Report of the Ocean Acidification and Oxygen Working Group

SCOR Biological Observatories Workshop

Venice, September 2009.

BACKGROUND AND CONTEXT FOR OBSERVING APPROACHES RELATED TO THE GROUP'S TOPIC

The Keeling Curve (Fig. 1) illustrates a continuing rise in the amount of carbon dioxide (CO_2) in the atmosphere as humans use ever-larger quantities of coal, oil, and natural gas as energy sources. However the atmosphere is not the only sink for the CO_2 produced by burning these fuels: the oceans have taken up at least one third of the total amount of CO_2 produced by human activities since 1800 and one half of all fossil fuel emissions (Sabine et al., 2004). This addition of CO_2 to the surface ocean changes seawater chemistry, resulting in a decrease in pH (Fig. 2) and carbonate ion concentration, and an increase in the concentrations of bicarbonate and hydrogen ion – ocean acidification. The level of CO_2 in the atmosphere seems likely to double over its pre-industrial value by the middle of this century: in response the chemistry of the ocean is changing more rapidly than at any time in the past 20 million years (Feely et al., 2004). Indeed this process of ocean acidification has reduced the surface ocean pH by about 0.11 already (a change of about 30% in hydrogen ion concentration), and is expected to reduce pH by up to another 0.3 units this century if nothing is done to curb the release of CO_2 to the atmosphere from human activities (Orr et al., 2005).

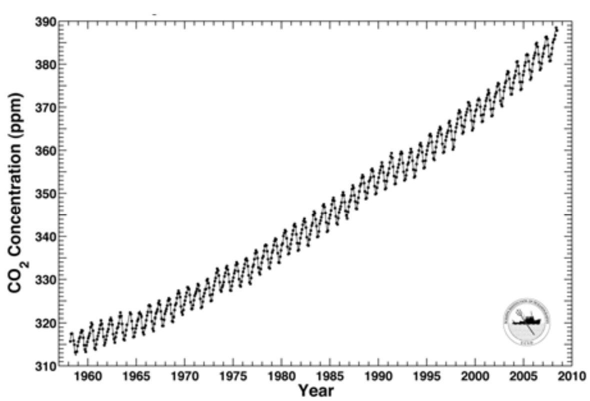


Fig. 1. Monthly average CO_2 concentration at the Mauna Loa Observatory, Hawaii (http://scrippsco2.ucsd.edu/home/).

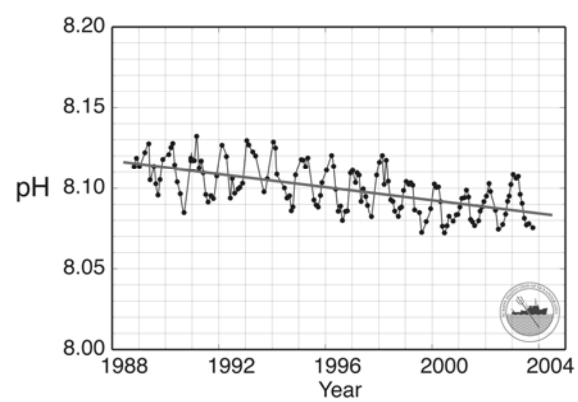


Fig. 2. Surface ocean pH at the Hawaii Ocean Time-Series site 100 km north of Oahu.

One consequence of this changing chemistry is a reduction in the saturation state of seawater with respect to calcite and aragonite: two common types of calcium carbonate formed by marine organisms. Evidence is now mounting that such changes in seawater chemistry can have consequences for a wide variety of marine organisms. Many calcifiers – including commercially important species such as oysters, mussels, and sea urchins as well as corals – exhibit reduced calcification rates in response to elevated CO_2 levels (Fabry et al., 2008). In contrast, growth rates of some seagrasses and nitrogen-fixing cyanobacteria appear to be enhanced by increased CO_2.

It has been suggested that organisms growing in waters along the west coast of the United States may already be experiencing large impacts as a result of the synergistic effects of coastal upwelling and ocean acidification (Feely et al., 2008). During upwelling along this coast, water with increased CO_2 levels (due to organic mineralization through respiration at depth) is brought onto the shelf and into the surface ocean. It appears that this water, in addition to its original high levels of CO_2 by virtue of its sub-surface source, is also enhanced with anthropogenic CO_2 as it was last in contact with the atmosphere only 50 years ago and thus has taken up additional CO_2 from the atmosphere. An immediate consequence of this is that the CO_2 concentration in upwelled water at any particular site will be greater, also the area of the coastal ocean that exceeds a particular threshold CO_2 value (or that is below a particular carbonate saturation state) will be greater, than it would have been in pre-industrial times. Furthermore, each year will draw on water that has been exposed to the atmosphere still more recently, resulting in yet higher CO_2 levels.

As a result, there is a potential for this enhanced level of acidification (especially when combined with the observed low O_2 levels found in the upwelled waters; Bograd et al., 2009) to exert impacts on organisms and their associated ecosystems both in the natural environment and in coastal mariculture facilities. However, as yet, little is known about this. Laboratory studies have been made on a variety of individual organisms at various stages in their life cycles, with many of these studies showing potentially problematic effects. However, almost nothing is known about these effects at a whole-of-ecosystem level or the ability of organisms to adapt to these changes (Fabry et al., 2008). Essentially we are embarking on a large-scale global experiment with – as yet – unknown consequences. There is some evidence for respiration stress caused by synergistic effects between O_2 and CO_2 (e.g. Brewer and Peltzer, 2009).

Oxygen is a limiting and fundamental requirement for all aerobic organisms living in the oceans as well as having a direct role in the biogeochemical cycling of carbon and nitrogen. At O_2 levels below ~60 µmol kg^{-1} (hypoxic conditions) most metazoans become severely stressed. Hypoxia triggers a range of sub-lethal effects and mortality of many species, especially in the benthos, and may create 'dead zones' depauperate in organisms and living marine resources. At levels below ~5 µmol kg^{-1} (suboxic conditions), nitrate becomes important in the respiration of the few organisms able to survive at these concentrations. When O_2 levels drop to zero, the water is termed 'anoxic', and biogeochemical processes are then dominated by sulfate-reducing microbes.

Anoxia is rare in the modern open ocean, but is important in some enclosed seas such as the Baltic. Hypoxic conditions occur, however, at mid depths (oxygen minimum zones, OMZs), over wide expanses of the North Pacific, in smaller regions of the north Indian Ocean, and in the eastern tropical Atlantic and Pacific Oceans. Suboxic conditions are restricted to more limited regions of the north Indian and eastern Pacific OMZs. There is evidence for an increase in the occurrence of hypoxic and suboxic conditions in coastal waters (Diaz and Rosenberg, 2008), where low subsurface O_2 levels can be generated by shoaling of the oxic/hypoxic boundary, natural high biological productivity in upper waters or by eutrophication from agricultural runoff or sewage inputs (Vaquer-Sunyer and Duarte, 2008).

There also exist numerous reports of decreasing oxygen levels in the open ocean. Thicker oxygen minimum zones (OMZs) will have an impact on the N cycle. Through both denitrification and nitrification processes, thicker OMZs will likely increase the flux from the ocean to the atmosphere of N_2O, a potent greenhouse gas. Low concentrations of oxygen also have adverse effects on marine life forms considered valuable by humans, ranging from reduced growth and reproductive capacity to habitat avoidance and ultimately death. The responses of benthic and pelagic animals in estuarine, semi-enclosed seas, and open shelves to hypoxia depend on the duration, repeatability, and intensity of oxygen depletion and on whether H_2S is formed. Tolerance to hypoxia and threshold values are species- and stage-specific and can vary enormously. While some fish species may suffer from oxygen values of less than 3 ml L^{-1} and show impact on growth, development and behaviour, other organisms such as euphausiids may survive DO levels as low as 0.1 ml L^{-1} (Vaquer-Sunyer and Duarte, 2008). In some eutrophic coastal systems, excess organic matter from primary production can overwhelm an ecosystem's assimilative capacity to the detriment of higher trophic levels and at the same time leading to increases in microbial activity (bacteria and archaea) that are well adapted to hypoxia or anoxia. Anoxic areas can conversely act as natural boundaries concentrating prey and limiting or changing trophic interactions which can lead to local areas of apparent high productivity (e.g. Wishner et al., 1995).

In addition to the increase in the temporal and spatial extent of hypoxic regions, changes in the oxygen saturation from fully saturated to under-saturated (for example 70% or 40%) can already have significant biological effects on growth and behaviour. The physiological, sub-lethal effects of adaptation to under-saturation, and the energetic cost of such adaptation, or alternatively of any migration to avoid affected areas, have to be considered at the level of species, population and ecosystem. In coastal and shelf sea areas, the occurrence of such oxygen depletion events is expected to increase as a consequence of climate change (Frölisher et al., 2009).

NEED FOR SYSTEMATIC LONG-TERM MEASUREMENTS OVER LARGE SCALES

Climate variability and change have coherent globally distributed impacts on marine ecosystems. Phenomena such as El Niño and El Viejo (Pacific Decadal Oscillation) influence the productivity and structure of marine ecosystems in some cases decreasing productivity (such as in the eastern Pacific and western Indian Ocean) and in others increasing productivity (western Pacific). The phenomena seem to occur in two unstable states (cold/warm, more productive/less productive). Duration (multi-decadal) has greater impact on the full ecosystem than intensity (El Niño). On glacial to interglacial scales, including the Little Ice Age, the globally cold/more productive eastern Pacific present day paradigm is different. A globally cool glacial condition seems to be associated with a warm, less productive eastern Pacific (and Atlantic). In addition rather dramatic changes have occurred over short (decadal) periods. Clearly there is significant uncertainty in predictions about how global change (specifically global warming) will impact eastern Pacific and other ecosystems. Although, individual regional research efforts exist and are valuable, if we are to fully determine impacts and potential feedbacks a globally integrated Ocean Biology Observatory is needed.

Laboratory and field data on individual species suggests there will be dramatic effects of acidification on ocean systems. Yet direct information about ecosystem-level effects of acidification are scarce, and the influence of pH on important ecological processes are hard to ascertain.

WHAT ARE THE PRIORITY OBSERVATIONS TO ADDRESS THIS ISSUE?

Ocean Acidification:

At present there are four parameters that can be reliably measured for the sea water carbon dioxide system (alkalinity, total inorganic carbon (TIC), pH, $p(CO_2)$), and one of these, pH, has multiple possible definitions which in turn can result in multiple values for acid-dissociation constants. It is possible to obtain a complete description of the acid-base composition of a seawater sample at a particular temperature and pressure provided the following is known:

- the salinity and temperature, and hence the solubility constant of carbon dioxide in the sea water as well as the equilibrium constant for each of the acid dissociation reactions that is assumed to exist in the solution,
- the total concentrations for each of these non-CO_2 acid-base systems,
- the values for at least two of the four CO_2-related parameters: A_T ,TIC , pH, $p(CO_2)$.

Although this is true for shipboard measurements, it is – as yet – not practical for autonomous measurement systems where – currently – systems only exist for $p(CO_2)$ and for pH. In certain regions it may also be practical to infer the total alkalinity of the sea water from measurements of temperature and salinity – provided that a well-tested calibration algorithm has been produced.

Oxygen:

The measurement of dissolved oxygen in seawater is now well-established and some oxygen sensors have now been deployed on Argo floats. The spatial coverage of the ocean needs to be expanded and equipping further Argo floats would be useful, even though there is a significant cost penalty. More measurements need to be made in existing areas of low oxygen (e.g. OMZs) to delineate any changes in spatial extent and to help define biotic responses.

Response of biota:

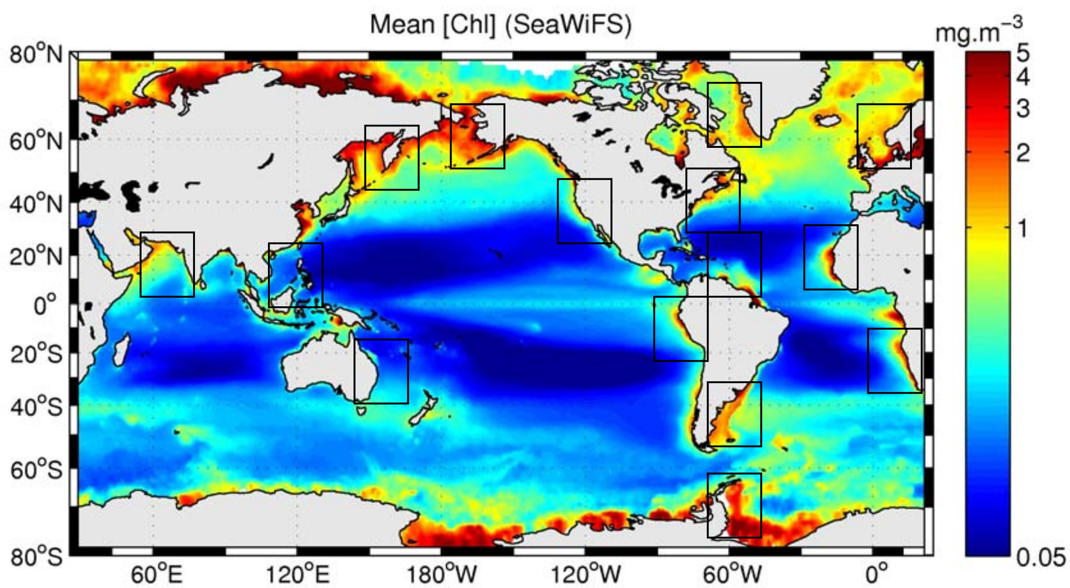
All biota are likely to be impacted by ocean acidification and reduced oxygen, but it is unclear at this time what groups in the biota from microbial community to the top predators including pelagic and benthic communities will be most affected. Therefore, key species representing each group from diverse ecosystems/biomes across the global ocean need to be observed. These should include examples of key species from individual ecosystems that drive the biogeochemical cycle in each region; for example, microbes, phytoplankton including cyanobacteria, zooplankton and benthos (calcifiers and non-calcifiers), nekton and marine mammals and birds. Measurements should include primary production, abundance and biomass, shifts in community structure and phenology, and levels of calcification. Along with these parameters, the microbial activity (production/oxygen consumption) needs to addressed. The challenge here is that the measurement of O_2 and pH are straight forward compared to the measurements needed to characterize biological changes. There is then further complexity in relating the observed changes to particular environmental effects, not just O_2 or pH.

WHERE SHOULD THE OBSERVATIONS BE MADE AND AT WHAT FREQUENCY AND DURATION?

There are differing observational needs for the open oceans and coastal areas and there are areas that are known to be high-risk / high-impact / high variability such as polar seas, coral reef systems, coastal upwelling zones, estuaries and enclosed seas. Open ocean strategies like those articulated in the OceanObs white papers by Gruber et al. (2009) for oxygen (on Argo floats) and Feely et al. (2009) for ocean acidification, that essentially leverage systems designed for physics, should be endorsed by the ocean biological observatory group. For coastal areas on the other hand there is no well developed global strategy even though there is significant work being done at regional and national level. There is a need for design and integration of a global coastal network of observations and data management and this may be one of the outcomes of the biological observatory group.

We advocate regional (large-scale, but potentially geographically limited) coverage for the coastal ocean/continental shelves, because interpretation of local changes in coastal systems requires a 3D context. A sensible approach may be to pick coastal regions that are known to be important from ecological or economic points of view, and pick representative cross-sections of different systems. We do not know the spatial and temporal de-correlation scales of oxygen or pH variability. Since pH seems to be well-correlated with O_2 and since O_2 is easier to measure than pH, one could possibly use O_2 to establish what the de-correlation scale for pH likely is. Ideally, the average distance separating various oxygen sensors should be commensurate with these de-correlation scales.

The sampling strategy at each location would include a few high resolution temporal (moorings), high precision measurements (ships), and slow spatially distributed (glider, tagged animals) sections. Ships of opportunity are equipped with underway sensors for T, S, p(CO_2), O_2, etc. The glider and tagged animal observations overlap with the open ocean Argo float coverage. Algorithms developed from the high resolution and precision measurements are used to estimate parameters from the few parameters that glider or tagged animal are able to measure. Models assimilating the full set of data provide high resolution 3D fields for biologists to interpret the impacts of the environment on ecosystem properties. The standardization of methods and measurements is key for the comparative exercise.



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- Fig. 3. The core of an observing strategy needs to include a broadly distributed set of regions over various latitudes, pH and oxygen. The boxes on this map are indicative only and the actual locations need further analysis.

Observational technologies now available and on the horizon, and gaps in available sensors to address the need

At this time, systems exist for autonomous measurement of p(CO_2). These take two forms: one based on equilibrating the water with a gas phase and measuring the CO_2 concentration in the gas phase using an infra-red technique (*e.g.*, the Seaology® Monitor of Battelle, Columbus Ohio, USA), the other is based on equilibrating the CO_2 through a membrane and measuring the resulting pH change in the solution (e.g., the SAMI instrument of Sunburst Sensors, Ltd., Missoula, Montana, USA).

pH can be measured using either a spectrophotometric approach (*e.g.* the SAMI-pH instrument) or a potentiometric approach (e.g., based on a Honeywell Durafet® as is being developed at the Monterey Bay Aquarium Research Institute, Moss Landing, California, USA). Although both systems show promise, additional work will be needed to provide high-quality stable calibrations over a range of temperature and pressure (such as might be experienced on a mooring or profiling float).

Unfortunately, using this pair of parameters is not ideal since both parameters are functions of temperature and pressure and they are significantly anti-correlated with each other. If one is to get a detailed picture of ocean acid-base chemistry, they need to be measured precisely with a low uncertainty, but to date such low uncertainties have not been demonstrated for oceanic pH measurements. Perhaps the ideal measurement pair would be pH and total inorganic carbon. At this time, work is progressing on developing an autonomous system for TIC (Sayles and Eck, 2009), but such an instrument is not yet commercially available.

ISSUES IDENTIFIED:

Any biological observatory needs to address the following questions / issues:

- How does ocean acidification and/or changing oxygen affect biological processes at species, population and ecosystem levels?
- Will acidification and/or reduced oxygen change biogeochemical cycling and impact ecosystem services and functions such as carbon cycles, the biological pump and the sequestration of CO_2?
- Are there areas that are particularly vulnerable or resilient and what rates of change can we expect?
- Which systems are able to adapt and which ones will not?
- What are the most appropriate ways to measure adaptation or change?
- Modelling needs to be an integrated part of the observatory with the data being used to inform and validate assimilation models and for the models to direct future observations.
- Any observatory must be able to measure the spatial and temporal extent of hypoxia and carbonate saturation.

SUMMARY:

1. There is a strong and demonstrable need to measure ocean chemistry on a regional and global scale, but we also need to measure the impact and response on biota. Part of any

design of an observing system needs to consider responses and adaptations at the level of organisms.

2. There are differing observational needs for the open oceans and coastal areas and there are areas that are known to be high-risk / high-impact / high variability such as polar seas, coral reef systems, coastal upwelling zones, estuaries and enclosed seas. Open ocean strategies like those articulated in the OceanObs white papers by Gruber et al. (2009) for oxygen (on Argo floats) and Feely et al. (2009) for ocean acidification, should be endorsed by the ocean biological observatory group. For coastal areas on the other hand there is no well developed global strategy even though there is significant research work being done at regional and national level. There is a need for the design and integration of a global coastal network of observations and data management and this may be one of the tasks of the biological observatory group.

3. A conceptual station design has been developed but this needs to be road tested with the other groups to ensure that a range of appropriate measurements are made at each location or set of locations (see Fig. 3).

4. There is currently no standard commercial off the shelf (COTS) set of sensors for alkalinity / pH / p(CO_2) and so work needs to be done on developing these to a point where they can be operationally deployed for reasonable deployment times (six months or more) and in a profiling mode. The work of this group may be in developing best practices with each of the main instruments and working with the manufacturer to refine and improve the instrumentation. The idea of using existing platforms, such as Argo, needs to be investigated.

5. Some areas are natural laboratories for acidification and so these could be good areas for experimental work and may produce experimental outcomes that may be more meaningful than smaller scale laboratory studies.

6. Data management and access is still a major, universal problem that needs to be addressed. One option is to put any observing system behind the IOC or equivalent (e.g. GOOS, Coastal GOOS, CoML) and leverage off their data management systems and framework as well as the inter-governmental arrangements in place for existing oceanographic work. We should aim for an international data centre that holds and gives access to ocean acidification data at a global level somewhat like Argo, but more collaborative so that in the future there are global centres responsible for particular variables or areas. Policies regarding data access and management need to be put in place that meets the needs of individual researchers and possible end users.

7. Any observation system needs to have a set of best practice methodologies and approaches including deployment, calibration, inter-calibration work, technology transfer and so on. These need to be applied to <u>all</u> deployed sensor systems and should be developed and propagated at the community level.

8. Any research on ocean acidification and O_2 will need to consider effects on both pelagic and benthic populations. These have traditionally been studied by different groups of scientists so appropriate research linkages will need to be put in place.

RECOMMENDATIONS:

- Our group supports the installation of O_2 sensors on the standard Argo float design and optimisation of this and other sensors into future designs;
- Development of a global strategy is needed for the implementation of long-term sustained O_2 and pH/p(CO_2) observatories in areas not covered by current proposals / projects together with articulation of possible outcomes from such a system and how an observatory would contribute to modelling work;
- A standard O_2 and pH/p(CO_2) sensor package needs to be developed together with best practices to support the collection of high quality data.
- Complimentary technologies including remote sensing (e.g. for coccolithophores and other algal blooms), continuous plankton recorder (CPR), biological indicators of acidification, and eco-genomics need to be developed to provide the suite of tools needed to characterize marine communities and their changes.
- Development of a number of O_2/pH/p(CO_2) reference stations is highly desirable. A suite of 10-12 global sites that are regularly maintained and calibrated along with a simpler down-scale set of observatories based on other platforms (e.g. gliders, existing moorings, modified Argo floats, ships of opportunity) is a minimum requirement.
- In relation to biological response a global system should be developed that takes note of the regions which are already, or are expected to be, most impacted. To resolve timing and community changes, sampling should be undertaken at least at monthly intervals at identified key locations over decadal periods to produce time series. Whenever possible biological sensors should be added to the autonomous platforms for continuous collection of data. These locations could be linked together with measurements from Argo floats, research cruises, ships/animals of opportunity and biological and instrumented sampling along Continuous Plankton Recorder routes. Particular attention needs to be paid to corals (reef and deep water) by interfacing studies on acidification with existing monitoring strategies. Benthic communities that are representative of estuarine, coastal and deep ocean conditions need to be monitored.

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Useful websites:

EPOCA 'Best practice in ocean acidification' http://www.epoca-project.eu.

NERC Ocean Acidification Project. http://www.nerc.ac.uk/research/themes/earthsystem/events/ocean-acidification.asp.

The Ocean Acidification Network. http://iodeweb3.vliz.be/oanet/Events.html

PANEL MEMBERS:

John Volkman – CSIRO Marine and Atmospheric Research, Australia (Panel Chair)

Scott Bainbridge – Australian Institute of Marine Science, Australia (Rapporteur)

Andrew Dickson – Scripps Institution of Oceanography, USA

Philip C. Reid – SAHFOS, United Kingdom

Denis Gilbert – Maurice-Lamontage Institute, Fisheries and Oceans Canada, Canada

Francisco Chavez – MBARI, USA

Haimanti Biswas – National Institute of Oceanography, India

Katja Fennel – Dalhousie University, Canada

Kelly Kryc – Moore Foundation, USA

Phillip Taylor - National Science Foundation, USA

Ralph Prien – Leibniz institute for Baltic Sea Research, Germany

Roberta Marinelli– Antarctic Sciences Division, National Science Foundation, USA

Silke Kröger – CEFAS, United Kingdom

Toshiro Siano – JAMSTEC, Japan