

Coastal Ocean Acidification and Carbon Cycling due to Geochemical and Biological Processes: Development of a Novel High-Resolution O₂ / H⁺ Eddy Correlation Technique

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The research developed a new and novel instrument (the Eddy Covariance Hydrogen ion and Oxygen Exchange System, ECHOES) that measures the exchange of metabolically important constituents between the ocean and organisms living on and within the seafloor. Oxygen is used as a tracer of benthic photosynthesis and respiration, providing the net metabolism of the benthic community. The pH is a net measure of the metabolism by benthic communities as well as the net rates of calcification and dissolution. Comparing these two flux rates (oxygen and pH, or the hydrogen ion (H⁺) concentration) and complementary measurements of the carbonate equilibria in seawater allows for the determination of the net ecosystem metabolism and the net ecosystem calcification.

The instrument relies on the vertical transport of dissolved chemicals that is mediated by ocean currents and their interactions with the bottom, or the turbulent vertical transport. The vertical water velocities were measured using Doppler principles and are combined with high frequency measurements of both oxygen and pH. One of the greatest challenges with this work was to develop sensors that can measure very quickly (up to ~ 50 times per second) and to do so with a very high precision. To achieve this we adapted fast oxygen (O₂) optodes and developed a new micro-flow cell H⁺ ion selective field effect transistor; these sensors displayed sufficient precision and rapid enough response times to measure concentration changes associated with turbulent exchange.

The ECHOES system was deployed in a eutrophic estuary (Waquoit Bay, Massachusetts, USA), and revealed that the benthos was a sink for acidity during the day and a source of acidity during the night. The individual H⁺ and O₂ fluxes were highly correlated and yielded H⁺ fluxes that could not be explained by O₂ metabolism alone, suggesting there are additional sources of acidity that influence coastal pH.

This new tool will be highly valuable for the evaluation of the health and status of coastal waters, which provide significant resources, shoreline protection, fisheries, and tourism for a large portion of the human population. The development of better tools for evaluating these systems will have an impact on the general environmental sustainability and management of these important coastal ecosystems. It is expected that this new instrument will be fundamental in the

analysis of carbon cycling, ecosystem metabolism, and calcification, especially in complex environments such as coral reefs and seagrass meadows.

The ECHOES system provides a new tool for determining the influence of benthic biogeochemical cycling on coastal ocean acidification and carbon cycling. The system will also have direct applications in carbonate-dominated ecosystems where the H^+ exchange rates can be used to determine rates of dissolution and calcification. Thus, in the future we plan to use this instrument to advance what is known about coastal carbon cycling and ocean acidification, particularly in relation to the primary production (e.g. algae, seagrasses) and calcification (e.g. corals, shellfish).

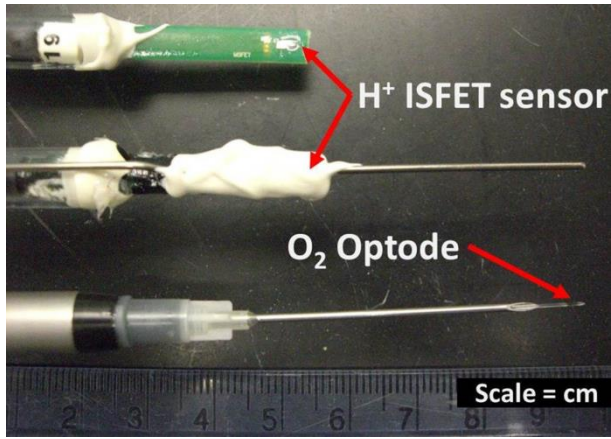
The first co-measured fluxes of O_2 and H^+ were presented at the international Ocean Science Meeting, along with many others presentations, and a manuscript validating the ECHOES was recently published:

Long MH, Charette MA, Martin WR, McCorkle DC. (2015) Oxygen metabolism and pH in coastal ecosystems: Eddy Covariance Hydrogen ion and Oxygen Exchange System (ECHOES). *Limnology and Oceanography: Methods*. DOI: 10.1002/lom3.10038

Link: <http://onlinelibrary.wiley.com/doi/10.1002/lom3.10038/full>



M. Long deploying the ECHOES system in the Waquoit Bay, Massachusetts.



The pH ISFET sensor, flow-through pH ISFET sensor, and O₂ optode (left). Initial ECHOES prototype being tested in Waquoit Bay, MA (right).