

# O<sub>2</sub>-MAVS: an Instrument for Measuring Oxygen Flux

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**Abstract** - With the awareness that the surface ocean is becoming more acidic due to the uptake of anthropogenic CO<sub>2</sub> and that the resulting decrease in carbonate ion concentration is contributing to a decline in the calcification rate of many organisms, there is a pressing need to develop methods that can easily and reliably measure the calcification rates of these organisms under natural conditions so that any changes that may be occurring can be detected. Recent advances in control volume [1] and benthic boundary layer eddy correlation methods [2, 3] promise to make continuous non-invasive measurements of net oxygen community production and respiration a reality. These methods, however, cannot be extended to the measurement of calcification rate because no suitable sensor for the measurement of total alkalinity (TA) exists at the present time. We have a solution that is based on measuring the vertical gradients in current velocity and the chemical constituent of interest in the boundary layer. The vertical gradient in velocity gives us  $K_z$  and  $K_z$  times  $\delta C/\delta z$  gives us the flux of constituent C into or out of the seafloor. The method can be applied to the measurement of calcification but could also be applied to the measurement of the flux of any chemical or biological constituent that can be determined from a water sample, in this case O<sub>2</sub>. Water samples could be collected with an automated water sampler preferably slowly over the period of an hour so that high frequency variability that cannot be sampled would be averaged out. Here we present preliminary data using an Acoustic Doppler Velocimeter (ADV), Modular Acoustic Velocity Sensor (MAVS) and two Aanderaa oxygen optodes. Three test deployments were made on shallow, warm-water coral reefs in La Parguera, Puerto Rico. Time series of net production obtained using the boundary layer gradient flux method (GF) were compared with measurements based on the Eulerian upstream-downstream flow respirometry method and a 1-D water column mass balance method with air-sea gas exchange. The agreement between methods was very encouraging, thus validating the O<sub>2</sub>-MAVS as an instrument capable of measuring oxygen flux.

## I. INTRODUCTION

Measurement of the rates of photosynthesis, respiration and calcification are fundamental to the understanding of coral reef ecosystems. The balance between photosynthesis and respiration tells us if the ecosystem is producing more organic matter than is required for daily maintenance, i.e. is it able to support some level of export production. Typically on a healthy reef nutrient fluxes limit net ecosystem production to a small positive number in the range of 0-50 mmol C m<sup>-2</sup> d<sup>-1</sup>. Equally important is the net ecosystem rate of calcification. If

this number is positive then the reef is accreting calcium carbonate. This means that corals and calcareous algae are producing CaCO<sub>3</sub> faster than the natural physical and bio-erosive processes are removing it and the reef is capable of keeping up with sea level rise. Rates of net calcification range from 20 mmol CaCO<sub>3</sub> m<sup>-2</sup> d<sup>-1</sup> in lagoon and back reef environments, to 100 in shallow reef flats, and to 300 in highly energetic fore reef environments [4, 5].

Historically measurements of carbon cycling on coral reefs have been made employing the flow respirometry method whereby a parcel of water is followed as it flows over a portion of a reef and the changes in oxygen and/or carbonate parameters are measured to determine the flux of carbon into and out of the organic matter and calcium carbonate pools. Variations of the method include Eulerian approaches and stagnant water approaches. All of these methods had the drawback of being very labor intensive. It was necessary to repeat the measurements at different times of the day and night. Often it took days to weeks to accumulate enough data to compile a single diurnal curve that could then be integrated to yield the desired 24-h cumulative rate of net community production or calcification. Further complication is introduced by measuring over several hundred meters to a kilometer in order to accurately resolve the change in total alkalinity (TA) and by natural variations in the current direction from day to day, making it difficult to obtain measurements over the same part of the reef from day to day.

Gattuso et al. [6, 7] introduced the innovation of fitting the net production (np) and calcification rate data to light response functions. Non-linear regression was used to determine the best-fit parameter values for the functions. The functions were integrated numerically over the period of interest using instantaneous incident irradiance data that had been collected nearby. While this technique made it much easier to obtain the desired daily rates it invokes the assumption that light alone is sufficient to accurately predict rates of net production. This is unrealistic because it is known that respiration can change independent of photosynthesis on time scales <1 month [8]. Basically variance in respiration responds to variance in light received over the past several days to weeks and not to the instantaneous light received during the previous

daylight period. Consequently, the method may not return accurate estimates of 24-h net community production.

Recently a highly innovative control-volume approach was described by Falter et al. [1]. A triangular array of ADCPs and Aanderaa optode oxygen sensors were deployed on the Kaneohe Bay Barrier Reef, HI. Continuous measurements of the rate of net oxygen evolution were measured over an 18-d period in December 2006. Lagrangian measurements of oxygen flux made by following oxygen changes in a dye patch as it drifted through the control volume were shown to be in excellent agreement with the control volume oxygen fluxes. Net community production (NCP) averaged over the study period was  $5 \pm 123 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  and ranged from -200 to  $190 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  indicating the extent of day to day variability that can be experienced and the need for a method that can make continuous measurements over an extended period of time. While this method is clearly a major advancement it does have some limitations. The authors suggest that the minimum length scale to ensure a measurable horizontal gradient in oxygen is approximately 250 m and that the maximum depth is on the order of 3-4 m. The duration of the study is limited by oxygen sensor drift due to biofouling. Perhaps the greatest drawback is that the control volume approach is not easily modified to make measurements of calcification. Sensors that measure total alkalinity are not yet available although they are in development and may become available in 2-5 years. There are sensors that measure pH and  $\text{pCO}_2$ . However, assuming reasonable values for the precision of each measurement the propagated precision in TA is  $\pm 15 \text{ uEquiv kg}^{-1}$ , which is not adequate for the rates of calcification that can be expected. One group in Australia is taking the brute-force approach of pumping seawater from each of the vertices of the control volume for analysis at a nearby laboratory facility [9]. The results of this approach have not been published so it is not possible to judge the success of the approach.

The eddy-correlation method is another innovative method that is revolutionizing the field of oceanography by making it possible to make completely noninvasive measurements of sediment-water oxygen fluxes on a continuous basis [2, 3]. The method requires a single point velocimeter such as an Acoustic Doppler Velocimeter (ADV) or Modular Acoustic Velocity Sensor (MAVS) and a fast-response oxygen sensor. The technique has been used in sandy and muddy bottom environments where the oxygen uptake has varied from 40 to  $200 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ .

It is also important to mention that different types of enclosures have been used to obtain *in situ* measurements of coral reef metabolism [10-13]. All these have the drawback of altering the hydrodynamic environment. While this is a concern we don't know how big the bias is until comparisons can be made with methods that do not alter the hydrodynamics.

In this paper we will not review the approaches that measure coral reef calcification on a broad spatial and long

temporal scale, or the so-called alkalinity depletion-water residence time methods. These approaches are valuable for characterizing the big picture of how a complete reef system is performing. Here we are interested in methods capable of measuring metabolism and calcification with high spatiotemporal resolution. We see these methods as vital to understanding how individual parts of the reef are contributing to the whole and how they are responding to short term physical and chemical forcing.

There is good reason to suspect that the metabolic rates that were established for coral reefs in the 1970s and 80s [4] have changed dramatically. This is based on three lines of evidence. First, is the well documented evidence that the percent of live coral cover has declined by 20% in the Indo-Pacific [14] and by 40% in the Caribbean [15] between the 1980s and 2003. It would be expected that calcification rates would decline in proportion to the decline in live coral cover unless new opportunistic calcifiers have moved into the system. Second, is the evidence that the calcification rate of individual coral colonies has also declined. This evidence is based the analysis of the skeletons of long-lived species of coral [16-18]. It is difficult to make a precise attribution for the cause of this decline in recent decades but the authors note that the decline is consistent with what would be predicted from laboratory studies of the effects of warming and ocean acidification on calcification rates. Finally, and the main motivation for this study, there is the experimental evidence that the projected increases in temperature and decrease in pH over the next 50-100 years could cause a dramatic decline in the health and abundance of scleractinian corals [19, 20].

The implications of significant change in coral reef ecosystems affects the economic and nutritional needs of millions of people in the US and worldwide, the preservation of marine biodiversity, the protection of coastal cities and communities, as well as innumerable other ecosystem services. To adequately determine and interpret these changes will require robust and efficient observational tools. On this basis, we have applied a novel boundary layer approach that utilizes the gradients in oxygen and total alkalinity concentration to estimate coral reef net production and calcification. The instrument package is light weight, small and easily deployable in any depth of water. The footprint of the measurement area is on the order of  $50 \text{ m}^2$ , big enough to average over a reasonable portion of a particular type of habitat but small enough to be used on typical coral reefs that are composed of a mosaic of different communities on fairly small length scales.

## II. BACKGROUND

### A. Calcification

Calcification is the process whereby corals, algae and, to lesser extent, protozoans and invertebrates take up  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  ions from the seawater and secrete various forms of calcium carbonate minerals. Approximately 10-20% of all the carbonate production in the ocean occurs in a region that

amounts to just 0.17% of the area of the seafloor [21, 22]. Since the production occurs in shallow supersaturated environments most of it does not dissolve and instead it accumulates building the framework that is home to all the other organisms living on the reef. An abiotic form of this reaction happens in the sediments in a process known as cementation. However, by far the greatest amount of carbonate is produced by living organisms. The parallel process of photosynthesis is key to the rapid rate of calcification. The organism may be photosynthetic itself in the case of calcareous algae or the animal may have a photosynthetic algal symbiont within its tissues in the case of corals and foraminifera. The mechanism for the connection between photosynthesis and calcification is not well known. Often the coupling can be quite loose as evidenced by the observation that the ratio of calcification to gross photosynthesis can vary from 0.2 to 1.5 [23]. A number of environmental factors are known to be important for maintaining a high rate of calcification by corals including high light, low nutrients, clear water, adequate water flow, water temperature within a narrow range and high carbonate saturation state. Two of these factors, water temperature and saturation state, are projected to move well outside the preferred optimal ranges within the next 50-100 years [24] i.e. temperature increase of 1-6 °C and a CO<sub>2</sub> partial pressure increase of 180 to 420 ppm.

The earliest field evidence that saturation state exerts a strong control on calcification in the ocean was a study performed on the Great Bahama Bank by Broecker and Takahashi [25]. They observed a relationship between the age of a parcel of water based on salinity or <sup>14</sup>C concentration and the total alkalinity draw down relative to the oceanic source water. A plot of calcification rate ( $\Delta\text{TA}/\text{age of water parcel}$ ) against the ion activity product of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> (effectively the saturation state) produced a strong, linear relationship. It was initially thought that this could only mean that the calcification over the Bank was abiotic. However, a mesocosm experiment where both Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> were manipulated independently proved that saturation state:  $[\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}}$ , exerts a strong control on the biocalcification rate of corals and calcifying macro algae [29].

Calcification is a key determinant of reef health as it is the process whereby corals and calcareous algae build the framework that forms the habitat for all the other species that are found on the reef. As an example, Watanabe et al. [54] combined measurements of dissolved inorganic carbon (DIC) and TA from a reef in Palau over the period 1992 to 2002 with estimates of the residence time of the water on the reef to compute the net calcification rate of the community. They found that calcification on the reef flat declined over this period from 110 to 60 mmol m<sup>-2</sup> d<sup>-1</sup> and in the lagoon from 35 to 20 mmol m<sup>-2</sup> d<sup>-1</sup>, a 30-40% decline in just a 10 year period. The time series for the reef flat showed a particularly strong dip between Jan. 1998 and Feb. 1999 corresponding with an El Nino-related mass bleaching event in the summer of 1998

that killed many corals in Palau and throughout the Pacific and Indian Oceans [25A, 26].

The chemical environment in the surface ocean is changing as the ocean takes up CO<sub>2</sub> from the atmosphere. This in turn lowers the pH and the carbonate saturation state of the water [27, 28], making it more difficult for organisms to secrete their CaCO<sub>3</sub> skeletons and shells. Carbonate saturation has a strong impact on calcification rates of corals [29-35]. Based on the projected CO<sub>2</sub> increase the saturation state of the tropical surface ocean could drop to 2.8 by the year 2100 [27]. It is feared that as the CO<sub>2</sub> in the atmosphere increases the saturation state of the ocean will drop to a point that calcification is no longer sufficient to replenish losses due to storms, grazers and borers.

#### *B. Boundary layer-chemical gradient flux measurements of respiration and calcification*

There is a growing recognition within the field of biological oceanography that transport of nutrients and other materials into and out of sessile animals, such as corals and benthic algae, is mass transport limited and strongly affected by the local flow field surrounding the organism [36-43]. This means there is a need to move away from methods for measuring metabolism that involve enclosing the organism and altering the hydrodynamic environment to methods that measure flux in the free and ambient environment. Two new methods have recently been shown to permit the continuous measurement of *in-situ* rates of oxygen evolution and consumption of benthic communities. These are the control-volume method and the eddy-correlation method. Both methods show great promise of revolutionizing our understanding of how the photosynthesis and respiration rates of natural benthic communities vary in time and space and what factors control those rates.

Control volume experiments are one approach [8]. This involves measuring the transport of water and material into and out of a water volume in all directions by deploying instruments in all corners of that volume. The method can be powerful, but involves a lot of equipment to measure the full water column for both material and velocity at different corners of the volume. Many different instruments are required, and they must be very accurate and precise in order to get accurate mass balances. This technique also uses the residual of what comes in and out of the vertical control surfaces to determine the flux from the top and bottom of the control volume – usually the benthic and air-water interface. The mass-balance technique requires some spatial and temporal averaging in the control volume as well.

The eddy correlation or direct covariance (DC) boundary layer flux technique has important advantages [2, 3]. The DC technique does not use an eddy diffusion model and measures a small footprint of substrate at high temporal resolution. This provides the necessary interrogation timescale to (1) resolve physical and biogeochemical processes and (2) provide the accumulation of net productivity to ascertain the metabolic state of the ecosystem.

The lack of a sensor that accurately measures total alkalinity directly or a pair of sensors (e.g. pH and pCO<sub>2</sub>) from which TA can be computed with sufficient accuracy and precision precludes the application of the control volume or direct covariance techniques to the budget of total alkalinity at this time. An alternative approach based on quantifying the vertical flux of material transported from the surface through the benthic boundary layer is the boundary layer gradient flux (GF) technique. Boundary layer techniques, including the GF, over corals to determine the momentum have been shown to be successful [44]. From the momentum flux, the friction velocity, drag coefficient, and eddy diffusivity can be computed.

The advantage of the method is that mean gradients in the boundary layer can provide a measurement of the benthic flux. Accurate gradients in current speed and dissolved chemical constituents over a small depth interval are used for the gradient flux technique. The GF method is very powerful because of its flexibility: it can be applied to any constituent for which a vertical gradient can be measured, and it does not require a fast-response (e.g. seconds or less) sensor. Lacking a fast-response sensor for TA, the GF method is most suited for TA fluxes. The GF method is less susceptible to wave motion because it averages out the wave motion and relies on a diffusion model so significant artifacts are mitigated. In recent years, several studies have made direct flux measurements in the aqueous boundary layer [2].

High-resolution, instantaneous boundary layer velocity profiles have been measured with acoustics and optics. Very high resolution dynamic profiles have been measured using a Particle Image Velocimeter (PIV) and a pulsed-laser light sheet to get the velocity profile by McGillis [45]. PIV is difficult and costly to perform in the field, particularly when the profile of the streamwise flow is required to measure boundary layer profiles to measure surface stress, drag coefficients, and near-wall eddy diffusivity. Near bottom velocity gradients and variance fluctuations can be measured with point measurements of high frequency, fast response water velocity sensors. Robust water velocity measurements include: Acoustic Doppler Velocimeter (ADV); time of flight, Modular Acoustic Velocity Sensor (MAVS); high resolution Dopbeam spatial velocity measurements; and Acoustic Doppler Current Profilers (ADCP). Note, Laser Doppler Velocimeter (LDV) and other optical systems (PIV and Holographic techniques) have shown high quality spatial and time response measurements in the field.

Boundary layer measurement techniques were used to measure fluxes at the air-water surface using the GF technique [46-49]. The gradients of carbon dioxide in the atmosphere are very small. To measure accurate gradients, the single detector differencing method was performed. When the boundary layer formulation requires stability corrections, the GF technique needs structure functions for stability. We used GF and DC methods in the boundary layer over water for the first time to generate formulations for the stability structure functions [50].

The GF technique is used in the benthic boundary layer by measuring vertical gradients of velocity, temperature, and chemical constituents to calculate the flux of momentum, heat, respiration and calcification. If the boundary layer is not neutral and buoyancy influences the boundary layer, then the turbulent flux-profile relationship would require a stability correction. If waves or shear forcing erode significant buoyancy, and the critical Richardson number is not achieved, corrections to the surface flux are not required. A pertinent example of the GF technique is provided using the vertical gradient of mean quantities  $\bar{x}$ , where the method predicts that the normalized gradient should be a universal function of  $\xi$  such that:

$$\frac{\kappa z}{x_*} \frac{\partial \bar{x}}{\partial z} = \Phi_x(\xi) \quad (1)$$

where  $\Phi_x$  is an empirically determined dimensionless gradient function for  $x$ . If wall layer turbulence holds and no stability corrections are required,  $\Phi_x$  is unity. The scaling parameter ( $x_*$ ) can be determined from the slope of the solution to (1). The flux is then calculated by combining this scaling parameter with the friction velocity

$$F_x = x_* u_* \quad (2)$$

For net production or calcification, the flux is calculated using gradients of DO and TA. The GF can also be related to the gradient with the eddy diffusivity that is directly proportional to the flux:

$$F_x = K_z \frac{\partial \bar{x}}{\partial z} \quad (3)$$

where  $z$  is the height above the surface and  $K_z$  is the variable of proportionality known as the eddy diffusivity for mass.

As a proof of concept three studies were conducted in a shallow warm water reef environment in La Parguera, Puerto Rico. An ADV, MAVS, and two Aanderaa optode oxygen sensors were deployed on a frame at 0.20 m above the bottom (mean height of the surrounding corals) and at 1.2 m above the bottom (Fig. 1). Deployments were made on Media Luna Reef Jan. 10-12, 2008 and on Enrique Reef Feb. 24-26 and Mar. 24-29, 2009. During the study on Media Luna discrete oxygen samples were also collected upstream and downstream of the location of the boundary layer flux measurements so that oxygen flux could also be determined by the Eulerian upstream-downstream mass balance method [51]. An RDI ADCP was deployed to obtain the currents along the reef between the upstream and downstream sampling locations. At the beginning and end of the deployment the oxygen sensors were positioned side by side to obtain data so that any small offset or biases in the signals could be corrected in the time series and discrete oxygen samples were collected to provide a check on the accuracy of the oxygen signals. Fig. 2 shows that the oxygen flux computed by the boundary layer gradient flux method (GF) is in good agreement with the rates determined by the conventional Eulerian method.

Fig. 3 shows the data from a 6-day deployment in Mar. 09 on Enrique Reef. Note how the gradient in DO shifts between day and night reflecting O<sub>2</sub> production at the seafloor-water interface during the mid-day and O<sub>2</sub> consumption at night. Note that the GF method yields reasonable rates despite swings in DO that may be due to tidal or lateral advection events. The daily rates of np integrated over 24-h for the Feb. and Mar. 09 deployments of the CROSS in La Parguera are given in Table 1.

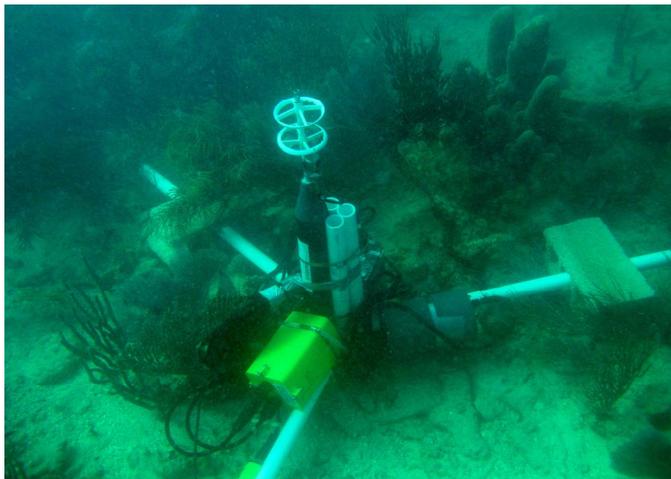


Fig. 1: The Coral Reef Oxygen Sensor System (CROSS) deployed in the reefal system of Cayo Enrique, La Parguera, Puerto Rico. The noninvasive PVC frame minimizes flow distortion. The CROSS includes a near surface ADV, an upward facing MAVS, 2 optodes at 20 cm and 120 cm, and an AMT fast-response oxygen sensor. Water sampling equipment (not shown) for TA to perform BLG flux measurements of calcification and respiration. The CROSS contains an internal and external battery pack for extended operation and an Autonomous Low Power System that simultaneously measures all instruments on a single purpose processing chip.

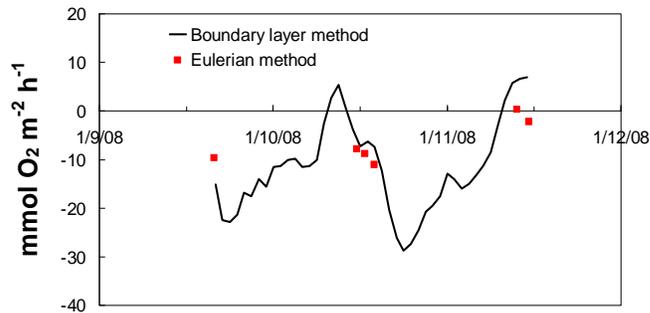


Fig. 2: Oxygen flux rates from Media Luna Reef, La Parguera, Puerto Rico. The comparison shows good agreement between boundary layer GF and Eulerian upstream-downstream methods.

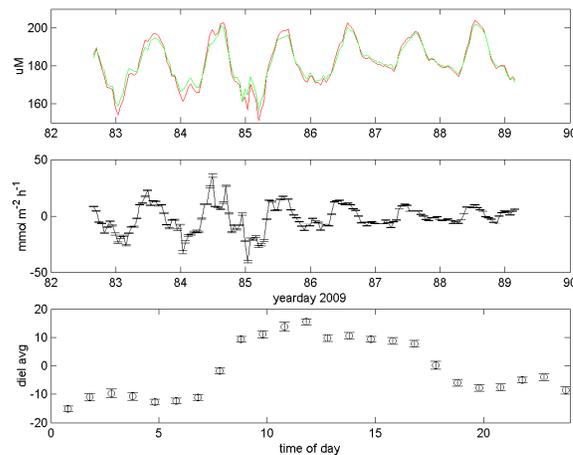


Fig. 3: Time series of data from Cayo Enrique Reef in La Parguera, Puerto Rico collected using the boundary layer flux method March 2009. Red line is DO at 0.2 m above the bottom and green line is DO at 1.2 m above the bottom. Data show periods of net oxygen production (photosynthesis) at mid day and net oxygen consumption (respiration) at night. The top plot shows the simultaneous dissolved oxygen measurements. DO is measured every 10 seconds. Data shown are hourly averages. The middle plot shows the GF net O<sub>2</sub> production measured using the simultaneous gradients in oxygen and velocity. The bottom plot shows the average diel net O<sub>2</sub> production from the week long deployment.

TABLE 1. Daily rates of np

Date	np, mmol C m <sup>-2</sup> d <sup>-1</sup>
2/24/2009	3.5
2/25/2009	7.0
3/24/2009	-27.7
3/25/2009	-39.1
3/26/2009	-15.7
3/27/2009	38.1
3/28/2009	32.1
3/29/2009	60.7

Rates of np are highly variable from day to day but averaged 8.1 mmol C m<sup>-2</sup> d<sup>-1</sup> over the period 3/24-3/29/09. These data

illustrate the value of methods (control volume or GF) that measure  $np$  continuously over long enough time to obtain a useful long term average.

As a check on the GF method,  $np$  was computed from the oxygen time series shown in Fig. 3 by computing changes in the water column oxygen inventory over time and estimating the air-sea gas exchange based on the Wanninkhof et al. [52] gas exchange velocity-wind speed relationship:

$$np \times PQ = h \frac{\partial O_2}{\partial t} + k_{O_2} (O_2 - c_s) \quad (4)$$

where  $np$  is the hourly rate of net community production ( $\text{mmol C m}^{-2} \text{h}^{-1}$ ),  $h$  is the water depth (5.4 m),  $\partial O_2 / \partial t$  is the time rate of change of oxygen concentration in the water column ( $\text{mmol m}^{-3}$ ),  $k_{O_2}$  is the gas exchange velocity for oxygen computed as function of temperature and wind speed,  $c_s$  is the surface equilibrium oxygen concentration computed for the ambient temperature and salinity according to Benson and Krause [53] and  $PQ$  is the photosynthetic quotient (Fig. 4). Note that  $np$  computed based on the temporal changes in oxygen concentration (mass balance method) are substantially in agreement with the rates estimated from the vertical gradient in dissolved oxygen (GF method).

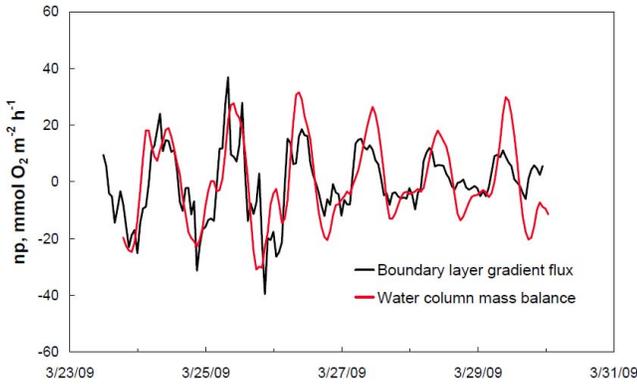


Fig. 4: Comparison of  $np$  computed by the GF method and by a mass balance method based on changes in water column oxygen concentration, Eq 4.

Fig. 5 shows the vertical eddy diffusivity  $K_z$  computed from the turbulent boundary layer vertical gradient in current velocity based on the Mar. 09 data. Note that  $K_z$  varies from 2-6  $\text{m}^2 \text{h}^{-1}$  depending on current speed. We use this range in  $K_z$  and estimates of typical coral reef calcification rates to estimate the magnitude of the TA gradient we may expect to observe in La Parguera and our work in the Florida Keys (Table 2).

The values in column 3 of Table 2 come from Smith and Kinsey [4] and Kinsey [5] and have been converted to hourly rates assuming a 12-h day and the light calcification rate 3-times the dark rate and that the TA flux is twice the  $\text{CaCO}_3$  flux.  $K_z$  is computed from measurements of the turbulent boundary layer velocity gradient made at Enrique Reef, La

Parguera, Puerto Rico. Note the magnitude of the TA gradient is 4 to 60-times our best analytical precision for the TA analysis.

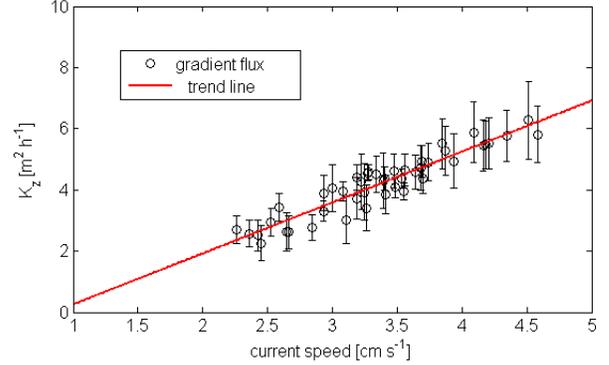


Fig. 5: Comparison of the eddy diffusivity computed for the March 2009 deployment of CROSS boundary layer fluxes on Enrique Reef, Puerto Rico. Eddy diffusivity  $K_z$  [ $\text{m}^2 \text{h}^{-1}$ ] and  $\pm$  standard deviations are plotted versus current speed.

TABLE 2. Estimated TA gradients based on expected rates of calcification.

Date	Environment	kg $\text{CaCO}_3$ $\text{m}^{-2} \text{y}^{-1}$	mmol $\text{CaCO}_3$ $\text{m}^{-2} \text{h}^{-1}$	$K_z$ , $\text{m}^2$ $\text{h}^{-1}$	dTA/dz
2/24/09	Reef flat	4	6.8	2.0	12.3
2/25/09	Reef flat	4	6.8	6.0	4.1
3/24/09	Reef crest	10	17.1	2.0	30.8
3/25/09	Reef crest	10	17.1	6.0	10.3

### C. $O_2$ -MAVS Instrumentation

The eddy correlation technique for  $O_2$  can be done in a single instrument that measures both velocity fluctuations and  $O_2$  fluctuations. The MAVS [55, 56] current sensor is capable of measuring vector velocity fluctuations with 0.1 cm/s resolution and accuracy 1% of the measured value. To this has been added a fast response oxygen sensor [57]. The oxygen sensor made by AMT has such low analyte consumption relative to other oxygen sensors that streaming of the sensor membrane or stirring of the analyte is not necessary. It has a 200 ms response time to 90% of the amplitude of a step in oxygen presented to the membrane covering the electrode. The 0-5 volt output of the oxygen sensor is digitized at 21 Hz and added to the data stream of temperature, velocity, and sensor orientation. Fig. 6 shows correlations of the velocity and oxygen signals in a still environment in the laboratory and indicates the noise floor. The noise floor in this case is given by  $\delta \text{cm/s} * \delta \text{mV}$  where the mV reading is scaled by the reading of 455 mV for saturated atmospheric concentration in the tank. The average of the four standard deviations is  $0.7 \text{ cm mV s}^{-1}$ .

Performance of the oxygen sensor in the field is demonstrated by Fig. 7 showing the tracking of oxygen compared to two Aanderaa optode sensors on the reef. The fast response time of the AMT sensor does not prevent it from following the longer term fluctuations of oxygen as shown by the optode sensors 844 and 845. The final illustration of the

oxygen sensor's ability to follow natural fluctuations of oxygen is shown in Fig. 8 where concentration response to daylight and night over grass is displayed. Current is plotted along with the incident photosynthetic active radiation (PAR). Fig. 9 shows cospectra of velocity and of vertical velocity with oxygen concentration in arbitrary units showing that the vertical flux of oxygen is correlated with the flux of

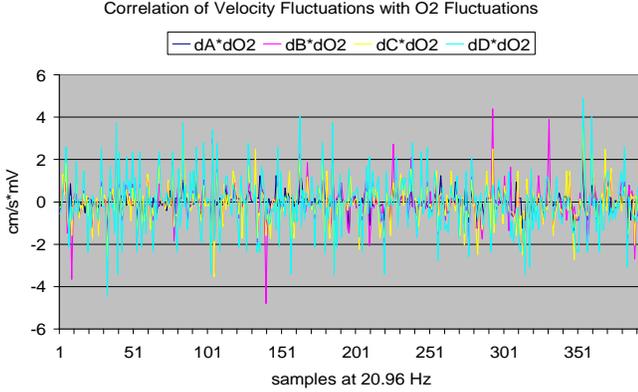


Fig. 6 shows correlation of each of the four acoustic velocity measuring paths with fluctuations in oxygen signal in mV from the sensor. Full scale in the tank from atmospheric saturation was 455 mV.

momentum.

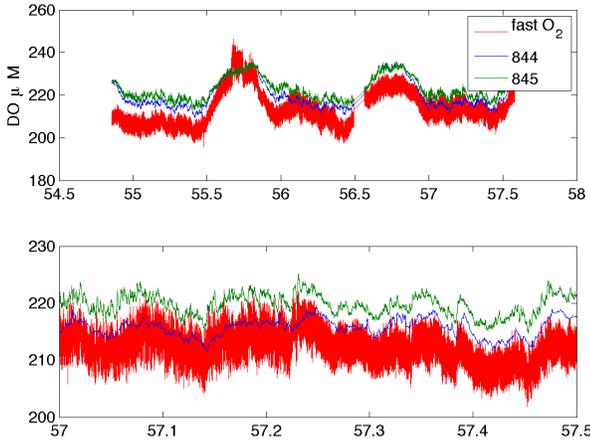


Fig. 7 is a comparison of the AMT oxygen sensor on O<sub>2</sub>-MAVS with two Aanderaa optodes on the reef. The fast oxygen sensor tracks the lower frequency fluctuations of oxygen as well as the optodes and also captures high frequency fluctuations.

### III. FUTURE WORK PLAN

Net community production, calcification, and momentum measurements can be made using O<sub>2</sub>-MAVS and CROSS-Talk. A frame of thin tubing carrying the current meters, oxygen sensors, water samplers, pumps, control system, data

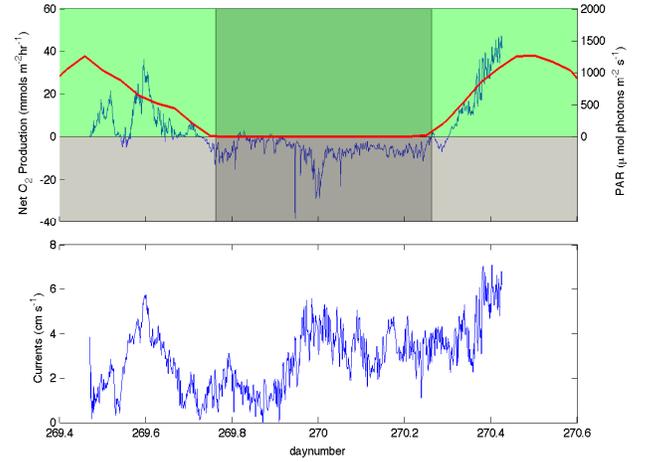


Fig. 8 demonstrates that the oxygen sensor behaves in an expected way when sunlight on a grass bed gives rise to increased oxygen concentration. Production stops and consumption occurs when the PAR goes to zero at night. Velocity is plotted as well.

acquisition system, and batteries can be placed in the reefal

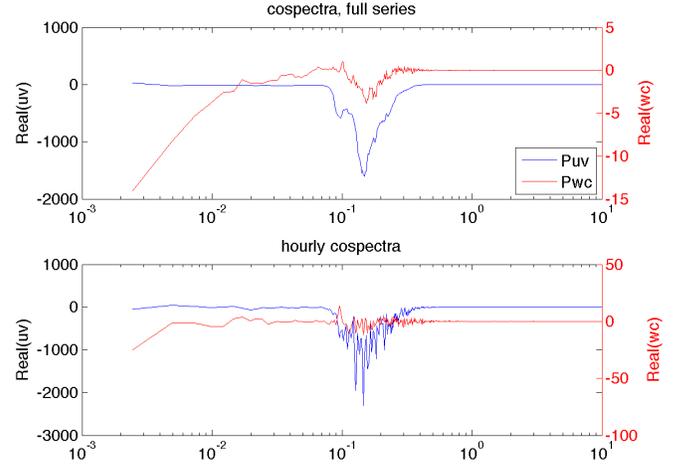


Fig. 9 shows the cospectra of velocity and of vertical velocity with oxygen concentration demonstrating that the vertical flux of oxygen is correlated with the flux of momentum.

system by divers. We will be able to calculate robust estimates of the vertical concentration gradients of TA and DO in the benthic boundary layer. Net production and calcification will be computed from the product of  $K_z$  times the vertical concentration gradient using the GF technique. Using  $K_z = u_* \kappa z$ ,  $np$  and  $g$  can be calculated as:

$$np = \frac{\rho u_* \kappa (DO_{z=2} - DO_{z=1})}{PQ \ln(z_2 / z_1)} \quad (5)$$

$$g = -0.5 \rho u_* \kappa \frac{(TA_{z=2} - TA_{z=1})}{\ln(z_2 / z_1)} \quad (6)$$

where  $np$  is the hourly rate of net community production ( $\text{mmol C m}^{-2} \text{h}^{-1}$ ),  $\rho$  is the density of the seawater ( $\text{kg m}^{-3}$ ),  $u_*$  is the friction velocity,  $\kappa$  is the Kármán constant,  $DO_z$  is the

dissolved oxygen concentration ( $\text{mmol kg}^{-1}$ ) at 0.2 or 1.2 m above the seafloor,  $PQ$  is the photosynthetic quotient (assumed to be 1.0),  $g$  is hourly rate of net community calcification,  $-0.5$  accounts for the fact that 2 Equivalents of TA are consumed per mole of  $\text{CaCO}_3$  produced and  $TA_z$  is the total alkalinity ( $\text{mEq kg}^{-1}$ ) measured at 0.2 or 1.2 m above the seafloor. The friction velocity,  $u_*$ , is calculated using the boundary layer gradient flux technique at the same time and spatial scale as the chemical constituents. The boundary layer velocity gradient and current speed are used to determine  $u_*$ , and the corresponding drag coefficient,  $C_d = (u_*/U)^2$ , and the eddy diffusivity  $K_z$ , estimating the boundary layer flux from wall layer.

The O<sub>2</sub>-MAVS/CROSS-Talk system can be deployed for extended periods on bottom substrates to determine the environmental forcing and conditions of net community production and calcification.

#### IV. SUMMARY

To assess the impact of climate change on the health of coral ecosystems new methods are needed to extend the spatial and temporal coverage of coral reef studies to ascertain whether observed changes are global in scope and temporally coherent with observed changes in climate and ocean chemistry. In this study, a method was implemented to help advance the synopticity of reef metabolic studies by providing a relatively inexpensive tool for evaluating reef calcification. Calcification is a key determinant of reef health. It is the process whereby corals and calcareous algae build the framework that forms the habitat for the rich diversity of species found on the reef. In order for a reef to persist through time the rate of calcification must be great enough to keep up with sea level rise and the normal destructive forces that are constantly eroding the framework away. The chemical conditions in the ocean that have favored extensive reef development throughout the tropics and have been fairly stable for the last 5000 years are starting to deteriorate at an alarming rate. Results from our work will contribute to understanding whether coral reef ecosystems can cope with this stress or if corals will experience a phase shift to a community dominated by non calcifying organisms.

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