AN INTERNATIONAL OBSERVATIONAL NETWORK FOR OCEAN ACIDIFICATION

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ABSTRACT

An integrated international interdisciplinary program of ship-based hydrography, time-series moorings, floats and gliders with carbon system, pH and oxygen sensors, and ecological surveys is recommended to determine the large-scale changes in the properties of ocean water and the associated biological responses to ocean acidification. By carefully coordinating ocean acidification requirements with the future research plans of the ocean carbon and biological communities, and adding additional sensors and moorings where needed, many of the research requirements of the ocean-acidification community can be met for open-ocean regions. For coastal environments, a large network of new hydrographic and ecological surveys, moorings and floats will be required to provide a coastal observing system for ocean acidification. These activities will require a coordinated international research effort that is closely linked with other international carbon research programs, such as the CLIVAR/CO_2 Repeat Hydrography Program. Many of the data synthesis activities, data archiving and international data management activities could be shared between the carbon and ocean acidification programs. Presently, many countries are engaged in ocean acidification research and monitoring activities. For example, the European ocean acidification community has developed a major multi-nation program (EPOCA). The total cost of the present observational efforts for ocean acidification is estimated at about $10 Million US dollars per year. We estimate that the cost of an expanded international observational program as described below to be approximately $50 Million US dollars per year.

1. INTRODUCTION

Since the beginning of the industrial revolution the release of carbon dioxide (CO_2) from our industrial and agricultural activities has resulted in an increase in atmospheric CO_2 concentrations from approximately 280 to 391 parts per million (ppm). The atmospheric concentration of CO_2 is now higher than experienced on Earth for at least the last 800,000 years, and is expected to continue to rise at an increasing rate, leading to significant temperature increases in the atmosphere and the ocean surface in the coming decades. During this time, the ocean has absorbed nearly 500 billion tons of carbon dioxide from the atmosphere, or about one-third of anthropogenic carbon emissions. This absorption has benefited humankind by significantly reducing greenhouse gas levels in the atmosphere, thereby partly minimizing global warming. However, when the anthropogenic CO_2 is absorbed by seawater, chemical changes occur that increase the CO_2 partial pressure $p(CO_2)$ and reduce both seawater pH and the concentration of carbonate ion in a process commonly referred to as ocean acidification (Fig. 1). As a result, the pH of ocean surface waters has already decreased by about 0.1 unit since the beginning of the industrial revolution [1 and 2], with a decrease of ~0.0018 y^{-1} observed over the last quarter century at several open

ocean time-series sites [3, 4 and 5]. The gradual process of ocean acidification has long been recognized [6, 7, 8, 9 and 10] but the ecological implications of such chemical changes have only recently been examined. By the middle of this century atmospheric carbon dioxide levels could reach more than 500 ppm, and near the end of the century they could be over 780 ppm [11]. This would result in an additional decrease in surface water pH of approximately 0.3 pH unit by 2100, implying that the ocean would increase acidity by a factor of about 2.5 relative to the beginning of the industrial revolution.

The decline in the carbonate ion concentration as a consequence of ocean acidification is of particular concern with respect to many shell-forming marine organisms. Carbonate ion is a basic building block of skeletons and shells for a large number of marine organisms, including corals, shellfish, and marine plankton [12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32 and 33]. Some of the smaller calcifying plankton are important food sources for marine organisms at higher trophic levels. In addition, increased CO_2 and its concomitant changes in ocean chemistry may alter species composition and succession of primary producers and other microbes. Thus ocean acidification could have profound impacts on some of the most fundamental geochemical and biological processes of the sea in coming decades. A decline in coral reef accretion rates due to simultaneous increases in temperature and decreases in carbonate ion concentration [34] would have negative impacts on fisheries, tourism, coastal protection, and other fundamental biogeochemical processes. The abundance of commercially important shellfish species could also decline, and if the planktonic prey of larger fish were affected, this too would have serious consequences for marine food webs. Increased $p(CO_2)$ can also impact the physiology of marine biota through acid-base imbalance and reduced oxygen transport capacity [13 and 35]. On the other hand, not all biological impacts from rising atmospheric CO_2 are necessarily deleterious for a species. Nitrogen-fixation by *Trichodesmium*, for example, is enhanced by elevated CO_2 [36]. Growth and light-saturated photosynthetic rates of seagrasses are also increased under high CO_2 conditions [37 and 38]. There will likely be ecological "winners" as well as "losers" among taxa indigenous to specific regions as well as invasive species, but it is largely unknown how these changes will impact ecosystems and biogeochemical cycles. This rapidly emerging scientific issue has raised serious concerns across the scientific and fisheries resource management communities as to possible ecological and economic impacts [39 and 40].

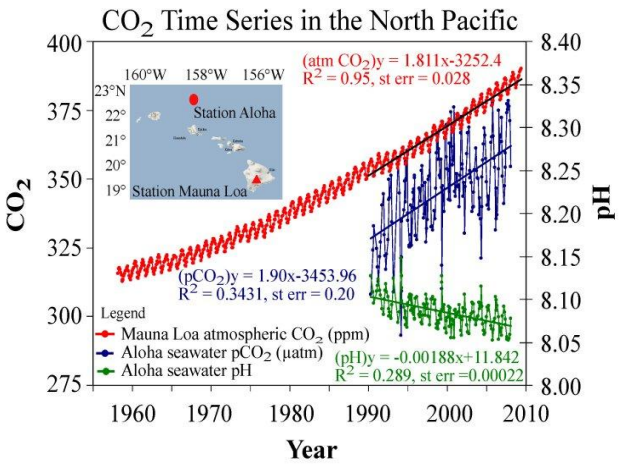

Figure 1. Time series of atmospheric CO_2 at Mauna Loa (in ppm; mole fraction in dry air) and surface ocean pH and p(CO_2) (µatm) at Ocean Station Aloha in the subtropical North Pacific Ocean. Note that the increase in oceanic CO_2 over the last 19 years is consistent with the atmospheric increase within the statistical limits of the measurements.

Mauna Loa data: Dr. Pieter Tans, NOAA/ESRL (http://www.esrl.noaa.gov/gmd/ccgg/trends);

HOTS/Aloha data: Dr. David Karl, University of Hawaii (http://hahana.soest.hawaii.edu) (modified after [41]).

A coordinated multidisciplinary approach to observations and modelling is key to achieving a successful research strategy for ocean acidification. This will facilitate the development of our capability to predict present and future responses of marine biota, ecosystem processes, and biogeochemistry [13]. Critical research elements require regional and global networks of observations and process studies, manipulative experiments involving a suite of organisms in laboratory experiments, mesocosm and field studies, technological advances, and new modelling approaches. One of the key questions regarding responses to ocean acidification is whether or not there are geochemical thresholds for ocean acidification (e.g., $CaCO_3$ mineral saturation state levels) that will lead to irreversible effects on species and ecosystems over the next few decades? Can we develop new biological methodologies to determine whether organisms and ecosystems can adapt sufficiently to changing seawater chemistry in ways that will reduce potential negative impacts of ocean acidification? Indices for ocean acidification beyond basic water-column physics and chemistry have yet to be adequately developed. Parameters that can be measured routinely onboard ships include temperature, salinity, oxygen, nutrients, CO_2 partial pressure [$p(CO_2)$], pH, total

alkalinity (A_T), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and particulate organic- and inorganic carbon (POC, PIC). While some of these chemical species can now be measured on moorings they are not yet broadly utilized on a global scale. Moreover, new method development is required for routine measurements of DIC and A_T and proxies that may indicate stress on biological organisms. 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.

2. SCIENTIFIC OBJECTIVES AND RATIONALE

The principal scientific objectives for a sustained ocean acidification observational network are to: 1) improve assessment of the oceanic and coastal ocean acidification that has transpired across the anthropocene, 2) establish critical base-lines necessary to track further acidification, 3) characterize natural variability of carbonate chemistry particularly in coastal ecosystems to serve as a prerequisite to appropriate threshold designation, 4) monitor and track continued ocean acidification in support of improved geochemical model development and validation, and 5) monitor and characterize ecosystem responses to ocean acidification. An observation program must be designed to integrate the new methodologies and approaches as they become available.

2.1 Understanding ocean carbonate chemistry changes and pH over time

Results from the global ocean CO_2 surveys over the past two decades have shown that ocean acidification is a predictable consequence of rising atmospheric CO_2. Seawater carbonate chemistry is governed by a series of chemical uptake, dissolution, speciation and precipitation reactions:

Air-sea exchange:

$$CO_{2\,(atmos)} \rightleftharpoons CO_{2\,(aq)} \qquad (1)$$

This exchange is relatively rapid (occurring within months) so that the increase in the $p(CO_2)$ of surface waters parallels the average change in atmospheric concentration.

Dissolution and Speciation:

$$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad (2)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (3)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (4)$$

these reactions are very rapid, and for most applications the partitioning of inorganic carbonate species can be assumed to be in equilibrium. For typical surface ocean conditions today (2009), about 90% of the total carbon dioxide is in the form of the bicarbonate anion (HCO_3^-) and ~9% as carbonate(CO_3^{2-}), with only ~1% remaining as undissociated $CO_{2(aq)}$ and H_2CO_3.

Calcification:

$$[Ca^{2+}] + [CO_3^{2-}] \rightleftharpoons CaCO_{3(s)} \qquad (5)$$

The saturation state of calcium carbonate is defined by $\Omega = [Ca^{2+}][CO_3^{2-}] / K'_{sp,}$ and differs for different mineral forms of the precipitating carbonate due to their differing solubility constants (K'_{sp}).

Photosynthesis $\rightleftharpoons$ Respiration (simplified):

$$CO_2 + H_2O \rightleftharpoons CH_2O + O_2 \qquad (6)$$

Reaction 1 occurs on time scales of months, while reactions 2 - 4 occur on time scales of 10s of seconds for hydration and microseconds for acid base chemistry. Since CO_2 is a weak acid, it reacts with seawater to form carbonic acid (H_2CO_3), a weak acid. Most of the H_2CO_3 dissociates to form a hydrogen ion (H^+) and a bicarbonate ion (HCO_3^-). A smaller portion of the H^+ reacts with carbonate ion (CO_3^{2-}) to produce HCO_3^- ion. As a result, CO_2 uptake by the ocean causes an increase in H^+ concentration and decreases pH and the CO_3^{2-} concentration. The decrease in CO_3^{2-} reduces the carbonate saturation state of calcium carbonate ($CaCO_3$), which directly affects the ability of some $CaCO_3$-secreting organisms to produce their shells or skeletons (Reaction 5). This is true even though most surface waters in the global ocean are currently super-saturated (e.g., Ω values of 2-4 for aragonite and 4-6 for calcite), because many organisms have optimal carbonate precipitation rates at these or higher saturation states. Photosynthesis by marine photosynthetic organisms to form plant matter (Reaction 6) consumes CO_2 and thus reduces the acidity of surface waters. It also produces a large fraction of the annual global supply of oxygen (and consumes other nutrients such as nitrate, phosphate, and iron, all of which can be limiting in different parts of the ocean). As this plant matter sinks into the subsurface layers of the ocean it is re-oxidized by respiration back to CO_2, thereby sequestering CO_2 from the atmosphere but also acidifying the deep sea. Reactions 5 and 6 dominate the natural cycles of carbon in the ocean and produce large gradients in CO_2, pH and carbonate ion concentrations.

These processes are well verified and can be seen in models, open-ocean hydrographic surveys, and time series data [3, 4, 2, 1, 42, 41, 14, 15, 11 and 44]. At the Hawaii Ocean Time-Series (HOT) station ALOHA the increases of surface water $p(CO_2)$ parallels that of atmospheric CO_2 (Fig. 1), indicating uptake of anthropogenic CO_2 as the major cause for long-term increases in dissolved inorganic carbon (DIC) and

decreases in $CaCO_3$ saturation state [45]. While ocean acidification is a global-scale phenomenon, there are areas that already experience low pH conditions naturally; e.g., modelling studies have suggested that the high latitude oceans (Arctic and Southern Oceans) will experience aragonite undersaturation by the middle of the century [46, 47 and 11]. Reference [48] argues that the surface Arctic will start experiencing localized aragonite undersaturation within the next decade. In fact a recent paper documents seasonal undersaturation already [49]. Figure 2 shows an example of moored observations of $p(CO_2)$ and pH in the subarctic Pacific. The wintertime pH values are significantly lower than in the subtropics, as the models predicted.

A recent study [41] presented new observations showing that organisms growing in coastal upwelling along the continental shelf of the west coast of the North America may already be experiencing significant biological effects resulting from the combined impacts of coastal upwelling and ocean acidification. Here the seasonal upwelling of subsurface waters along the coast brings CO_2-enriched waters onto the shelf and, in some instances, into the surface ocean. It appears that this water, in addition to its high level of natural CO_2 resulting from respiration processes in the subsurface layers, is also significantly enriched with anthropogenic CO_2 above what it would have been in pre-industrial times. Since these "acidified" upwelled waters are undersaturated with respect to aragonite they are already a potential threat to many of the calcifying aragonitic species that live in these coastal regions. Because seasonal upwelling is a common phenomenon in many coastal regions, this process may be affecting coastal ecosystems in other locations as well. Shoaling of undersaturated waters has been observed in the North Pacific [9], and the Chukchi Sea in the Arctic [50] where the biological pump enhances the seasonal undersaturation of carbonate minerals in subsurface waters.

2.2 Developing an Ocean Acidification Observational Network

The existing global oceanic carbon observatory network of repeat hydrographic surveys, time-series stations and volunteer observing ships in the Atlantic, Pacific and Indian Oceans can provide a strong foundation of observations of the carbonate chemistry needed to address the problem of ocean acidification. Indeed, much of our present understanding of the long-term changes in the carbonate system is derived from such repeat sections and time series measurements [3, 41 and 14]. Enhancing these activities and expanding the global time-series network with new carbon and pH sensors [51] will provide important information on the changing conditions in both open-ocean and coastal environments that are presently undersampled. At this time, most of the current moored carbon observatories only measure $p(CO_2)$, which is of itself unable to constrain the carbon system adequately for effective monitoring and for forecasting ocean acidification and the concomitant biological effects.

Ideally, this network would also have the capability to measure $CaCO_3$ saturation states and $CaCO_3$ production and dissolutions rates. Additional sensors for dissolved inorganic carbon and total alkalinity would also be beneficial for detecting changes in the marine inorganic carbon system as well as deposition of other non-CO_2 sources of acidification, particularly in coastal regions [52 and 53]. Measurements of net primary production, either directly or from nutrient or oxygen inventories, along with an understanding of water movements in coastal zones, are also important for identifying physical and biological modifications to ocean acidification.

Leveraging existing infrastructure and monitoring programs will enable research to be conducted efficiently and quickly. For example, additional inorganic carbon system measurements and process studies could be conducted at the OceanSITES time series stations [54] and at the Long-Term Ecological Research sites such as those in the California Current, Palmer West Peninsula Antarctica and at Moorea. Additional time series stations, repeat surveys and underway measurements [55 and 56] are also urgently needed in other open-ocean and coastal regions. Consequently, new moored buoys equipped with carbon system sensors and ancillary technologies (e.g. autonomous water samplers, nutrient analyzers) for ocean acidification should be added to the present carbon network. Sites which also deploy deep sediment traps offer additional advantages, in allowing the links between calcification and biological carbon to the deep sea to be evaluated [57], and by providing seasonally resolved sampling of biogenic carbonate-forming organisms, such as forams which have been shown to exhibit reduced shell thicknesses in response to acidification [58].

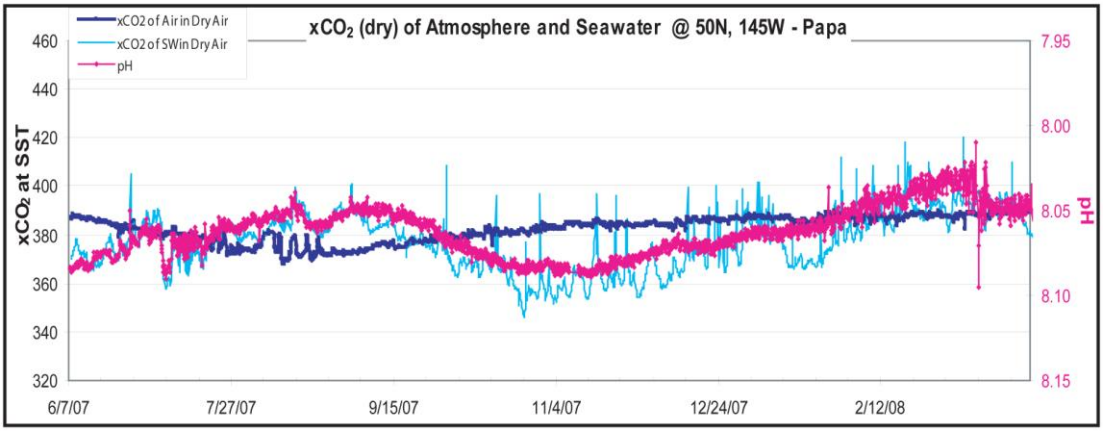

Figure 2: Time Series of p(CO_2) and pH measurements from a mooring located at Ocean Station PAPA in the subarctic North Pacific (data from Chris Sabine, NOAA/PMEL).

2.3 Measurement requirements for the Ocean Acidification Observational Network

2.3.1 DIC, $p(CO_2)$, A_T and pH

On surface ship oceanographic cruises, such as the CLIVAR/CO_2 Repeat Hydrography Program cruises (see [78]), DIC, $p(CO_2)$, A_T and pH can be measured with very high accuracy and precision [59, and references therein]. The methods are well established and described in great detail in the "Guide to Best Practices for Ocean CO_2 Measurements" [60]. In addition, appropriate reference materials are available for DIC, A_T and $p(CO_2)$. 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. International data synthesis efforts, such as those being carried out as part CLIVAR/CO_2 Repeat Hydrography Program, must be continued to ensure the precision and accuracy required to determine the anthropogenic CO_2 contributions to ocean acidification. Documentation of the equations used [61] and dissociation constants used to calculate [CO_3^{2-}] and carbonate saturation states (Ω) should always be detailed.

Emerging Issues and implications for sampling: For other platforms, including moorings and floats, commercially-available systems are also available for $p(CO_2)$ and pH (see http://www.ioccp.org/ for a list of available sensors). However, the combination of $p(CO_2)$ and pH sensors does not allow for the most accurate measurement of $CaCO_3$ saturation state and some of these systems are not well suited for sustained deployments especially in coastal environments. Consequently, there is an immediate need to improve upon existing technologies and to develop autonomous sensors for DIC and A_T for moorings and floats.

2.3.2 Particulate Inorganic Carbon (PIC), Particulate Organic Carbon (POC) and Bio-Optical Measurements

A full evaluation of the response of ocean ecosystems to ocean acidification will require a wide range of measurements of existing and evolving community compositions, interactions, and distributions, and experimental studies of the responses of organisms and communities to elevated CO_2. Here we emphasize PIC and POC because they can be measured accurately, play important roles in assessing the overall impact of ocean production on atmospheric CO_2, and offer the possibility of being measured at large scales using both satellite and in-situ sensors. New procedures have recently been developed for obtaining information on the distributions of PIC and POC from bio-optical sensors that have been calibrated against the 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 [64]. Similarly, [65] 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 (Fig. 3). 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

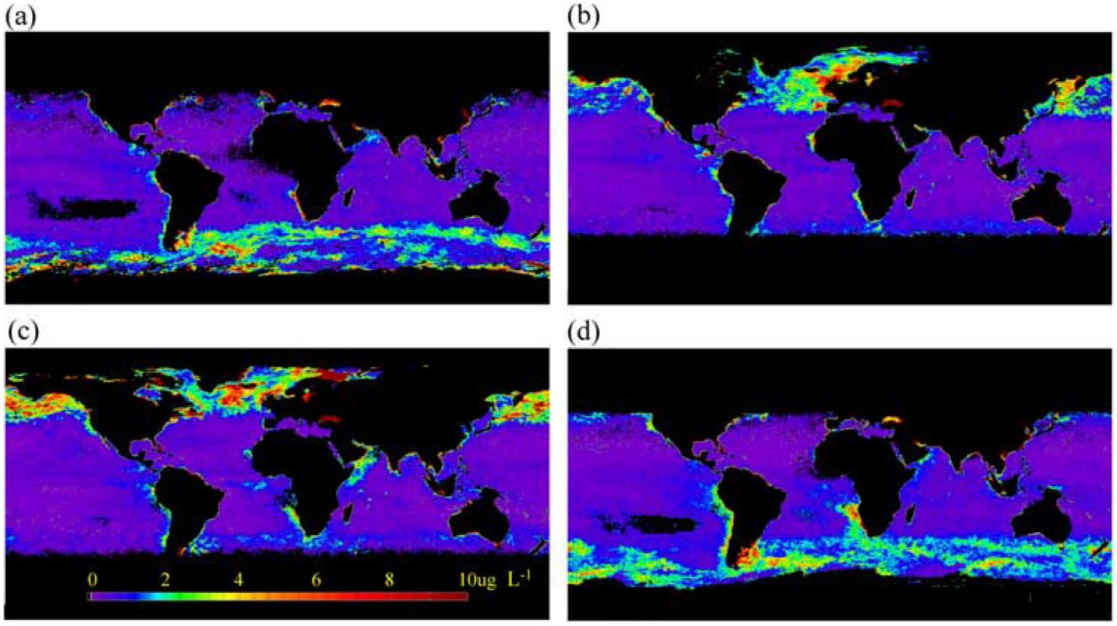

Figure 3. Global composite images of suspended PIC concentration calculated from MODIS/ Terra data using a two-band calcite algorithm. The color scale is highlighted in Fig. 3c. These data were binned into 36 km^2 and 90 day averages, and thus the standard error will be <0.08 mg PIC L^{-1}, well below the average seawater concentration of 2 mg PIC L^{-1}; (a) January–March. (b) April–June. (c) July–September. (d) October–December (after Balch et al., 2007).

coccolithophores (phytoplankton) and foraminifera (zooplankton) via size fractionation [66].

2.3.3 Oxygen

As noted above, biologically driven uptake of CO_2 is intimately linked to oxygen production, so that monitoring oxygen assists in assessing both the processes that move CO_2 into the ocean and the response of the ocean to acidification. In this regard, it is possible that the combined impacts of increased stratification due to global warming and changes in ocean biology caused by increased CO_2 and decreased pH, could cause a decline in oceanic oxygen concentrations [57]. These changes have significant implications for organisms because they will enhance the potential for expanded respiratory stress near oxygen minimum zones in open oceans and also in hypoxic regions in coastal zones [67]. Consequently, oxygen levels should be routinely measured along with the carbon system parameters. In coastal regions, the interaction of low pH waters from upwelling regions with hypoxic waters will cause the water to have lower pH and lower saturation state. Thus, coastal regions will be impacted by a combination of stressors that possibly could magnify biological impacts. Furthermore, in coral reef systems $p(CO_2)$ is elevated as a function of both respiration and calcification. It is necessary to ensure that we incorporate oxygen measurements if we are to assess the relative effects of ocean acidification on the metabolic performance of coral reefs.

Emerging issues and implications for sampling: The oceanographic community should strive to integrate existing and new sensors onto autonomous platforms (e.g., floats, gliders, etc).

2.3.4 Other Biological Measurements

In addition to the seawater carbonate chemistry measurements of the proposed Ocean Acidification Observational Network, it is essential to establish a corresponding observational network to monitor and assess ecological impacts of ocean acidification in oceanic, coastal, and insular marine ecosystems around the globe. Most importantly, this biological observing system should be designed to cost-effectively and efficiently assess changes in calcification rates across taxa and in biodiversity, abundance, and distributions of marine organisms across ecosystems. Such biological measurements should have concurrent measurements of seawater CO_2 chemistry.

In key regions such as the high latitudes, abundances and vertical distributions of calcifying planktonic organisms should be tracked at spatial and temporal scales that enable the detection of possible shifts and allow us to distinguish between natural variability and anthropogenic-driven changes. Rapid, high throughput

methods to identify marine organisms include optical plankton imaging systems [68]. Such systems can be deployed on drifting, towed or moored platforms. Optical plankton samplers should be benchmarked carefully with quantitative plankton tows. The occurrence of functional groups in surface waters has been tracked by repeated Longhurst-Hardy Continuous Plankton Recorder surveys over the past 60 years and should be continued. The use of specific DNA sequences for marine bar-coding would be valuable in coastal areas and regions projected to become undersaturated with respect to aragonite in the coming decades (e.g., Southern Ocean, Arctic Ocean, subarctic Pacific) to monitor changes in biodiversity, either from the loss of species of the addition of invasive species. At selected regions, rates of calcification and other physiological processes known to be strongly impacted by high CO_2 should be measured. In a carefully selected subset of coral reefs, high-resolution surveys of species abundances, reef calcification, and photosynthesis should be conducted.

In the case of coral reefs, adequate methods exist for measuring calcification and extension rates from cores of massive reef-building scleractinian corals. These methods need to be applied systematically to both older massive corals and younger branching and encrusting corals broadly distributed across gradients of aragonite saturation state. In addition, a global array of simple calcification plates (or similar devices) should be deployed to monitor the calcification rates of sessile calcareous organisms, such as crustose coralline algae, a major reef builder that often acts as the cement holding reefs together. As one example of a tool to assess spatial patterns and to monitor temporal shifts in biodiversity, the Census of Marine Life Coral Reef Ecosystems project developed Autonomous Reef Monitoring Structures (ARMS) as systematic collecting devices, and continues to develop mass parallel molecular sequencing capabilities to allow comparative and time series analyses of indices of invertebrate biodiversity of hard-bottom habitats around the globe [69]. Similar systematic collecting devices should be employed to assess biodiversity changes in soft-bottom and planktonic communities. Other cost effective tools for monitoring biological shifts in community structure include passive acoustic Ecological Acoustic Recorders EARs) [70, 71, and 72].

It has already been well established that rates of calcification at the scale of whole coral reef communities are sensitive to changes in ambient aragonite state of saturation and temperature and that rates of $CaCO_3$ dissolution impact their $CaCO_3$ budget significantly [73, 34 and 74]. Thus, in concert with assessing the community structure of both shallow and deepwater corals, it is equally important to make measurements of community calcification and dissolution to establish a baseline for these important environmental indicators as well as to demonstrate the effects of acidification in situ and in real time using relatively simple and non-destructive methods. Changes in the phototrophic/heterotrophic balance of coral reef ecosystems can also be discerned by monitoring variations in the photosynthesis to respiration ratio, which can be observed using continuous dissolved oxygen measurements [74].

Emerging issues and implications for sampling: For critical regions such as the high latitudes and coastal areas, abundances and distributions of key taxa should be tracked with sufficient precision and resolution to detect possible shifts corresponding to observed changes in the geochemical parameters. There is an immediate need for such baseline data on calcifying organisms in regions that are projected to become undersaturated with respect to aragonite in the coming decades. Rapid, cost-effective technologies for quantifying abundances of targeted organisms should be a central component of any integrated ocean acidification observation network.

2.4 Evaluating Ocean Acidification Models

Ocean general circulation models (OGCMs) that include biogeochemical parameterizations have been used to assess the past, present and future state of ocean acidification [1, 2, 11, 46 and 47]. Because they were established as coarse-resolution models, the present models have only been applied to open-ocean conditions. Nevertheless, the models have been useful for identifying regions of high vulnerability to ocean acidification in the future, such as the Southern Ocean and the subarctic Pacific [11]. The data from repeat hydrographic surveys and time-series measurements of the ocean acidification observational network will provide an excellent means of testing and evaluating model outputs.

Emerging issues and implications for sampling: For coastal environments, several existing higher-resolution models could be modified to include carbon system dynamics and water-sediment interactions and then used to predict local to regional impacts of ocean acidification. An example of such a model is the Regional Ocean Model System [75 and 76]. Furthermore, to address ocean acidification impacts on organisms the models will need to be enhanced to include responses and feedbacks between lower- and higher trophic levels of the marine food web and implications for ecosystem function. An integrated approach employing both a detailed observational network together with high-resolution physical-biogeochemical-ecosystem models is required for coastal regions.

3. STRATEGY FOR AN OBSERVATIONAL NETWORK FOR OCEAN ACIDIFICATION

3.1 Repeat Surveys of Chemical and Biological Properties

In developing an observational network for ocean acidification most of the same sampling principles and strategies that are being developed for open-ocean and coastal carbon [55] apply here as well. For example, the decadal surveys are extremely useful for determining basin scale changes in the aragonite and calcite saturation states over timescales of 10-15 years. The sampling plans for the next phase of the CLIVAR/CO_2 Repeat Hydrography Program could effectively provide the required information. Figure 4 shows the repeat sections we believe to be most critical for the decadal survey (solid) and for the high frequency repeat lines (dashed). Spatial sampling should continue to repeat the transect lines carried out in the Atlantic, Pacific, and Indian Oceans, with the Southern Ocean integrated as part of the other basins. The Arctic is of increasing importance and should be emphasized, adding new transects where appropriate. We recommend adding additional chemical and biological measurements to the repeat surveys to address ocean acidification issues, such as highly-resolved depth distributions and abundances of calcifying plankton, estimates of calcification rates, $CaCO_3$ dissolution rates and other CO_2-sensitive processes as appropriate.

For the coastal environment, a similar sampling strategy to that outlined for the coastal carbon measurements [55] is recommended for the ocean acidification coastal network. Underway sampling on research vessels and VOS ships should include the additional pH and carbon parameters necessary to address ocean acidification [56]. These data will help to establish large-scale trends in acidification in much the same way [77] have established basin-scale trends in $p(CO_2)$.

3.2 Time-Series Measurements on Floats and Gliders and at Fixed Stations

Carbon and pH sensors on moving platforms such as Argo-type systems or gliders could resolve shorter space-time scale variability of the upper ocean than is possible from repeat sections, but that technology must be developed and tested in the field before it can be implemented on a large scale. Time-series measurements on fixed moorings appear to be a reasonable alternative for more limited time-space variability studies. These studies could be conducted at the OceanSITES time-series stations [54] and at the Long-Term Ecological Research sites such as those in the California Current, near Palmer West Peninsula Antarctica and at Moorea. Time-series stations are also urgently needed in other open-ocean and coastal regions. Consequently, new moored buoys equipped with carbon system sensors for ocean acidification should be added to the present carbon network. Bio-optical sensors and optical plankton imaging systems should be deployed to track possible shifts in abundances of key functional groups. When automated, in situ samplers for DNA bar-coding are available, we recommend that they be used at time series stations.

Seasonal measurements of calcification rates and other CO_2-sensitive processes not currently measured at time series sites should be conducted in order to assess the long term response of ecosystems to ocean acidification. Figure 5 and Tabs. 1 and 2 provide our recommended distribution of time-series sites based on the national plans for ocean acidification research and discussions of what is needed by the Ocean Acidification Working Group. The coral reef monitoring sites have a unique label in Fig. 5 to help distinguish them from the open-ocean and coastal time-series sites. By integrating these ocean acidification activities with the various international ocean carbon programs much of the work can be carried out without duplication of effort. As soon as carbon and pH sensors on floats and gliders are fully tested and deemed ready for large-scale deployment we recommend their implementation into the next phase of the Argo Program. Sites of potential ocean acidification vulnerabilities are indicated by ovals in Fig. 5. The entire Arctic Ocean and Southern Oceans are also likely to experience aragonite undersaturation in the near future. These regions of vulnerabilities are shown for planning future ocean acidification time-series measurements.

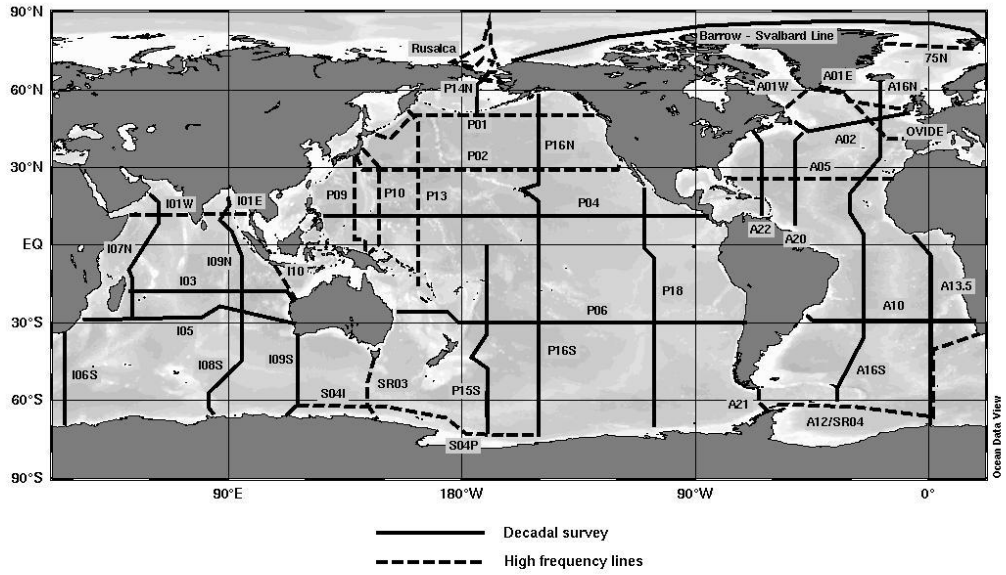

Figure 4. Planned repeat hydrography surveys and high-frequency lines for carbon and ocean acidification measurements. We recommend full water column measurements of at least 3 carbon parameters on each of the transect lines.

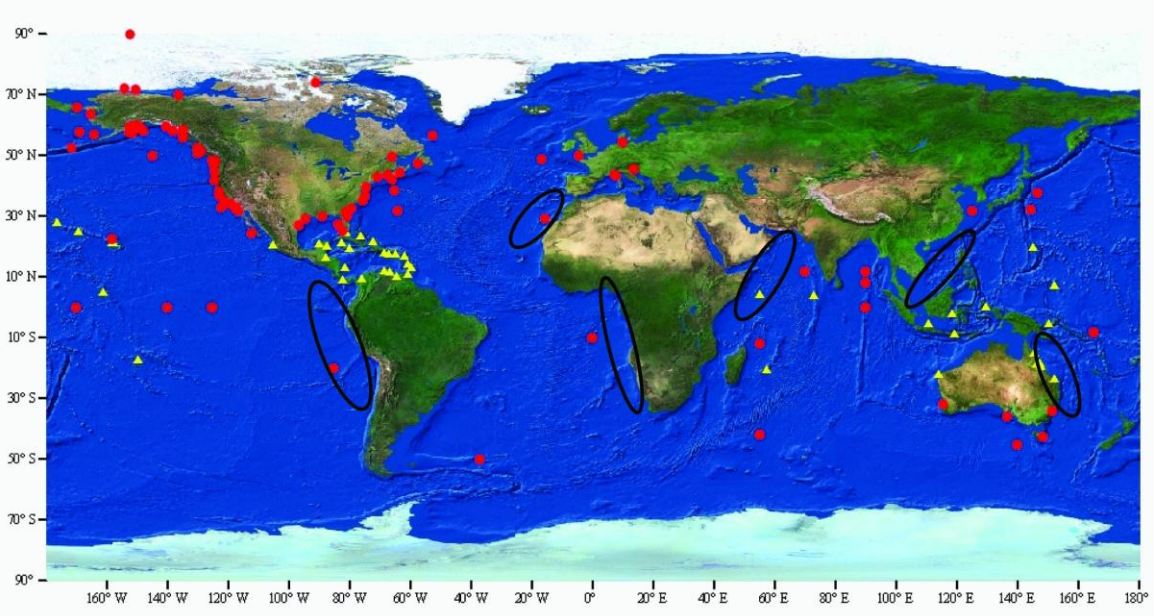

Figure 5. Potential ocean acidification monitoring sites in open-ocean and coastal regions, and potential coral reef ocean acidification monitoring sites. The station locations are given in Tables 1 and 2. Red circles represent deployed or planned open-ocean monitoring sites; yellow triangles represent deployed or planned coral reef monitoring sites. Future sites likely to experience aragonite undersaturation in the near future are indicated by ovals.

Longitude	Latitude	Site Name	Country	Deployed*	Mooring Project
-125.00	0.00	125W, 0	Pacific - equator	Dep	NDBC TAO
-140.00	0.00	140W, 0	Pacific - equator	Dep	NDBC TAO
-170.00	0.00	170W, 0	Pacific - equator	Dep	NDBC TAO
-117.20	33.10	Agua Hedionda	USA - Pacific	P	COAST
-171.45	52.43	Amukta Pass 1	USA - Gulf of Alaska	P	PMEL/OSU, NOAA OA Monitoring Moorings
55.00	-42.00	ARC	South Indian	P	NOAA OA Monitoring Moorings
-112.16	24.56	Bahia Magdalena	Mexico - Pacific	Dep	UABC/CICESE/CICIMAR
-134.64	56.24	Baranof Island	USA - Gulf of Alaska	P	PMEL/NURP
-154.00	72.22	Barrow Canyon	USA - Chukchi Sea	P	PMEL/UAF
-91.03	74.08	Barrow Strait	Canada - Arctic	Dep	DFO-BIO
-150.08	71.65	Beaufort Sea	USA - Beaufort Sea	P	PMEL/UAF
-169.33	65.88	Bering Strait	Arctic	P	PMEL/UW, NOAA OA Monitoring Moorings
-88.77	30.09	Biloxi	USA - Gulf of Mexico	Dep	PMEL/USM, NOAA OA Monitoring Moorings
-123.02	38.27	Bodega Bay	USA - Pacific	Dep	UC Davis
54.52	10.03	Boknis Eck Time Series Station	Baltic Sea	Dep	IFM-GEOMAR
-52.48	56.67	Bravo mooring	Canada - Labrador Sea	P	DFO-BIO
-64.20	31.70	BTM	Bermuda - Atlantic	Dep	MOSEAN - Bermuda Testbed Mooring, NOAA OA Monitoring Mooring
-124.75	47.34	Cape Elizabeth (NDBC 46041)	USA - Pacific	Dep	PMEL/OSU, NOAA OA Monitoring Moorings
-75.40	35.01	Cape Hatteras	Atlantic	P	NOAA OA Monitoring Moorings
-117.47	32.74	Carlsbad	USA - Pacific	P	CSUSM
-122.00	33.00	CCE1	USA - Pacific	R 2/22/2009	PMEL/Scripps, NOAA OA Monitoring Moorings
-74.84	36.61	Chesapeake Bay	Atlantic	P	NOAA OA Monitoring Moorings
-151.44	57.52	Chiniak Bay 3	USA - Gulf of Alaska	P	PMEL/OSU
-134.67	55.91	Coronation Island	USA - Gulf of Alaska	P	PMEL/OSU
-96.70	26.97	Corpus Christi, Texas	Gulf of Mexico	P	NOAA OA Monitoring Moorings
165.00	-8.00	CSIRO	Pacific - South	P	CSIRO/PMEL
-4.33	50.04	E1	Atlantic - NW European Shelf	P	Western Channel Observatory
-116.72	31.82	Ensenada	Mexico - Pacific	Dep	UABC/Cicese
-15.50	29.18	ESTOC	Canary Islands - Atlantic	Dep	ESTOC, NOAA OA Monitoring Moorings
-82.22	25.25	Everglades National Park, FL	USA - Gulf of Mexico	P	NOAA OA Monitoring Moorings
-37.00	-50.00	Falklands	South Atlantic	P	NOAA OA Monitoring Moorings
-147.67	58.28	FATE-1	USA - Gulf of Alaska	P	PMEL/OSU, NOAA OA Monitoring Moorings
-125.27	48.55	Folger Passage	Canada - Pacific	P	IOS
-94.41	29.23	Galveston, Texas	USA - Gulf of Mexico	P	NOAA OA Monitoring Moorings
-67.5	43.75	GNATS	USA - Gulf of Maine	P	Bigelow/NASA
-65.9	42.33	GoMoos	USA - Atlantic	Dep	UNH/UMontana/GoMOOS
-80.87	31.40	Gray's Reef (NDBC 41008)	USA - Atlantic	Dep	PMEL/UGA, NOAA OA Monitoring Moorings
-149.47	59.85	Gulf of Alaska 1	USA - Gulf of Alaska	P	PMEL/UAF
-148.22	58.54	Gulf of Alaska 2	USA - Gulf of Alaska	P	PMEL/UAF
-70.75	43.08	Gulf of Maine	USA - Atlantic	Dep	PMEL/UNH, NOAA OA Monitoring Moorings
-65.00	38.50	Gulf Stream	North Atlantic	P	NOAA OA Monitoring Moorings
-63.251	44.296	Halifax Harbour	Canada - Atlantic	Dep	Dalhousie U
125.00	32.00	Iedo	Korea - Pacific	P	KORDI Korea Ocean Research Development Inst.
146.60	37.90	JKEO	Japan - Sea of Japan	R 3/24/2008	JAMSTEC - Japanese Kuroshio Extension Observatory
-152.18	59.53	Kachemak Bay, Alaska	USA - Gulf of Alaska	P	
136.45	-35.83	Kangaroo Is	Australia - southern	P	CSIRO/PMEL
-151.52	59.47	Kasitsna Bay	USA - Gulf of Alaska	P	PMEL/NURP
144.50	32.30	KEO	Japan - Sea of Japan	Dep	PMEL Kuroshio Extension Observatory mooring, NOAA OA Monitoring Moorings
-140.29	59.41	Khantaak Island	USA - Gulf of Alaska	P	PMEL/OSU
-152.39	57.79	Kodiak	USA - Gulf of Alaska	P	PMEL/NURP
-134.77	58.39	Lena Point	USA - Gulf of Alaska	P	PMEL/NURP
-74.25	39.47	LEO-15	Atlantic	P	NOAA OA Monitoring Moorings
-122.39	36.70	M1/M2	USA - Pacific	Dep	MBARI
-164.05	56.87	M2	USA - Bering Sea	Dep	PMEL, NOAA OA Monitoring Moorings
-168.87	57.85	M4	USA - Bering Sea	Dep	PMEL
-136.11	69.94	Mackenzie mouth	Canada - Arctic	P	UNH?/DFO?
148.23	-42.65	Maria Is	Australia - eastern	P	CSIRO/PMEL
-158.10	22.70	MOSEAN	USA - Pacific	R 7/31/2007	HALE-ALOHA mooring at Hawaii Ocean Time station
-152.00	89.85	North Pole	USA - Central Arctic	P	PMEL/UAF
-122.83	37.76	off San Francisco Bay	Pacific	P	NOAA OA Monitoring Moorings
13.57	45.62	PALOMA	Europe - Mediterranean	Dep	VECTOR
-144.80	50.10	PAPA	USA - Pacific	Dep	NOAA OA Monitoring Moorings
0.00	-10.00	Pirata 5	South Atlantic	P	NOAA OA Monitoring Moorings
-120.70	34.40	Point Conception	USA - Pacific	P	PMEL/CSUSM, NOAA OA Monitoring Moorings
-16.50	49.00	Porcupine	North Atlantic	P	NOAA OA Monitoring Moorings
151.25	-34.08	Port Hacking	Australia - eastern	P	CSIRO/PMEL
70.00	12.00	RAMA - Arabian	North Indian	P	NOAA OA Monitoring Moorings
90.00	12.00	RAMA - Bengal	North Indian	P	NOAA OA Monitoring Moorings
90.00	0.00	RAMA - Equator	Equatorial Indian	P	NOAA OA Monitoring Moorings
115.42	-32	Rottnest Is	Australia - western	P	CSIRO/PMEL
13.55	45.55	Slovenia-Gulf of Trieste	Mediterranean	Dep	MBS/NIB - VIDA
140.00	-45.00	SOFS	South Indian	P	NOAA OA Monitoring Moorings
-79.10	32.501	South Atlantic Bight (NDBC 410	USA - Atlantic	P	UGA

Table 1. Planned or Deployed Open Ocean and Coastal Ocean Acidification Monitoring Sites

* Dep: Deployed; P: Potential Site; R (date): Recovered Date

Longitude	Latitude	Site Name	Country	Deployed*	Mooring Project
-87.30	20.41	Akumal	Mexico - Caribbean	P	Centro Ecological Akumal
-157.80	21.30	Alawai	USA - Pacific	Dep	UH - Coral Reef Instrumented Monitoring Platform
-66.78	11.86	Archipelago Los Roques	Venezuela - Caribbean	P	Fundation Los Roques
-90.03	21.17	Arrecife Alacranes	Mexico - Caribbean	P	UNAM
-80.06	19.70	Bloody Bay Marine Park	Little Cayman - Caribbean	P	Little Cayman Research Center
-82.10	9.33	Bocos del Toro	Panama - Caribbean	P	Smithsonian
-68.29	12.16	Bonaire NMP	Bonaire - Caribbean	P	Bonaire National Marine Park
-60.83	11.18	Buccoo Marine Park	Tobago - Caribbean	P	USGS
152.00	7.50	Chuuk State	Micronesia - Pacific	P	KORDI Korea Ocean Research Development Inst.
-157.80	21.40	CRIMP	USA - Pacific	Dep	UH - Coral Reef Instrumented Monitoring Platform
-68.63	18.17	Del Este; Punta Cana	Santo Domingo	P	NCORE
118.30	-2.00	Derawan	Indonesia - Pacific		
-81.10	24.62	Dry Tortugas	USA - Gulf of Mexico	P	USGS
-67.05	17.94	Enrique	USA/Puerto Rico - Caribbean	Dep	UPR
-59.65	13.19	Folkstone Marine Reserve	Barbados - Caribbean	P	UWI
-87.78	16.83	Glovers Reef	Belize - Caribbean	P	Wildlife Conservation Society
152.00	-23.50	Heron Island	Australia - Southern GBR	P	CSIRO/UQ/PMEL
-82.65	21.50	Isle of Pines	Cuba - Caribbean	P	Inst. Invest.Ocean.
110.50	-5.08	Karimunjawa Islands	Java Sea	P	Center for Marine Studies, University of Queensland
-157.90	21.30	Kilo Nalu	USA - Pacific	Dep	UH - Coral Reef Instrumented Monitoring Platform
150.09	-5.33	Kimbe Bay	Pacific - Coral Triangle	P	NOAA Coral Reef Conservation Program
119.30	-8.38	Komodo Island	Pacific - Coral Triangle	P	NOAA Coral Reef Conservation Program
-76.14	23.79	Lee Stocking Island	Bahamas - Caribbean	P	Perry Institute for Marine Science
145.27	-14.69	Lizard Island	Australia - Great Barrier Reef	P	CSIRO/PMEL
73.00	4.00	Maldives	Maldives - Indian	P	NOAA Coral Reef Conservation Program
-169.00	25.00	Maro Reef	USA - Hawaii	P	NOAA Coral Reef Conservation Program
145.23	20.01	Maug Islands	Marianas Trench	P	Marianas Trench Marine National Monument
57.43	-20.20	Mauritius	Mauritius - Indian	P	NOAA Coral Reef Conservation Program
-64.48	10.31	Mochima	Venezuela - Caribbean	P	Univ. Oriente
-149.50	-17.00	Moorea	Moorea - Pacific	P	NSF LTER
147.20	-18.20	Myrmidon Reef	Australia - Central outer GBR	P	Center for Marine Studies, University of Queensland
-61.74	17.16	North Sound	Antigua - Caribbean	P	UM/TAMU
146.30	-18.40	Orpheus Island	Australia - Central Inner GBR	P	Center for Marine Studies, University of Queensland
-161.00	5.00	Palmyra Atoll	USA - Pacific	P	NOAA Coral Reef Conservation Program
-176.00	28.00	Pearl Reef	USA - Hawaii	P	NOAA Coral Reef Conservation Program
-105.23	20.62	Puerto Vallarta	Mexico - Pacific	P	UABC/Cicese/UAG
129.35	0.33	Raja Ampat	Pacific - Coral Triangle	P	NOAA Coral Reef Conservation Program
-64.76	17.78	Salt River Canyon (NPS)	St. Croix - Caribbean	P	UVI
-75.87	9.79	San Bernado	Colombia	P	Invesmart
-81.34	13.37	Seaflower Biosphere Reserve	Colombia - Caribbean	P	Coralina (NGO)
55.30	4.40	Seychelle Islands	Seychelles - Indian	P	NOAA Coral Reef Conservation Program
-60.83	14.42	South Island area	Martinique - Caribbean	P	IFREMER/IRD
113.94	-21.89	Ningaloo	Australia	P	western CSIRO
147.62	-19.31	Yongala	Australia	P	eastern CSIRO/PMEL/AIMS
-72.02	21.96	Three Mary Cays	Turks and Caicos - Caribbean	P	Turks and Caicos School for Field Studies

Table 2. Planned or Deployed Coral Reef Ocean Acidification Monitoring Sites

*Dep: Deployed; P: Potential Site

4. DATA MANAGEMENT, SHARING, AND PRODUCT DEVELOPMENT

4.1 Data Management

The strategy proposed for data management for ocean acidification studies is to provide the additional data and information to the existing data assembly and archive centers, to develop new tools and indices for addressing ocean acidification issues, to coordinate data management activities with those of the operational programs such as CLIVAR/CO_2, Argo and OceanSITES, and to improve the technology to release data in a more timely manner. It is also proposed to develop a single international ocean acidification information center that will serve as a central communication and coordination forum and directory to the data assembly centers. Several data centers currently provide data management services for particular types of hydrography data and biogeochemical data. We recommend establishing some of these centers as archives for ocean acidification data.

- **Ocean Acidification**

  European Project on Ocean Acidification (EPOCA)
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- **Biogeochemical Measurements**

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  Email: cchandler@whoi.edu
  Website: http://bco-dmo.org/

- **CTD and bottle data**

  CLIVAR and Carbon Hydrographic Data Office
  Principal Contact: Jim Swift, Director
  Email: jswift@ucsd.edu
  Website: http://cchdo.ucsd.edu/index.html

- **Oceanic Carbon Data from Discrete Samples**

  Carbon Dioxide Information Analysis Center - Ocean CO_2 (World Data Center for Atmospheric Trace Gases)
  Principle Contact: Alex Kozyr
  Email: ako@ornl.gov
  Website:
  http://cdiac.esd.ornl.gov/oceans/home.html

- **Oceanic Carbon Data from Underway Measurement Systems**

  Carbon Dioxide Information Analysis Center - Ocean CO_2 (World Data Center for Atmospheric Trace Gases)
  Principle Contact: Alex Kozyr
  Email: ako@ornl.gov
  Website:
  http://cdiac.esd.ornl.gov/oceans/global_pco2.html

4.2 Data Products and Joint Synthesis Activities

The Ocean Acidification Observation Network will need to continually provide data products, indices, publications, and data synthesis activities and products. Data synthesis activities should include standardizing and merging of basin and global scale data sets, synthesis with data from other platforms and model outputs, and integrated synthesis reports. The synthesis process should include: science and technical workshops; product development workshops; and international synthesis meetings. An international program on ocean acidification would provide the necessary framework for producing coordinated global basinwide, and regional scale data products and synthesis reports on a regular basis and provide the right forum to provide integrated synthesis products to resource managers and policymakers.

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