by significantly reducing atmospheric CO₂ levels, thereby partly minimizing climate change due to the increased atmospheric burden of greenhouse gases including CO₂.

Inorganic carbon occurs naturally in seawater as a suite of carbon compounds including dissolved carbon dioxide (CO_{2(aq)}), carbonic acid (H₂CO₃), bicarbonate ions (HCO₃⁻), and carbonate ions (CO₃²⁻). The relative proportions of ions in this "CO₂ system in seawater" adjust to maintain ionic charge balance (often referred to as "carbonate equilibrium" of seawater or the "carbonate buffering system"). However, when seawater absorbs so much anthropogenic CO₂ over such a relatively short time period, both seawater pH and the concentration of carbonate ions decrease in a process commonly referred to as ocean acidification (Caldeira and Wickett, 2003; Feely et al 2009, 2004; Orr et al., 2005). Addition of CO₂ to seawater alters the carbonate equilibrium, with an associated decline in pH and changes in the relative concentrations of bicarbonate and carbonate ions.

The main concern about ocean acidification is its impact on marine life. Ocean acidification represents a suite of chemical changes and thus a suite of impacts on marine organisms. Ocean acidification includes changes in the concentrations of dissolved carbon dioxide, bicarbonate ion, carbonate ion, and hydrogen ion, all of which can directly affect marine biological processes:

pH. Since pH is reported on a logarithmic scale, small changes in pH indicate large changes in hydrogen ion concentration. The 0.1 pH unit decrease in average pH of the surface ocean since preindustrial times is equivalent to about a 30% increase in the hydrogen ion concentration. Biochemical processes of virtually all living organisms are regulated by pH, so most organisms expend energy to regulate their cellular and internal pH. Some organisms are better equipped to handle changes in pH than are others.

CO_{2(aq)} and HCO₃⁻. Concentrations of both dissolved carbon dioxide and bicarbonate increase with ocean acidification. Marine primary producers use both forms of carbon, and production of at least some species is likely to increase. Sea grasses, for example, use CO_{2(aq)} for photosynthesis and have been shown to increase production with CO₂ fertilization, at least when light and nutrients are not limiting. Some microscopic phytoplankton also seem to benefit from increases in CO_{2(aq)} or HCO₃⁻.

CO₃²⁻. Changes in the carbonate ion concentration affect the availability of carbonate minerals used by marine organisms to produce their shells or skeletons. The carbonate

ion concentration decreases dramatically with ocean acidification – by about 30% once atmospheric carbon dioxide concentration is twice the preindustrial level. This will limit shell and skeletal formation of many organisms, including corals, shellfish, sea urchins, and many algae.

All marine organisms are vulnerable to the indirect effects of ocean acidification, such as:

Chemical speciation of nutrients and metals. Changes in pH, a fundamental chemical property of seawater, can alter the availability of nutrients, trace elements and trace organics that support marine life. The chemical form of several trace metals, for example, can be altered by changes in pH, making them more or less available (or more or less toxic) to marine organisms.

Biogeochemical processes. The major nutrient cycles in the ocean, which include geological, chemical, physical, and biological processes, determine the availability of nutrients that support all ocean life, as well as the ability of the oceans to sequester CO₂ from the atmosphere. Ocean acidification has the potential to alter both chemical and biological processes that will affect nutrient and carbon cycles, such as by altering the rate of nitrogen fixation by certain marine algae.

Food web effects. Because marine food webs are complex, changes in one or more key species can have repercussions throughout the food web. This is one of the main concerns regarding U.S. fisheries, but predicting such changes may also be one of the greatest research challenges within ocean acidification research. Even those organisms that are not directly impacted by ocean acidification can be indirectly affected by changes in their food supply, competitors, or predators. Considering the direct effects of “CO₂ fertilization” on primary production described above, while this may initially seem favorable, the ultimate outcome is unpredictable, since increases in CO_{2(aq)} and HCO₃⁻ may favor certain types of algae over others and thus change the nature of marine food webs.

Changes in ecosystem substrate. In some communities, particularly bottom dwellers, decreases in calcium carbonate production alter the structural fabric of the ecosystem. Many marine plants and animals depend on the structural habitat provided by coral reefs and cold-water coral communities. Oyster banks, clam beds, etc. may also be affected by substrate changes associated with decreased carbonate production.

Another challenge is that ocean acidification is acting simultaneously with other natural and human-induced changes that hasten localized declines in pH and carbonate mineral saturation states, such as periodic mesoscale circulation events, eutrophication, hypoxia, and altered freshwater runoff (Doney et al., 2007; Feely et al., 2008; Salisbury et al., 2008; Miller et al., 2009; Feely, Alin, et al., in press). Furthermore, ocean acidification is not the only stress presently acting on ocean ecosystems: nonchemical factors like temperature change, fishing, and physical alterations also affect marine species and communities (Pörtner, 2008; Hoegh-Guldberg et al. 2007; Waldbusser et al. in press). In many cases the effects are not simply additive, but are either synergistic or antagonistic. Any classification of natural waters as threatened or

impaired by ocean acidification should therefore also take into account all the acute and chronic stressors that could contribute to altering pH or carbonate ion concentration. Ideally, such a classification would also include an integrated assessment of all the stressors (chemical and otherwise) acting on an ecosystem.

At present, many uncertainties remain concerning the status of ocean acidification in coastal zones, nearshore ecosystems' tolerances to these changes, and the potential long-term effects of ocean acidification. We explore these unknowns in detail in OCB (2009) but we also mention primary uncertainties in the answers below.

2. If EPA issues guidance regarding the listing of waters as threatened or impaired for ocean acidification under the 303(d) Program, what are the specific elements that EPA should consider? Should the Agency specifically consider the following:

Main points:

- Substantial scientific guidance on methods for monitoring ocean acidification have been published over the last five years, and a major NRC report is nearly complete which details a national strategy for monitoring both ocean acidification and its impacts.
- Monitoring of ocean chemistry is now fairly straightforward, but monitoring of biological impacts remains challenging. This is because ocean acidification impacts marine life in multiple ways, the impacts are compounded by other impacts that occur simultaneously, and because the complexity in ecosystem interactions renders the impacts difficult to predict.
- Several technologies currently exist for monitoring ocean acidification and its impacts. Several autonomous sensors are currently available for monitoring changes in one or more of the CO₂-system parameters, and more sensors are being developed. Some of these sensors are well suited by deployment on buoys, gliders and other remotely operated vehicles. Remote monitoring of biological responses to ocean acidification are less developed. Satellite-based remote sensing has been developed for examining changes in calcium carbonate production by bloom-forming phytoplankton. Autonomous sensors for calcium carbonate particulates are also available and have been deployed on buoys. Future developments in biological monitoring (e.g. DNA bar-coding of marine communities to capture species diversity) are anticipated but are not yet available for broad application in monitoring the impacts of ocean acidification.
- Various U.S. agencies are undertaking programs for monitoring ocean acidification and its impacts, and efforts to coordinate such activities are underway via JSOST.

Any assessment of natural waters as threatened or impaired from ocean acidification must incorporate high-quality water chemistry data to identify changes in the chemical environment, and it must be based on knowledge of how the evolving chemical environment will influence aquatic communities in the region. With these two key information categories in hand, managers may take appropriate measures to preserve ecosystem function. At present, existing knowledge of the “baseline” status of natural waters (mean values, natural variability, “hazardous” conditions) is limited, but establishment of ongoing monitoring programs now using methods proven to deliver high-quality water chemistry data (reviewed below in response to 2a) will

provide the datasets needed to assess whether acidification is affecting a particular region (NRC, 2010). Then, information about the diverse biological responses to increased water CO₂, decreased pH, CO₃²⁻, and the saturation state of aragonite (Ω_{ar}), a biologically important calcium carbonate mineral, emerging from ongoing studies will enable new conclusions about biological responses to acidification to be applied as they emerge from present studies and programs (reviewed below in response to 2a).

a. What surface water monitoring methods and programs are available to States to measure ocean acidification impacts?

This question was recently addressed by two reports (NRC 2010, Riebesell et al. 2010). The NRC report “Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean” lays out a strategy for monitoring ocean acidification in marine and coastal waters. The Riebesell et al (2010) “Guide to best practices in ocean acidification research and data reporting” provides in detail the recommended methods for monitoring and experimentation of ocean acidification and its effects on marine life. In addition, OCB’s response to the EPA NODA on ocean acidification (2009) provided a summary of monitoring methods for measuring ocean acidification (restated below), as well as a few methods for monitoring biological response to ocean acidification. The biological monitoring methods remain much less developed than those for seawater chemistry, an important gap recognized in the NRC report.

Assessments should allow for the possibility that estuaries may respond differently to ocean acidification than the open ocean, as highlighted in a recently completed study. For example, Feely, Alin, et al. (in press) studied the impacts of ocean acidification in Puget Sound during cruises in winter and summer of 2008. Anthropogenically acidified coastal waters upwelling along the western North American continental margin enter Puget Sound through the Strait of Juan de Fuca. Observed pH and aragonite saturation state values in surface and subsurface waters were substantially lower in parts of Puget Sound than would be expected from anthropogenic carbon dioxide (CO₂) uptake alone. The authors estimated that ocean acidification can account for 24–49% of the pH decrease in the deep waters of the Hood Canal sub-basin of Puget Sound relative to estimated pre-industrial values. The remaining decrease in pH that occurs between the time when seawater enters the sound and when it reaches this deep basin is from remineralization of organic matter during natural or anthropogenically stimulated respiration within Puget Sound. Over time, however, the relative impact of ocean acidification could increase significantly, accounting for 49–82% of the pH decrease in subsurface waters by the time atmospheric CO₂ doubles. These changes may have profound impacts on the Puget Sound ecosystem over the next several decades. These estimates suggest that the role ocean acidification will play in estuaries may be different from the open ocean.

The following description from the OCB response to EPA’s NODA on ocean acidification (OCB, 2009) of the available monitoring methods is repeated below for completeness.

Chemical monitoring

Although pH in seawater has been measured for many decades, a reliable long-term trend of ocean water pH cannot be established in most locations due to data quality issues, in particular

the lack of strict and stable calibration procedures and standards. Moreover, seawater pH is very sensitive to temperature, and temperature is not always recorded or measured at sufficient accuracy to constrain the pH measurement. Therefore in order to reconstruct long-term pH trends, pH values (or $[H^+]$ activity or concentration) are computed using chemical models with measured values of dissolved inorganic carbon (DIC or CT), CO_2 partial pressure (pCO_2), and/or total alkalinity (TA or AT) in seawater.

With major analytical advances over the last two decades, the four so-called inorganic carbon system parameters can be measured with very high accuracy and precision aboard oceanographic research vessels or from water samples collected at field sites. Of the four parameters, pCO_2 and pH can be measured remotely on moorings or other platforms using autonomous sensors. The analytical procedures for making CO_2 parameter measurements are documented in great detail in the “Guide to Best Practices for Ocean CO_2 Measurements” (Dickson et al., 2007). For ocean acidification research at least two, and preferably three of the four carbon parameters should be measured at each of the sampling depths to ensure internal consistency of the data sets. Accuracy and precision can be obtained from replicate measurement of certified standards, which are available for all four parameters (Table 1 in OCB, 2009).

Direct Measurement of pH

Direct measurements of pH in seawater have traditionally been performed using an electrode, most commonly a glass-calomel electrode pair. However, these data cannot be used to document a long-term trend because of the lack of electrode accuracy. The major problems, detailed in OCB (2009), include the following:

- a) Stable electrodes with sufficient sensitivity ($pH \sim 0.001$) that are suitable for long-term measurements in seawater are unavailable.
- b) Standard hydrogen electrodes cannot be used for seawater samples, since the hydrogen gas passed through the sample purges CO_2 and alters pH.
- c) pH electrodes may be calibrated using standard solutions (e.g. the TRIS-buffer), but eliminating systematic errors arising from junction and asymmetry potentials is difficult.
- d) Errors are often introduced when CO_2 gas in the air in a cell's headspace exchanges with a sample during measurement.
- e) Determining errors due to failures in maintaining the samples and electrodes at the same temperature is difficult.
- f) There are four pH scales, and the pH scales used for measurements are often not defined in data reports. These pH scales are not interchangeable and thus the pH scale should always be noted.

The current preferred method of pH analysis is measuring pH spectrophotometrically (Clayton and Byrne, 1993; Wang et al., 2007) because the problems with electrodes are circumvented (see a, c, and d above). Measurements can be made with high precision (± 0.0005), and accuracy is only limited by errors associated with maintaining and measuring temperature, accurate knowledge of the indicator's thermodynamic and spectroscopic constants, and accounting for addition of indicator. Long-term, accurate pH_T measurements can now be made on moorings using autonomous spectrophotometrically based pH sensors (Seidel et al., 2008). However, the working range of spectrophotometric measurements is tied to the range of the buffers used,

which for seawater spans about 0.4 pH units. For inland and estuarine waters with wider pH ranges, other indicator buffers must be sought and cross-calibrated with the TRIS buffers.

Indirect Methods for the Determination of pH

Alternative methods can also be used for computing pH (or $[H^+]$ activity or concentration) in seawater. Commonly used methods are briefly described below, and their strengths and weaknesses are discussed in detail in OCB (2009).

DIC-TA method: $[H^+]$ may be computed using a chemical model for seawater with the total concentration of CO_2 species dissolved in seawater (DIC), titration or total alkalinity (TA or AT), temperature and salinity data. When the concentrations of nutrient salts (i.e. phosphate and silicate) are high, these concentrations are also needed. DIC and TA may be measured with sufficiently high precision and long-term stability.

Because of the complications of measuring TA, the resulting $[H^+]$ values may be less precise and subject to more systematic errors than the DIC- pCO_2 method, which is discussed below. Based on the accuracy limits listed in Table 1 of OCB (2009; or $1 \mu mol kg^{-1}$ for DIC and $2 \mu mol kg^{-1}$ for TA), the pH in surface waters (SST= $20^\circ C$, SSS = 35 PSU, TA= $2300 \mu mol kg^{-1}$, DIC= $2030 \mu mol kg^{-1}$) can be calculated with a precision of 0.004 and the aragonite saturation state to 0.02.

DIC- pCO_2 method: $[H^+]$ may be computed using a chemical model for seawater with DIC, pCO_2 , temperature and salinity data. DIC and pCO_2 can be measured with sufficiently high precision and long-term stability (e. g. Olafsson et al., 2009).

The $[H^+]$ values obtained by the DIC- pCO_2 and DIC-TA methods depend on the pH scale used for dissociation constants. However, the advantage of the pCO_2 -DIC method is that it requires only the solubility of CO_2 gas in seawater and the first and second dissociation constants for carbonic acids. In contrast, the TA-DC method requires not only the dissociation constants for carbonic but also those for boric, phosphoric, and silicic acids, and, as stated above, organic acids are often neglected.

TA- pCO_2 method: $[H^+]$ values computed using this pair are subject to the strengths and weaknesses described for TA and pCO_2 (OCB, 2009). However, the seasonal variability of TA appears to be small and may be parameterized with sufficient precision as a function of salinity and nitrate concentration, and extensive seasonal and interannual pCO_2 observations are available. The precision of the calculated pH using TA- pCO_2 is ~25% better than that of the DIC- pCO_2 method, as pH is not as sensitive to variations in TA as it is to variations in pCO_2 or DIC.

pH-DIC and pH-TA methods: Recent advancement of pH measurements via colorimetric methods has yielded high precision data (Byrne et al., 1989) that are comparable to, or better than the precision of pCO_2 measurements. These spectrophotometric measurements are relatively cheap and easy to perform but require appropriate standards, indicator solutions, and strict protocols to obtain the precision and accuracy necessary to discern multi-year trends caused by uptake of anthropogenic CO_2 . However, since these high quality measurements did not

commence in the field until the late 1990s, data are very limited and insufficient to determine a long-term trend or characterize geographical variability for seawater pH.

The pH value computed by the DIC-pCO₂ and DIC-TA methods depends on the pH scale used for the determination of the dissociation constants of carbonic, boric and other acids. The pH values measured by colorimetric methods have been found to be consistent with those computed from the DIC-pCO₂ or DIC-TA during cruises when three or more inorganic carbon system parameters are measured (Byrne et al. 1999).

Multiple Linear Regression Approach: There are a few empirical approaches that have been used for estimating carbon chemistry from hydrographic data sets from field observations. For example, the multilinear regression (MLR) analysis method has often been used to fill data gaps in data-sparse basins via interpolation and extrapolation (Lee et al., 2000; 2006). The MLR method takes advantage of statistical correlations between frequently measured properties (e.g., temperature, salinity) and the target property of interest (OCB, 2009). A similar approach can be used to estimate other carbon system parameters from hydrographic data sets collected from shipboard and moored observations in coastal waters. However, since coastal ecosystems have varying amounts of freshwater inputs with uniquely different alkalinity-salinity relationships, this approach should be validated locally with high-quality carbon chemistry measurements on a seasonal basis.

Conclusions about direct & indirect measurement methods:

- a) Application of a pH criterion alone will be inadequate to monitor ocean acidification and its impacts on coastal marine ecosystems. It is therefore recommended that additional criteria such as carbonate ion concentration and saturation state be considered.
- b) Direct measurements of pH using spectrophotometric indicators are the most reliable and straightforward method for quantifying the changes in [H⁺] due to ocean acidification. Thus far, however, these measurements have limited spatial and temporal coverage.
- c) Full characterization of the seawater inorganic chemistry system and ocean acidification requires simultaneous measurement of temperature, salinity and at least two of the four CO₂ system parameters (pH, DIC, TA and pCO₂). The pH scale used must also be reported.

Biological monitoring

Biological studies of both calcifying and noncalcifying species thus far have assessed a variety of responses to ocean acidification, which vary by species, location, and biological process. No universal indicators of ocean acidification biological effects have been identified yet (NRC 2010), but experimental results show a range of responses that can be grouped generally into those relating to survival, growth, and reproduction (OCB, 2009). Most of these studies have been performed in carefully controlled laboratory experiments, but methods for determining calcification rate, physiological performance, etc. can be applied in natural waters as well. Monitoring biological responses alongside the chemical changes in seawater chemistry is essential if we are to attribute the responses to ocean acidification. As noted above, this is complicated by the fact that ocean acidification is acting simultaneously with other global,

regional and local changes in surface waters. Some responses (e.g. effects on marine calcification) are likely to be more strongly associated with ocean acidification, and should be monitored.

Methods currently used or being explored:

Numerous species-specific assessments of biological responses to chemical changes representative of ocean acidification have been performed to date (see, e.g., OCB, 2009). Calcification has often been studied using microscopy, spectrometry, radioisotope uptake, growth bands, or chemical anomalies/mass balances. Photosynthesis and nitrogen fixation have been studied using oxygen or isotopic uptake methods. Respiration and metabolic status have been measured using metabolic proxies and electrodes. Although still in the developmental states, several microbiological methods are likely to prove useful in monitoring physiological responses to ocean acidification. Genomics-based tools, such as quantitative PCR and DNA microarrays, measure gene expression in organisms exposed to ocean acidification (Hofmann et al. 2008).

Ongoing Programs

The following ongoing programs are providing high-quality inorganic carbon chemistry data that will provide useful information to determine natural baseline conditions and developing changes associated with ocean acidification. These programs are primarily focused on monitoring chemical parameters and not all examine the potential effects of ocean acidification on marine biota.

- NOAA National Ocean Service coastal monitoring (<http://oceanservice.noaa.gov/observations/monitoring/>)
- Ecosystem studies [e.g., the U.S. Long-Term Ecological Research (LTER) Network] (<http://www.lternet.edu/>)
- Moorings and floats (e.g., NOAA Moored pCO₂ program; but need more than pCO₂) (<http://www.pmel.noaa.gov/co2/moorings/>)
- NOAA Ocean Acidification Monitoring Program (<http://www.pmel.noaa.gov/co2/OA/>)
- U.S. CO₂/Repeat Hydrography Program (CLIVAR/CO₂) (<http://ushydro.ucsd.edu/>)
- OceanSITES (<http://www.oceansites.org/>)
- Regional multiyear research projects led by scientists at non-federal institutions that include ocean CO₂ sampling programs:
 - Georgia coast work (W.J. Cai, UGA; <http://www.marsci.uga.edu/facultypages/cai/>)
 - Gulfs of Maine and Mexico repeat surveys (J. Salisbury, UNH; <http://csg.sr.unh.edu/projects.html>)
 - Gulf of Mexico monitoring (S. Lohrenz, USM; http://ocean.otr.usm.edu/~w301130/research/research_bioocean.htm)

Historical datasets

EPA is encouraged to seek out long-term coastal States' and Federal datasets (e.g., USGS, NOAA) on water quality or any monitoring studies that have included pH data collected in coastal State waters. These datasets often have been collected as ancillary data for long-term water quality monitoring (e.g., in conjunction with *E. coli* monitoring), but may be available for

other monitoring studies as well. Technically, pH data collected within coastal environments in the U.S. for the past 4-5 decades may not be optimal in resolution and accuracy; however, they might provide EPA with information on long-term trends and seasonal and annual variability of pH that the coastal environments are likely to demonstrate, provided consistent calibrations were performed through time (see technical information above regarding pH measurements). Rigorous statistical evaluation of the data must be applied and metadata must be scrutinized. Many of the historical pH datasets lack sufficient detail on protocol and accuracy to be useful to estimate long terms trends.

Caveats

The majority of historical coastal ocean pH data have been measured using glass electrodes, which suffer from liquid junction potential problems due to salinity variations (Whitfield et al., 1985; Cai et al., 1998). The spectrophotometric method, which is widely used in open ocean research, needs further validation in coastal waters. While there are limited sustained measurements of pH and other inorganic carbon chemistry parameters in the coastal ocean, there are sufficient observations from a variety of sources to obtain a first-order idea of variations and expected increases. The main drivers of pH variability in the coastal ocean are changes in temperature, salinity, currents/upwelling, and biological processes. Often a combination of these

Table 1. Approximate ranges of inorganic carbon system parameters for seawater and fresh water^a.

	SST	SSS	DIC	TA	pCO ₂	pH ^b	Ω _{arg} ^c	Annual pH change ^d
Fresh water	0	0	329	300	375	7.591		0.0023
	25	0	329	300	860	7.360		0.0023
Seawater	4.3	34.6	2069	2300	232	8.24	2.41	-0.0027
	23.2	35.2	2003	2319	350	8.09	3.52	-0.0026
Mississippi	20	0	2468	2500	375	8.290		-0.0022
Eastern Boundary	10	34	2345	2400	1000	7.692	1.02	-0.0008
	20	34	2035	2300	375	8.061	2.97	-0.0019

^a These values are for illustrative purposes only. For each scenario the SST, SSS, pCO₂ and TA are prescribed to representative values encountered in the environment. The DIC, pH, and aragonite saturation state, Ω_{arg}, are calculated with the functional dependence of dissociation constants with temperature and salinity as described in Dickson and Millero (1987) using the program developed by Lewis and Wallace (1998). DIC and TA have units of μmol kg⁻¹ and pCO₂ is μatm.

^b pH at in situ temperature on the seawater scale.

^c Saturation state of aragonite. Values <1 indicate that the mineral phase will dissolve. Saturation state values for fresh water are poorly constrained and therefore not presented.

^d This is the annual change in pH for surface water assuming the pCO₂ increases by 2 μatm yr⁻¹. The example shows that seasonal and interannual changes in pH due to changes in temperature and inorganic carbon chemistry can be up to two orders of magnitude greater than the annual decrease in pH due to uptake of anthropogenic CO₂.

processes acts synergistically on pH. Table 1 provides a rough estimate of expected ranges of variability in $p\text{CO}_2$, pH, and aragonite saturation state compared with annual pH decrease due to anthropogenic CO_2 uptake. Upwelling heavily influences the U.S. West Coast and thus large ranges in pH and $p\text{CO}_2$ have been observed (Feely et al., 2008). These upwelled waters have a decreased buffering capacity due to high DIC values. Many fresh waters have limited buffering capacity as well because of the low alkalinities of these waters. The greatest excursions along the East and Gulf Coasts are attributed to fresh water input and annual temperature and biological changes. Since variations in seasonal temperature and biological productivity are greater in coastal regions, larger excursions in pH, $p\text{CO}_2$, and saturation states are encountered than in the open ocean.

i. Are there emerging remote sensing technologies that might be particularly suited to gathering information about acidification of ocean waters?

We describe here the variety of technologies that allow for autonomous measurements of ocean acidification. The region of greatest development has been in sensors that can be used for long-term deployment. We summarize here information from the recent document “Sensors and systems for in situ observations of marine carbon dioxide system variables” (Byrne et al. in press).

Autonomous sensors for measuring $p\text{CO}_2$ (or $f\text{CO}_2$, CO_2 fugacity), total alkalinity, DIC, and pH are being developed. Autonomous $f\text{CO}_2$ and pH sensors are well established, while DIC and TA sensors are not yet reliable. $f\text{CO}_2$ and pH sensors are already being deployed (but as noted below, $f\text{CO}_2$ and pH are not a recommended pairing of CO_2 -system parameters). While problems still exist in terms of instrument calibration and biofouling, it is reasonable to expect further improvements in precision and accuracy that approach those of shipboard measurements. An important consideration in deploying such sensors is that at least two of the CO_2 -system components need to be measured, and some sensor pairs are more compatible than others: DIC + $f\text{CO}_2$; DIC + pH; TA + $f\text{CO}_2$; and TA + pH. Another goal of future sensor development is to adapt sensors to the various observing platforms available, such as floats (including profiling floats) and gliders.

Combinations of space-based observations have been successfully used to map the CO_2 system in surface waters. Gledhill et al. (2008, 2009) developed a tool that uses observations of sea surface temperature, sea surface salinity, sea level pressure, atmospheric CO_2 , and chlorophyll *a* measurements to determine the CO_2 system parameters in seawater. While the model performs well in open ocean environments, it is probably not appropriate in regions dominated by riverine or coastal processes.

As noted in Feely et al. (2010), new procedures have recently been developed for obtaining information on the distributions of particulate inorganic carbon (PIC, or calcium carbonate) and particulate organic carbon (POC) from bio-optical sensors that have been calibrated against discrete samples. Such information is essential to evaluate how different phytoplankton groups respond to ocean acidification. These new bio-optical sensors can be deployed on moorings and floats (Bishop et al. 2002). Similarly, Balch et al. (2007) have employed bio-optical methods to obtain data on PIC distributions from satellite-based observations. When properly calibrated

against discrete measurements, these new approaches hold the promise of providing highly resolved data on the production and dissolution of biogenic carbonate phases in the oceans. This will be very useful for studying global-scale changes in phytoplankton groups and PIC over time. Filtration of underway seawater supplies from research and volunteer observing ships (VOS) offer pathways to calibration of these remote sensing approaches, as well as the possibility of easy extension to additional functional groups of phytoplankton (e.g. diatoms by adding biogenic silica measurements), and the separation of key carbonate forming taxa such as coccolithophores (phytoplankton) and foraminifera (zooplankton) via size fractionation. An autonomous PIC sensor has also been developed and deployed on multiple oceanographic platforms (Bishop 2009).

ii. Are there new programs for collecting information about acidification of marine waters off the U.S. coasts that could provide information useful to EPA or States in the next few years?

Several US agencies have programs for monitoring ocean acidification and/or its impacts. NOAA has been the most active in this regard and has recently developed a 6-year program to address ocean acidification. The US Geological Survey (USGS) has also supported ocean acidification research in coastal regions, and particularly on coral reefs, and continues to do so. NSF recently solicited proposals to directly address ocean acidification and its impacts (NSF-10530) with expected funding of \$12-15 million. In anticipation of the appropriation of funds authorized by the Federal Ocean Acidification and Monitoring Act (FOARAM Act 2009) to support ocean acidification research, the Joint Subcommittee on Ocean Science and Technology (JSOST) has formed an interagency working group on ocean acidification to “provide input to the JSOST on matters related to ocean acidification, including coordination of Federal activities on ocean acidification and other interagency activities as outlined in the Federal Ocean Acidification Research and Monitoring Act of 2009” and is writing a “comprehensive interagency plan to monitor and conduct research on the processes and consequences of ocean acidification on marine organisms and ecosystems.”

We anticipate that these efforts will lead to improvements in ocean acidification monitoring of both marine and coastal waters, and that much of this information will be both available and useful to EPA or States within the next few years.

b. What assessment methodologies are available for States to make attainment determinations consistent with water quality standards related to ocean acidification?

The OCB is not aware of States’ capacities to make attainment decisions, and does not feel qualified to answer this question beyond the recommendation that States partner with federal programs, Universities, etc. to conduct monitoring. In its response to the EPA NODA on ocean acidification (OCB 2009), the OCB provided extensive background information on methodologies for measuring ocean acidification and its effects on marine organisms. We recommend the States refer to this material, as well as the recent National Research Council report (NRC 2010) for guidance on what methodologies are available.

c. How can States incorporate additional information on ocean acidification beyond site-specific measurements? (e.g. offshore and global surveys, experiments and field studies on representative species or ecosystems, models for ocean acidification and carbon dioxide emission trends, etc.)

Numerous studies are presently underway to examine species- and region-specific responses of aquatic organisms to acidification. As the results from these experiments are published, EPA should combine the lessons learned about regionally important species with the emerging datasets from ongoing monitoring, so that potential biological thresholds can be anticipated.

Modeling studies are also underway to identify ways in which individual and regional responses may affect coastal ecosystems. EPA may also be able to forecast regional biological thresholds from the results of these studies as they are completed. In order to use current models as diagnostic tools, more work is needed to tightly couple chemical models and ecosystem-scale models with mechanistic relationships. As noted above, these are still being discovered.

d. What other data and information is available for States to use in making decisions regarding whether waters are threatened or impaired for ocean acidification?

As outlined in the response to 2a, available studies of biological responses to ocean acidification indicate that responses are often location- or species-specific. Ecosystem-scale studies will help clarify how individual responses will result in geographic or trophic shifts within marine environments, allowing conclusions to be drawn about the possible large-scale effects of acidification.

If reduced calcification decreases a calcifying organism's fitness or survivorship, then some calcareous species may undergo shifts in their distributions as the inorganic carbon chemistry of seawater changes. Calcifying species that are CO₂-sensitive could potentially be replaced by non-calcifying species and/or those species not sensitive to elevated pCO₂. By 2100, surface waters of polar and subpolar regions are projected to become undersaturated with respect to aragonite (Orr et al., 2005). Shelled pteropods are important components of the plankton in high latitude systems, with densities reaching thousands of individuals per cubic meter (e.g., Bathmann et al., 1991; Pane et al., 2004). If pteropods require seawater that is supersaturated with respect to aragonite, then their habitat would become increasingly limited, first vertically in the water column and then latitudinally, by the shoaling of the aragonite saturation horizon over the next century (Feely et al., 2004; Orr et al., 2005). If high latitude surface waters do become undersaturated with respect to aragonite, pteropods could eventually be eliminated from such regions, with consequences to food web dynamics and other ecosystem processes (Fabry et al., 2008). In the subarctic Pacific, for example, pteropods can be important prey for juvenile pink salmon (*Oncorhynchus gobuscha*). Armstrong et al. (2005) reported that a single species of pteropod (*Limacina helicina*) comprised 15 to 63% by weight of the diet of juvenile pink salmon. Planktonic ecosystems are complex, nonlinear, and the consequences of ocean acidification on this ecosystem are largely unknown (Guinotte and Fabry, 2008). The interactive effects of elevated pCO₂ and other climate change variables such as temperature could result in substantial changes to species diversity and abundances in many regions. Species interactions may be

altered on multiple trophic levels, potentially impacting ecosystem productivity, as well as the cycling of organic carbon and calcium carbonate.

3. How can States or EPA otherwise aid in monitoring ocean acidification and its impacts on marine life and ecosystems?

Main points:

- EPA and States can provide invaluable information on ocean acidification and impacts by leveraging on existing water sampling programs to include quality measurements of the CO₂-system in seawater.
- These existing programs could also be expanded to regions identified as being particularly vulnerable to ocean acidification or presently undersampled.

When establishing routine methods and standard operating procedures (SOPs) for measuring water quality and assessing the quality of those data, States and EPA should select methods and instrumentation that have been proven to achieve the detection limits, accuracy, and precision necessary to discern acidification signals (Dickson et al., 2007; Riebesell et al. 2010).

EPA and States that have been monitoring pH or other CO₂ system chemistry–related water quality parameters, and/or biological variables that are sensitive to ocean acidification, have procedures in place that, if conducted in accordance with SOPs, would provide invaluable long-term data on changes in seawater chemistry and biology. This is particularly true for estuarine and coastal waters. The sampling design could be tailored to assess regional concerns (e.g., the timing of settlement of mollusk and oyster larvae on benthic substrates.) Some previously collected data made by EPA and States may also prove valuable to understanding historical changes in ocean acidification, although the extent and quality of such data have not been fully established by the scientific community.

Programs initiated now or in the future should include monitoring of ocean acidification-relevant variables (pH, pCO₂, etc.) as well as evaluation of ecological changes. For example, the Great Lakes Restoration Initiative, a \$450 million effort started in 2009, should include efforts to assess acidification in the Great Lakes, given that this region is historically undersampled for these parameters, yet as large bodies of fresh water, are likely to experience impacts (see above).

4. If waters were determined to be threatened or impaired for ocean acidification under 303(d), what issues should EPA and States take into account when considering how to address TMDL development for such waters?

Main points:

- In establishing TMDLs for waters that have been deemed threatened or impaired, EPA and States should consider issues such as the natural variability of chemistry in the waters, as this will vary considerably from region to region.

- EPA should also consider the natural ability of organisms to cope with changes in CO₂-system chemistry. Some organisms are accustomed to very small variations in pH and other CO₂ system variables, while others naturally experience large variations.
- Within such variations, we do not yet know whether organisms are more likely to respond to lower maxima (e.g. reduced calcification rates during peak times of calcification) or lower minima (e.g. exposure to corrosive waters or anomalous CO₂-chemistry conditions). Specific guidelines must therefore be tailored to local conditions and knowledge of the biological responses (some of which will need to be determined experimentally or by other means). Also, the synchronization of the timing of various life stages with seasonal changes in the CO₂-system in seawater should be considered. Thus, developing TMDLs should consider timing of loads as well as overall loads.
- The capacity of organisms to acclimate or adapt to future changes in ocean acidification will be determined by many factors, including their evolutionary history, generation times, and the differences in susceptibility of various life stages. Adaptation to ocean acidification may lead to loss of other functions in some marine organisms.
- The impact of ocean acidification in combination with other stressors (warming, eutrophication, freshwater runoff, toxins, etc.) is a very important consideration, but unfortunately there are as yet few studies that can directly inform TMDL development about how to address multiple stressors.

Natural variability

Ocean acidification will affect the concentrations of multiple CO₂-system species (pH, HCO₃⁻, CO₃²⁻), and each of these has been shown to affect marine organisms. However, we know the most about the geochemical effects of ocean acidification and our answers are biased toward this aspect. pH, the carbonate ion concentration, and calcium carbonate saturation state exhibit large geographical variations from the tropics to the poles under pre-industrial conditions, reflecting variations in temperature and seawater chemistry. In cold polar waters, aragonite saturation is lower and closer to a threshold of 1, the boundary between undersaturated (<1) and oversaturated (>1). It is expected that undersaturated conditions with respect to aragonite (a more soluble form of calcium carbonate) will occur in the next 1-2 decades in the Arctic and in the next 2-4 decades in the Antarctic (e.g., Orr et al., 2005; Steinacher et al., 2009). The crossing of this geochemical threshold to undersaturated conditions in polar regions could result in calcium carbonate dissolution unless the organism has some mechanism(s) to prevent dissolution. However, many of the laboratory studies discussed above document biological sensitivity to reduced carbonate ion concentration simply when the extent of the calcium carbonate supersaturation is reduced, but remains well above 1. Therefore, the biological consequences of reduced calcium carbonate saturation state are complex and may differ among particular biological species, communities, and ecosystems. The rate and magnitude of chemical change may be more relevant to biological impacts than simply an absolute value of specific parameters of the inorganic carbon system. More research on field populations is needed to identify areas of particular susceptibility.

Adaptability

Because of inherent temporal limitations in experimental work, the type of organismal response to ocean acidification that we know most about is that of acclimation. Acclimation in this context is the short-term ability of existing individuals and populations to rapidly adjust their physiology to cope with changing pH. True adaptation is a longer-term evolutionary process of stable, long-

term phenotypic shifts that contribute to organismal fitness, as well as the selection for favorable new variant traits arising through mutation. The potential for marine organisms to adapt and evolve in response to selection by changing pH remains one of the least understood aspects of the ocean acidification field.

Changes in populations mediated by adaptation and evolution usually occur only over many hundreds or thousands of generations, and so typically require extended periods of time. Important clues about how the marine biota may respond to the current anthropogenic acidification event can be found in the paleo-oceanographic literature, since analogous events involving ocean-wide acidification and warming are thought to have occurred in the geological past (Zachos et al., 2005). Sedimentary records of changes in communities of calcareous plankton suggest that marine assemblages likely adapted to some degree to such a natural event, and so suffered only moderate losses of diversity (Bown and Pearson, 2009).

However, even those past ocean acidification events that are considered to be very rapid on geological timescales probably occurred over at least 1000 to 10,000 years (Zachos et al., 2005; Ridgwell and Schmidt 2010). In contrast, the current anthropogenic acidification is happening much more quickly, over mere decades or centuries. It is far from clear if or how marine organisms will be able to adapt to pH changes happening at this unprecedented rate. Evolutionary adaptation to acidification also seems much less likely in organisms such as vertebrates and some invertebrates that have long generation times relative to the timescales of ongoing chemical changes in the ocean. Microorganisms, with their short generation times of hours to days, would seem to have the best chance to truly adapt and evolve in response to ocean acidification. Long-term projects using genomic and metagenomic methods are needed to assess whether accelerating anthropogenic acidification is indeed driving microbial evolution.

A way to address these questions experimentally is by maintaining long-term cultures of model marine organisms at altered pH levels. An example of this type of study was presented by Collins and Bell (2004), who examined the long-term evolutionary responses of cultured marine phytoplankton to high CO₂ over 1,000 generations. Perhaps not surprisingly, they found that no new specific adaptations to low pH appeared over the course of their selection experiments; novel complex metabolic pathways and capabilities probably take much longer than this to arise through evolution. However, they did find that some cell lines in their experiments lost capabilities such as photosynthetic carbon-concentrating mechanisms (CCMs) that allow them to grow at today's lower CO₂ concentrations. Once the selective pressure to retain these low-CO₂ adaptations was removed through long-term growth at high CO₂, random mutational degradation of CCM genes occurred, rendering these cell lines incapable of growth at lower CO₂ levels. One implication of these findings is that if today's marine organisms are forced to adapt to a higher CO₂ environment, some may lose crucial physiological capabilities that would allow them to survive if and when human remediation efforts are eventually able to return ocean pH to normal pre-industrial values.

Another approach to looking at adaptation is to examine "natural experiments" in which organisms are subjected to low pH, high CO₂ conditions in situations such as when seawater chemistry is influenced by submarine volcanic venting. Since these vents subject local benthic marine organisms to long-term acidification, presumably they can be used as indicators of the

capacity for adaptive responses. Hall-Spencer et al. (2008) showed that such naturally acidified communities responded in ways that support some of the conclusions of short-term experiments. That is, acidic conditions reduced the ability of calcifying organisms to survive and build shells, effectively minimizing their contribution to the benthic community. In these acidified sites, their place was taken by the proliferation of non-calcareous, invasive brown algae. Tunnicliffe et al. (2009) found that calcifying mussels were able to grow near highly acidic vents, but they had much thinner shells and would therefore likely be more vulnerable to predation. The results of these natural acidification experiments must be interpreted cautiously for a number of reasons. For instance, other changes to seawater chemistry accompany volcanic venting that are unlikely to occur with anthropogenic ocean acidification, such as sulfide and trace metal enrichment. Nevertheless, these pioneering studies of low pH-adapted marine communities caution us against making the simplistic assumption that most marine organisms can fully compensate for acidification impacts through evolved resistance, if given enough time to adapt.

Interactions of OA with other stressors

One of the least understood aspects of the ocean acidification problem concerns the effect of ocean acidification when combined with other environmental stressors. The impact of multiple stressors is most acute for sessile organisms such as coral reefs (Anthony et al., 2009; Desalvo et al., 2008; Maynard et al., 2008; Zeevi-Ben-Yosef and Benayahu, 2008). Moreover, if calcification of reef-formers is inhibited by ocean acidification, then the ability of such reefs to withstand the more extreme storm events (expected with global warming scenarios; Huntington, 2006) would be diminished. Thus, increased erosion would be expected to result as the reef's ability to rebuild was compromised by ocean acidification. A more intensified water cycle would also result in greater freshwater runoff, which would exacerbate coastal ocean acidification impacts, since freshwater runoff doesn't have anywhere near the buffering capacity of seawater, thus causing even greater pH fluctuations.

Another environmental variable that is expected to be changing due to anthropogenic CO₂ emissions is temperature. Warming can cause acute stress to organisms, such that when combined with lower pH, might yield highly non-linear interactions. The literature on the impacts of thermal stress is enormous, too much to review here. Thermal stress can occur at the cellular level (causing disruption in cell physiology) or the community level (indirect changes in the environment). For example, increases in ocean temperature can affect ocean stratification, which will inhibit the vertical diffusion of nutrients in the sea, leading to nutrient-limited growth (Goes et al., 2004). Gregg et al. (2003) showed reduced global ocean chlorophyll levels corresponding with increases in sea surface temperature, which was hypothesized to be a function of increased stratification. Compounding these impacts with the additional physiological stress imposed by ocean acidification could mean dramatic changes in the ability of specific communities of algae to grow and survive.

Another example of compound effects of multiple stressors is the introduction of toxins to the marine environment along with ocean acidification, for which little work has been done. Much more work has been done on the recovery of lakes from multiple stressors (toxins, acidification, temperature, UVB) (Gunn and Sandoy, 2001; Keller et al., 2003; Keller, 2007). This body of literature has shown that the impact of multiple stressors at the community level is extremely difficult to predict, especially when there is the potential for arrival of exotic species (both

competitors and predators) into the ecosystem (Keller, 2007). Optimal approaches for studying the first-order effects of multiple stressors will likely utilize controlled experiments with multifactor analysis of variance (which will also include interaction terms). For whole ecosystem studies, however, such an approach will be much more difficult to design, and reproducibility of the experiments likely more tenuous, due to the stochastic nature of invading species. The time-scales of these multiple stressors could be equally difficult to demonstrate if one stressor has a short-term impact (*e.g.*, temperature) while the other has a longer-term impact (*e.g.*, acidification).

5. What other Federal ocean acidification programs and initiatives (e.g. National Ocean Policy, Subcommittee on Integrated Ocean Resources (SIMOR), Joint Subcommittee on Ocean Science and Technology (JSOST), National Research Council report on Marine pH) should EPA take into account when deciding how to approach ocean acidification under the 303(d) program?

US Interagency Working Group on Ocean Acidification FY 2010 Report.

This document will outline a strategic plan for Federal research and monitoring of ocean acidification and facilitate cooperation among the national and international participating organizations. It will outline specific activities to be conducted for both information gathering and analysis, and prioritize these efforts.

NOAA Ocean and Great Lakes Acidification Research Plan

This plan will identify critical uncertainties and key science questions about ocean acidification's progress and outlines a strategy for OA research, monitoring, and assessment through a comprehensive multi-organization effort. It is expected to provide integrated assessments of the ecological and societal impacts of ocean acidification for the U.S. coastal and Great Lakes regions to inform decisions about effective mitigation and adaptation strategies.

“An international observational network for ocean acidification”, Feely et al., (2010)

This paper provides “a community-based plan to address a strategy for a global ocean acidification observing system in the major ocean basins and marginal seas, warm water coral reefs, coastal margins, tropical to subtropical open-ocean regions, and high-latitude regions.” The system depends on a combination of direct and indirect quantifications of inorganic carbon parameters, biological measurements, model analyses, and maintenance of time-series datasets.

References

- Anthony KRN, Hoogenboom MO, Maynard JA, Grotto AG, Middlebrook R (2009) Energetics approach to predicting mortality risk from environmental stress: a case study of coral bleaching. *Funct Ecol.* 23(3):539-550
- Armstrong JL, Boldt JL, Cross AD, Moss JH, Davis ND, Myers KW, Walker RV *et al.* (2005) Distribution, size, and interannual, seasonal and diel food habits of northern Gulf of Alaska juvenile pink salmon, *Oncorhynchus gorbuscha*. *Deep Sea Res II* 52:247–265
- Balch W, Drapeau D, Bowler B, Booth E (2007) Prediction of pelagic calcification rates using satellite measurements. *Deep-Sea Research Part II- Topical Studies in Oceanography.* 54(5-7) 478-495.
- Bathmann UV, Noji TT, von Bodungen B (1991) Sedimentation of pteropods in the Norwegian Sea in autumn. *Deep Sea Res* 38:1341–1360
- Bishop JKB (2009) Autonomous observations of the ocean biological carbon pump. *Oceanography* 22: 182-193.
- Bown P, Pearson P (2009) Calcareous plankton evolution and the Paleocene/Eocene thermal maximum event: New evidence from Tanzania. *Marine Micropaleontology* 71:60-70
- Byrne RH, Breland JA (1989) High-precision multi-wavelength pH determinations in seawater using cresol red. *Deep-Sea Res. A* 36:803-810
- Byrne RH, McElligott S, Feely RA, Millero FJ (1999) The role of pHT measurements in marine CO₂- system characterizations. *Deep-Sea Res* 46:1985-1997
- Byrne RH, DeGrandpre MD, Short RT, Martz TR, Merlivat L, McNeil, C. Sayles FL, Bell R, Fietzek P (in press, 2010): Sensors and systems for in situ observations of marine carbon dioxide variables. In Proceedings of the “OceanObs’09: Sustained Ocean Observations and Information for Society” Conference (Vol. 2), Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306.
- Cai W-J, Wang Y (1998) The chemistry, fluxes and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia. *Limnol Oceanog* 43:657-668
- Caldeira K, and Wickett ME (2003). Anthropogenic carbon and ocean pH. *Nature.* 425(6956):365-365.
- Clayton TD, Byrne, RH (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Res* 40: 2115–2129
- Collins S, Bell G (2004) Phenotypic consequences of 1,000 generations of selection at elevated CO₂ in a green alga. *Nature* 431: 566-569
- Desalvo MK, Voolstra CR, Sunagawa S, Schwarz JA, Stillman JH, Coffroth MA, Szmant AM, Median M (2008) Differential gene expression during thermal stress and bleaching in the Caribbean coral *Montastraea faveolata*. *Mol Ecol* 17(17):3952-3971
- Dickson AG and Millero FJ. (1987). A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research Part A – Oceanographic Research Papers.* 34(10): 1733-1743.
- Dickson AG, Sabine CL, Christian JR (Eds.) (2007) Guide to best practices for ocean CO₂ measurements, PICES Special Publication, 3, 191 pp. (and pH references within) http://cdiac.ornl.gov/oceans/Handbook_2007.html
- Doney, SC, Mahowald N, Lima I, Feely RA, Mackenzie FT, Lamarque J-F, Rasch PJ (2007) Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system, *Proc Nat Acad Sci USA* 104:doi 10.1073 pnas.0702218104
- Doney, S.C., W.M. Balch, V.J. Fabry, and R.A. Feely (2009a): [Ocean acidification: A critical emerging problem for the ocean sciences.](#) *Oceanography*, 22(4), 18–27.
- Doney SC, Fabry VJ, Feely RA, Kleypas JA (2009b) Ocean acidification: the other CO₂ problem. *Ann Rev Mar Sci* 1:169-192
- Fabry VJ, Langdon C, Balch WM, Dickson AG, Feely RA, Hales B, Hutchins DA, Kleypas JA, Sabine CL (2009) Present and future impacts of ocean acidification on marine ecosystems and biogeochemical cycles, Report of the Ocean Carbon and Biogeochemistry Scoping Workshop on Ocean Acidification Research (UCSD, Scripps Institution of Oceanography; 9–11 October 2007).
- Fabry VJ, Seibel BA, Feely RA, Orr JC (2008) Impacts of ocean acidification on marine fauna and ecosystem processes. *ICES J Mar Sci* 65:414–432
- Feely, R.A., S.R. Alin, J. Newton, C.L. Sabine, M. Warner, C. Krembs, and C. Maloy (in press, 2010): The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. *Estuar. Coast. Shelf Sci.*
- Feely, R.A., S.C. Doney, and S.R. Cooley (2009): [Ocean acidification: Present conditions and future changes in a high-CO₂ world.](#) *Oceanography*, 22(4), 36–47.

- Feely, R.A., V.J. Fabry, A. Dickson, J.-P. Gattuso, J. Bijma, U. Riebesell, S. Doney, C. Turley, T. Saino, K. Lee, K. Anthony, and J. Kleypas (2010): An international observational network for ocean acidification. In *Proceedings of the "OceanObs '09: Sustained Ocean Observations and Information for Society" Conference (Vol. 2)*, Venice, Italy, 21–25 September 2009, Hall, J., D.E. Harrison, and D. Stammer, Eds., ESA Publication WPP-306. [In press]
- Feely RA, Sabine CL, Lee K, Berelson W, Kleypas J, Fabry VJ, Millero FJ (2004) Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. *Science* 305:362-366
- Feely RA, Sabine CL, Hernandez-Ayon JM, Ianson D, Hales B (2008) Evidence for upwelling of corrosive "acidified" water onto the continental shelf. *Science* 320:1490–1492
- Gledhill DK, Wanninkhof R, Millero FJ, Eakin CM (2008) Ocean acidification of the Greater Caribbean Region. *Journal of Geophysical Research* 13, C10031, doi:10.1029/2007JC004629.
- Gledhill DK, Wanninkhof R, Eakin CM (2009) Observing ocean acidification from space. *Oceanography* 22: 48-59
- Goes JI, Gomes H, Limsakul A, Saino T (2004) The influence of large-scale environmental changes on carbon export in the North Pacific Ocean using satellite and shipboard data. *Deep Sea Res* 51:247-279
- Gregg WW, Conkright ME, Ginoux P, O'Reilly JE, Casey NW (2003) Ocean primary production and climate: Global decadal changes. *Geophys Res Lett* 30(15):1809
- Guinotte JM, Fabry VJ (2008) Ocean acidification and its potential effects on marine ecosystems. In *The Year in Ecology and Conservation Biology 2008*. RS Ostfeld & WH Schlesinger (Eds.) *Annals of the New York Academy of Sciences*
- Gunn J, Sandoy S (2001) Northern Lakes Recovery Study (NLRS) - Biomonitoring at the Ecosystem Level. *Water, Air, Soil Pollut* 130:1-4
- Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, Turner SM, Rowley SJ, Tedesco D, Buia MC (2008) Volcanic carbon dioxide vents show ecosystem effects of ocean acidification. *Nature* 454:96-99
- Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A, Hatziolos ME. (2007) Coral Reefs Under Rapid Climate Change and Ocean Acidification. *Science*. 318(1737): DOI: 10.1126/science.1152509.
- Hofmann GE, O'Donnell MJ, Todgham AE (2008) Using functional genomics to explore the effects of ocean acidification on calcifying marine organisms, *Marine Ecology-Progress Series*, 373: 219-225.
- Keller B, Heneberry JH, Dixit SS (2003) Decreased acid deposition and the chemical recovery of Killarney, Ontario, lakes. *Ambio* 32(3):183-189
- Keller W (2007) Implications of climate warming for Boreal Shield lakes: a review and synthesis. *Environ Rev* 15:99-112
- Kleypas JA, Feely RA, Fabry VJ, Langdon C, Sabine CL, Robbins LL (2006a, b) Impacts of ocean acidification on coral reefs and other marine calcifiers: A guide for future research. Report of a workshop held 18-20 April, 2005, St. Petersburg, FL, sponsored by NSF, NOAA, and the U.S. Geological Survey 88
- Lee, K., L.T. Tong, F.J. Millero, C.L. Sabine, A.G. Dickson, C. Goyet, G.-H. Park, R. Wanninkhof, R.A. Feely, and R.M. Key (2006): Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans. *Geophys. Res. Lett.* 33: L19605, doi:10.1029/2006GL027207
- Lee K, Wanninkhof R, Feely RA, Millero FJ, Peng T-H (2000): Global distribution of total inorganic carbon in surface water. *Global Biogeochem. Cycles* 14:979–994
- Lewis E, Wallace DWR (1998) Program developed for CO₂ system calculations, Oak Ridge National Laboratory, Oak Ridge.
- Maynard JA, Anthony KRN, Marshall PA, Masiri I (2008) Major bleaching events can lead to increased thermal tolerance in corals. *Mar Biol* 155(2):173-182
- Miller AW, Reynolds AC, Sobrino C, Riedel GF (2009) Shellfish Face Uncertain Future in High CO₂ World: Influence of Acidification on Oyster Larvae Calcification and Growth in Estuaries. *PLoS ONE* 4(5): e5661. doi:10.1371/journal.pone.0005661
- National Research Council (2010) *Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean*, Ocean Studies Board Division on Earth and Life Studies, National Research Council. http://www.nap.edu/catalog.php?record_id=12904
- Ocean Carbon and Biogeochemistry Program. 2009. [Responses to EPA Notice of Data Availability from Ocean Carbon and Biogeochemistry Program](#).
- OCB Subcommittee on Ocean Acidification (2009) *Ocean Acidification – Recommended Strategy for a U.S. National Research Program*, Ocean Carbon and Biogeochemistry Program, 14 pp.

- Olafsson J, Olafsdottir SR, Benoit-Cattin A, Danielsen M, Arnarson TS, Takahashi T (2009) Rate of Nordic Seas acidification from time series measurements. *Biogeosci Discussions* 6: 1-20
- Orr JC, Fabry VJ, Aumont O, Bopp L, Doney SC, Feely RA, Gnanadesikan A *et al.* (2005) Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. *Nature* 437:681–686
- Pane L, Feletti M, Francomacaro B, Mariottini GL (2004) Summer coastal zooplankton biomass and copepod community structure near the Italian Terra Nova Base (Terra Nova Bay, Ross Sea, Antarctica). *J Plankton Res* 26:1479–1488
- Pörtner, H.O. 2008. Ecosystem effects of ocean acidification in times of ocean warming: a physiologist's view. *Marine Ecology-Progress Series* 373:203-217.
- Ridgwell A, Schmidt DN (2010) Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release, *Nature Geoscience* DOI: 10.1038/NCEO755.
- Riebesell U, Fabry VJ, Gattuso J-P (2010) Guide to Best Practices in Ocean Acidification Research and Data Reporting, Report of international research workshop on best practices for ocean acidification research (19-21 November 2008 in Kiel, Germany)
- Salisbury J (2008) Coastal Acidification by Rivers: A Threat to Shellfish? *Eos* 89(50): 9
- Seidel MP, DeGrandpre MD, Dickson AG (2008). A sensor for *in situ* indicator-based measurements of seawater pH. *Mar Chem*109:18–28
- Steinacher M, Joos F, Folicher TL, Plattner GK, Doney SC (2009). Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model. *Biogeosciences*. 6(4):515-533.
- Tunnicliffe V, Davies KTA, Butterfield DA, Embley RW, Rose JM, Chadwick WW (2009). Survival of mussels in extremely acidic waters on a submarine volcano. *Nature Geoscience*. 2(5): 344:348.
- Wang ZA, Liu X, Byrne RH, Wanninkhof R (2007) Simultaneous Spectrophotometric Flow-Through Measurements of Multiple Inorganic Carbon Parameters in Seawater: At-sea Test and Comparison. *Analyt. Chimica Acta* 596:23-36
- Waldbusser GG, Voigt EP, Bergschneider H, Green MA, Newell RIE. (in press). Biocalcification in the Eastern Oyster (*Crassostrea virginica*) in relation to long-term trends in Chesapeake Bay pH. *Estuaries and Coasts*.
- Whitfield M, Butler RA, Coington AK (1985) The determination of pH in estuarine waters. I. Definition of pH scales and the selection of buffers. *Oceanol Acta* 8:423-432
- Zachos JC, Rohl U, Schellenberg SA, Sluijs A, Hodell DA, Kelly DC, Thomas E, Nicolo M, Raffi I, Lourens LJ, McCarren H, Kroon D (2005) Rapid acidification of the ocean during the Paleocene- Eocene thermal maximum. *Science* 308:1611-1615
- Zeevi-Ben-Yosef D, Benayahu Y (2008) Synergistic Effects of UVR and Temperature on the Survival of Azooxanthellate and Zooxanthellate Early Developmental Stages of Soft Corals. *Bull Mar Sci* 83(2):401-414