Carbon Cycling in Carbonate-Dominated Benthic Ecosystems: Eddy Covariance Hydrogen Ion and Oxygen Fluxes

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Study site and methods description

Background - The basis for the EC technique is that turbulent mixing, caused by the interaction of current velocity with the benthic, atmospheric, sea-ice, or cline interfaces, is the dominant vertical transport process in boundary layers. Therefore, vertical fluxes across the ecosystem interfaces can be derived from high-resolution measurements of the vertical velocity and a solute concentration. The time-averaged EC flux across an interface are determined by:

$$Flux \ = \overline{w'c'} \ + \int_0^h \frac{dc}{dt} \ dz \qquad \textit{Eq. 1}$$

where the overbar represents a time average, and w' and c' are the fluctuating components of the vertical velocity and scalar concentration (c), respectively. The second term is the flux caused by changes in the storage between the interface and the measurement location, represented by *dz* (Lorrai et al. 2010, Rheuban et al 2014, Long and Nicholson 2018).

Field Sites – The field sites were located ~7 km offshore of Key Largo, Florida, USA at the southern tip of Florida in the Florida Keys. The sites were located on or adjacent to Little Grecian Rocks Reef with a site on the reef crest (25.119016°N, -80.300504°W, Figure 1c) at 2.9 m mean depth, in a seagrass bed located ~225 m to the northwest of the reef site (25.120328°N, -80.302222°W, Figure 1b) at 4.8 m mean depth, and in a sandy site located ~300 m to the southwest of the reef site (25.117320°N, -80.303069°W, Figure 1a) at 6.3 m mean depth. The reef site is described in substantial detail (3-dimensional and species analyses) in Hopkinson et al. (2020), where the EC instrument can be seen near the center of the image analyses (in Figure 6 of Hopkinson et al. 2020) during its deployment in this study. This reef site is substantially degraded with its benthic surface and primary production dominated by octocorals, algae and rubble (Hopkinson et al. 2020). The seagrass site was dominated by dense *Thalassia testudinum* (turtlegrass) with a canopy height of 0.2 m underlain by carbonate sands. The sandy site was composed of carbonate sands with microalgal mats (Figure 1a) and migrating bedforms 0.1 m in height. Research was conducted from June 24 to June 29 in 2018 with the seagrass deployment beginning on the 24th and the sand and reef deployment beginning on the 25th of June, 2018.

Instrumentation – The EC systems used here, known as Eddy Covariance Hydrogen Ion and Oxygen Exchanged System (ECHOES, Long et al. 2015a) consisted of an Acoustic Doppler Velocimeter (ADV, Nortek) that was coupled to a FirestingO_2 Mini fiber-optic O_2 meter with a fast-response (~ 0.3 s) 430 µm diameter optode (Pyroscience) (Long et al. 2015a, Long and Nicholson 2018, Long et al. 2019) and a fast-response (~0.6 s, Figure S1) Honeywell Durafet® III pH sensor with a preamp Cap Adapter and a custom isolation amplifier (based on Texas Instruments ISO124P). The ECHOES systems logged the three-dimensional velocity, depth, O_2 optode, pH sensor, and triaxial Inertial Measurement Unit (IMU, MicroStrain model 3DM-GX3) at a frequency of 32 Hz continuously. Using 6 rechargeable lithium ion batteries (50 Watt h, Nortek #220007) the system could operate continuously for ~4.5 days. All instrumentation was mounted to a light-weight, passively rotating carbon fiber frame (Figure 1). A bubble level affixed to the ADV mount allowed for precise leveling during field deployment by SCUBA divers. Stakes (sand

and seagrass sites) or lead weights and zip ties (reef site) maintained instrument location and orientation. The measurement height, or location of the ADV measuring volume and sensors, above the sediment surface was determined by placing it at a height that was greater than twice the canopy or bedform height (Figure 1) as recommended by terrestrial EC guidelines where twice the canopy height, and up to 5 times the canopy height in patchy environments, is recommended (Burba and Anderson 2010, Long et al. 2015b).

The microfluidic flow-through sensor design has a small volume (0.33 cm^3) and a KNF Micropump (model NF10) with a flow rate (100 mL min^{-1}) that combine to have a quick flush rate (5 Hz) while protecting and preventing light interference for both O_2 and pH sensors. The microfluidic intake was located 0.025 m behind the ADV measuring volume (see Donis et al. 2015, Berg et al. 2015) to prevent disruption of ADV-measured flow rates (Long et al. 2015a). The microfluidic housing mounted tightly over the Durafet III sensor tip and has a small chamber for inserting the O_2 optode, that is located at the end of a 0.04 m long, 0.003 m inside diameter copper intake tube and filter, with the outlet of the microfluidic chamber connected to the pump intake (Figure S2). A passive flow meter (0-100 ml min^{-1}) connected to the pump outlet was used to confirm pumping rates during deployment.

A separate frame at each site contained an Odyssey (Dataflow Systems, New Zealand) photosynthetically active radiation (PAR) sensor and a Seabird SeapHOx (measuring salinity, temperature, depth, O_2, and pH). The SeapHOx was factory calibrated and the Odyssey PAR sensors were calibrated to a HR-4 spectroradiometer system (HOBI Labs HydroRAD-4) using the methods of Long et al. (2012b).

Eddy Covariance Analysis – The 32 Hz data were averaged to 8 Hz for analysis. The ECHOES O_2 and pH sensors were calibrated to the slow-response SeapHOx sensors by least-squares regression. The ADV velocity data was removed from analysis when the beam correlation was < 50%. The means for Reynolds decomposition were determined using a 5 minute moving average window. The period over which the flux was determined, or burst length, was 15 minutes, with subsequent averaging to hourly rates. Rotations were conducted automatically by Nortek software (Vector v1.39.09) to East, North, and Up coordinates based on the IMU data (see Long and Nicholson 2018) followed by a planar rotation (see Lorke et al. 2013) for each instrument deployment. Standard eddy covariance analysis was conducted to calculate O_2 $\overline{(w'O_2')}$, H^+ $\overline{(w'H^{+\prime})}$, and momentum $\left(\overline{(w'u')^2} + \overline{(w'v')^2}\right)^{1/2}$ fluxes (e.g. Eq. 1) where u and v indicate the horizontal components of the velocity and w represents the vertical velocity. Cross Power Spectral Densities were also used to calculate O_2, H^+ and momentum fluxes and were determined with the Matlab function "CPSD", with the removal of wave frequencies conducted by accumulating the CPSD at frequencies below approximately $1/(2T_d)$. A storage correction was applied to all biogeochemical fluxes due to the presence of biological canopies and the high measuring heights used (Eq. 1, Lorrai et al. 2010, Rheuban et al 2014, Long and Nicholson 2018). Power spectral densities were determined using the Matlab function "PWELCH". The T_d was determined by finding the maximum of the momentum CPSD at the frequencies where the waves were expected for the study sites (e.g. 0.1 > Hz < 1). Wave velocities were determined by:

$$wave\ velocity = \left(\overline{(u' - \bar{u})^2} + \overline{(v' - \bar{v})^2} + \overline{(w' - w)^2}\right)^{1/2} \qquad \text{Eq. 4}$$

where the prime indicates the instantaneous velocity and the overbars indicate averaging over each burst.

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