OS15D-12

Free Ocean Carbon Dioxide Enrichment (FOCE): Control and Measurement of Ocean Seawater to Simulate a Low pH-High CO_2 Ocean

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ABSTRACT

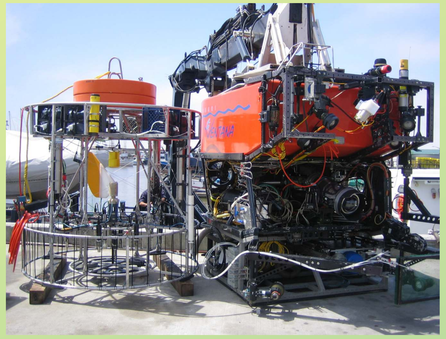
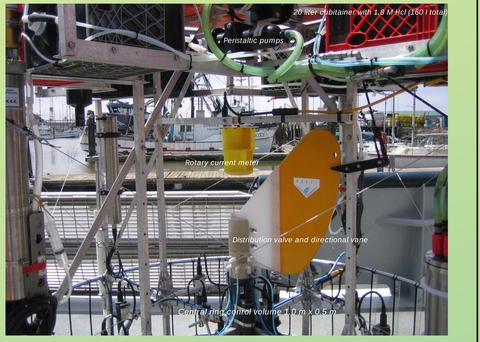
Scientists and Engineers at the Monterey Bay Aquarium Research Institute (MBARI) have undertaken a series of small-scale in-situ CO_2 enrichment experiments in order to simulate the present and predicted future effects of fossil fuel CO_2 emissions on ocean pH. In excess of 25 gigatons CO_2 are added to the atmosphere each year and the ocean has been the primary sink of these emissions. Presently, the ocean is absorbing on average 1 million tons of fossil fuel CO_2 per hour. The result of this process has been a lowering of the surface ocean pH by approximately 0.1 units during the past 100 years. Recent geochemical models project an additional drop of 0.2 units by the middle of this century.

The FOCE prototype was designed to create a controlled lowered pH condition for a freely exchanging volume of seawater 0.5 meters high by 1.0 meters diameter. A current meter and pH probes in the center of this volume provide the control feedback for driving the system to a desired pH set point (0.1 to 0.3 pH units below ambient seawater pH). The prototype system used a rotating mechanical vane and valve with eight ports, each port delivering acidified seawater to emitters that covered 1/8th the circumference of the 2-meter diameter framework. The directional valve delivered acidified seawater primarily to the upstream side of the FOCE structure. A second-generation FOCE system will use a current meter, directional resolver and electronic operation of up to 16 solenoid valves, allowing for significantly improved directional control at low flow conditions (< 10 cm/sec). For the two sea trials conducted with the FOCE prototype system, HCl was used to lower the pH of the seawater. We have now begun to envision a FOCE design that would use liquid CO_2 to change the local pH chemistry. A near shore cabled observatory could provide the power, communications, and a supply of piped CO_2 necessary for long term (weeks-months) observation and control of depressed pH levels in an ocean environment.

BACKGROUND

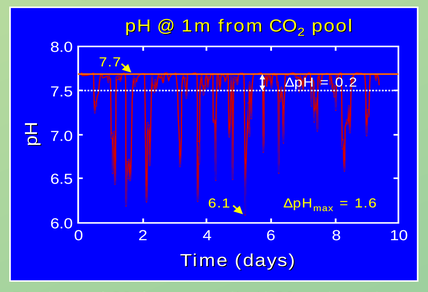
Terrestrial FACE (Free Air Carbon Dioxide Enrichment) experiments have been implemented for long term studies and are considered a worthwhile multi-discipline approach to global CO_2 research. Presently there are only a few oceanic facilities that have attempted to examine the hypercampic changes that global ocean ecosystems are expected to experience in the coming decades, and none have employed the FACE approach. Over the past two years, MBARI has used their extensive background in CO_2 research to develop a prototype oceanic system based on the scientifically accepted concepts of the terrestrial FACE experiments. Our initial effort has led to two deployments of a small system that allows real time feedback and modulation of pH in a small control volume. Our first deployment was in November 2004 at a depth of 250 meters while the second deployment was in July 2005 at a depth of 500 meters. These sites were located within the Monterey Bay National Marine Sanctuary. Once we had obtained the required permits from both MBNMS and NOAA, the prototype system imitated projected pH changes due to CO_2 using a low concentration mixture of HCl released into the ocean environment. These small scale experiments will likely become more common as scientists develop new research strategies for assessing the impact of higher CO_2 levels and lower pH conditions in the ocean.

Recent images from the benthic ecosystem near Davidson Seamount. Corals and sessile benthic communities are particularly sensitive to pH and climate fluctuations and have been considered the "canary in a coal mine" indicators as we begin to assess the impacts of a changing ocean chemistry.

ROV Ventana and FOCE system prior to deployment. Once on the sea floor the ROV and FOCE frame are connected via an underwater mateable connector (15 meter orange cable at left side of picture). This allows for real time power and data communications necessary to control the pH altering fluid. Blue dye was added to the acid solution to enhance visual detection of the plume and was contained in eight 20 gallon cubitainers. This was then plumbed to the central valve for distribution to the upstream side of the frame. Data from three pH probes at the center of the 1.0 m x 0.5 meter control volume was fed into our control algorithm (below left).

Above is a 20 minute frame grab from our control software GUI (Lab View). The plot shows all three pH probes (green, red, white) and the average pH value (blue) which was used to control the feedback loop once every second. The pH within our control area successfully oscillated around our chosen set point (0.1 pH units below ambient).



Dissolution of CO_2 from an open liquid CO_2 pool perturbs the nearby pH field in a highly irregular and uncontrolled manner. Short duration (tidal cycle) spikes in pH are up to 8 times larger than the 0.2-0.3 pH unit decreases predicted later this century.

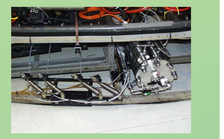
Photo from test tank trials conducted prior to FOCE field deployment. Dye was used to visually check on the performance of both the mechanical valve/vane assembly and the fluid emitters located around the perimeter of the frame. Quarter inch soaker hose was proven to work well as it created a diffuse cloud and minimized back pressure on our fluid delivery system.

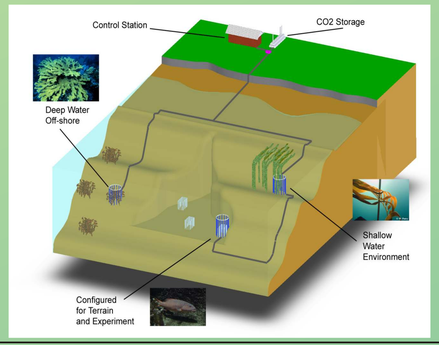
To compensate for the slow reaction time of CO_2 in seawater future FOCE designs will have to increase the emitter to control zone distance and also moderate bottom current speeds to match residence time to chemical equilibration times.

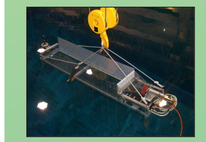
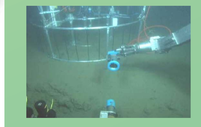
FUTURE OBJECTIVES FOR FOCE

Based on our initial successes of the two field deployments we are moving ahead with further refinements to the prototype FOCE system to achieve better operational methods and pH control. The original mechanical valve for fluid release will be replaced with individual solenoids for each section of the FOCE frame. This approach will insure proper section management for pH control along with closed sections able to be verified as closed. The mechanical valve demonstrated that we can perform the function of proper distribution of fluid without use of power if a particular deployment configuration requires that condition. We did experience some leakage from the valve and some acid bypass to additional (non-upstream) sections of the frame, which indicates the mechanical design and/or tolerances need to be improved.

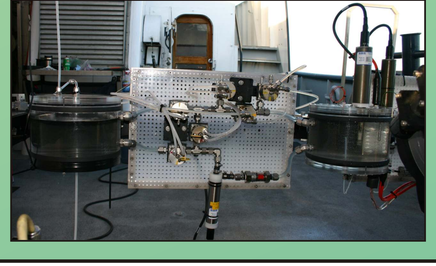
Further efforts include development of flow restriction panels, baffles or shutters. The implementation of these systems will allow more time for pH altering fluid (HCl or CO_2) to achieve equilibrium with surrounding seawater before entering our pH control area while keeping the hardware footprint as small as possible. Also being considered is a combination of active and passive controls that would allow adequate mixing through the system. These concepts are intended to maximize the operational zones of FOCE while minimizing physical disruption to the biological community within the region being studied.





MBARI has developed a variety of unique tools and techniques for handling CO_2 in the deep sea. Recent work has demonstrated we can create CO_2 rich fluids by pumping seawater thru chambers partially filled with liquid CO_2. Similarly, large reservoirs of CO_2 rich fluids to maintain a lowered pH field within a FOCE array could be formed by showering seawater through a CO_2 gas-space volume. We are now actively pursuing such designs for larger scale pH modification systems.



CO_2 hydration and kinetic disequilibrium: *In situ* effects of adding either HCl or CO_2 to seawater have been studied this past year (see poster OS45B-20). Reaction rates have been found to be on the order of minutes before steady state pH is achieved. Rates are dependent upon both temperature, pressure and pH.

Mathematical equations from Zeebe and Wolf-Gladrow (2001) for calculating reaction rates:

$$\frac{1}{\tau} = k_{+1} - k_{-1}(\partial_s b[H^+] + \partial_s h[HCO_3^-] - k_{-4}\partial_s b + k_{-4}([OH^-] + \partial_s oh[CO_2]$$

ACKNOWLEDGMENTS

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