Continuous measurements of dissolved O₂ and oxygen isotopes in the Southern California coastal ocean

Lauren Elmegreen Rafelski^{a,1,*}, Bill Paplawsky^a, Ralph F. Keeling^a

^a*Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA, 92093-0244, United States*

Abstract

Dissolved O₂/N₂, O₂/Ar, O₂ saturation and $\delta^{18}\text{O}$ were measured continuously near the surface ocean at the Scripps Institution of Oceanography pier in La Jolla, California, for five weeks. The data showed diurnal cycles in O₂ and $\delta^{18}\text{O}$, with amplitudes of 19 mmol m⁻³ and 1.1 per mil, respectively. The diurnal cycles are well described by a box model that includes photosynthesis, respiration, air-sea gas exchange, and mixing. The timing of the cycles can be explained using a photosynthesis rate proportional to photosynthetically active radiation, and the shapes of the cycles can be explained by mixing with a subsurface layer of water that is supersaturated in O₂. Based on the diurnal cycles in O₂ and $\delta^{18}\text{O}$, the average maximum daily photosynthesis rate was 3.7-4.7 mmol O₂ m⁻³ hr⁻¹, which is supported by the light-saturated photosynthesis rate estimated from the measured chlorophyll concentration. In the future, these continuous measurement techniques could be used at different locations and depths to improve the understanding of variability in

*Corresponding author.

Email address: lauren.rafelski@gmail.com (Lauren Elmegreen Rafelski)

¹Present address: AAAS Science and Technology Policy Fellow hosted by the U.S. Environmental Protection Agency, 1200 Pennsylvania Ave., NW, Washington, DC 20460

oceanic primary production.

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1. Introduction

Oceanic primary production is an important part of the global carbon cycle, with global net primary production totaling around 50 GtC yr⁻¹ (Westberry et al., 2008). Primary production can be measured using a variety of methods, including bottle incubations that measure ¹⁴C uptake or ¹⁸O production (Bender et al., 1999). In addition, satellite measurements of chlorophyll concentration in the surface ocean can be used to estimate global primary production (e.g. Antoine et al., 1996).

Measurements of dissolved O₂ and $\delta^{18}\text{O}$ have been used with models to determine rates of photosynthesis and respiration (e.g. Quay et al., 1993; Quiñones-Rivera et al., 2007; Levine et al., 2009), where $\delta^{18}\text{O}$ is defined as:

$$\delta^{18}\text{O} = \frac{(^{18}\text{O}/^{16}\text{O})_s}{(^{18}\text{O}/^{16}\text{O})_r} - 1 \quad (1)$$

where the subscripts s and r stand for sample and reference values, and $\delta^{18}\text{O}$ is multiplied by 1000 to give units of per mil. Photosynthesis increases the O₂ concentration and decreases $\delta^{18}\text{O}$, because photosynthesis produces O₂ with an isotopic composition similar to oxygen in water (Guy et al., 1993), which has less ¹⁸O relative to ¹⁶O than atmospheric O₂ (Kroopnick and Craig, 1972). Respiration decreases O₂ concentration and increases $\delta^{18}\text{O}$, because respiration preferentially uses ¹⁶O over ¹⁸O (Lane and Dole, 1956). Bender and Grande (1987) showed that the relationship between $\delta^{18}\text{O}$ and O₂ saturation is determined by the ratio of photosynthesis to respiration.

Previous studies have taken continuous measurements of dissolved gases such as O_2 and Ar using membrane inlet mass spectrometry (e.g. Tortell, 2005; Guéguen and Tortell, 2008) or equilibrator inlet mass spectrometry (e.g. Cassar et al., 2009). However, $\delta^{18}\text{O}$ of dissolved O_2 has only been measured by taking discrete samples of water for later gas extraction and analysis on a mass spectrometer (e.g. Hendricks et al., 2004; Sarma et al., 2005; Juranek and Quay, 2010; Stanley et al., 2010; Hamme et al., 2012). We instead developed a system for continuous, real-time measurement of dissolved gases, including $\delta^{18}\text{O}$, using an equilibrator designed for oxygen equilibration (Rafelski et al., 2013), and a mass spectrometer. This method allows for more frequent measurements of $\delta^{18}\text{O}$ over a longer period of time than previous work. To test this method, we collected data from the Scripps Institution of Oceanography (SIO) pier, in La Jolla, California. We measured dissolved O_2/N_2 , O_2/Ar , O_2 saturation, and $\delta^{18}\text{O}$ in the coastal ocean over a period of 5 weeks, and obtained observations at hourly resolution. Here we present these data, along with a model of O_2 and $\delta^{18}\text{O}$ that includes photosynthesis, respiration, air-sea gas exchange and mixing. We use this model to determine the processes contributing to the observed variability, and to estimate the photosynthesis rate.

2. Methods

2.1. Mass spectrometer

An isotope ratio mass spectrometer (Elementar Americas, Inc., IsoPrime) was used with a counterflow-type equilibrator to measure dissolved gases in seawater. The mass spectrometer has a flight tube, source, and detector inte-

grated into a single stainless steel enclosure, and can simultaneously measure ten m/z ratios: 28, 29, 30, 32, 33, 34, 36, 40, 44, and 45. The mass spectrometer inlet system allows for a continuous flow of sample and reference gases. A changeover valve switches between the sample and reference gases every 10 seconds, allowing for the calculation of delta values every 20 seconds, defined as:

$$\delta(A/B) = \frac{(A/B)_s}{(A/B)_r} - 1 \quad (2)$$

where A and B are two m/z ratios, $(A/B)_s$ is the mean of the sample gas during a 10-second collection period, and $(A/B)_r$ is the mean of the surrounding 10-second reference gas collection periods. The delta values are multiplied by 1000 to give units of per mil.

Previous studies measuring $\delta^{18}\text{O}$ of dissolved oxygen have used gas chromatography to separate O_2 and Ar from N_2 , in order to avoid changes in the ionization efficiency due to changes in the O_2/N_2 ratio, which can be highly variable in the ocean (Luz et al., 1999; Blunier et al., 2002). However, because we continuously sampled the gas, isolation of O_2 and Ar was impractical. Instead, we corrected for this and other interferences using:

$$\delta^{18}\text{O} = s_{18} \times (\delta(34/32) - n_{18} \times \delta(32/28) - c_{18} \times \delta(44/28)) \quad (3)$$

where n_{18} is the correction for N_2 interference (from variations in the O_2/N_2 ratio), c_{18} is the correction for CO_2 interference, and s_{18} is the span correction. The span correction corrects for scale contraction due to incomplete switching between the sample and reference gases. It was determined by measuring gas from cylinders of air that were highly enriched in O_2 or $\delta^{18}\text{O}$, as described in Rafelski (2012) and Rafelski et al. (2013). For $\delta(\text{O}_2/\text{N}_2)$ and

$\delta(\text{O}_2/\text{Ar})$, the N_2 and CO_2 interferences were so small that they could be neglected, and only the span correction was necessary.

The correction in $\delta^{18}\text{O}$ for N_2 interference is potentially very large and uncertain because of large variations in the O_2/N_2 ratio of air equilibrated with surface seawater. To reduce the need for a large correction, the mass spectrometer inlet system was modified so that N_2 gas could be added to the sample in automatically adjusted amounts to keep the O_2/N_2 ratio of the sample gas constant even while the O_2/N_2 ratio in the water was changing. A tank of pure N_2 gas was connected to a pressure controller (MKS Instruments Type 640 Absolute Pressure Controller) upstream of the changeover valve (Figure 1). The N_2 gas flowed through a 30 cm long, 0.005" diameter capillary tube into the sample stream. To allow for rapid shut off of the N_2 flow, the line was equipped with an evacuation port that caused flow to reverse directions at the N_2 injection point when the N_2 flow was turned off.

During sampling, the flow of added N_2 gas was adjusted via upstream pressure control using a feedback loop that targeted a measured $\delta(\text{O}_2/\text{N}_2)$ of zero (i.e. sample O_2/N_2 ratio equal to reference). The reference gas was compressed ambient air, with normal atmospheric O_2 isotopic composition. The system could only stabilize the measured $\delta(\text{O}_2/\text{N}_2)$ when the ambient $\delta(\text{O}_2/\text{N}_2)$ of the dissolved gas was above zero, but the ambient $\delta(\text{O}_2/\text{N}_2)$ was rarely below zero in the measurements reported here. We alternated between adding N_2 gas for 25 minutes so that $\delta^{18}\text{O}$ could be measured, and not adding N_2 for 20 minutes so that the O_2/N_2 ratio could be measured. On this mass spectrometer, when a cylinder of gas is sampled, the standard error of the mean of 20 minutes of data is ± 0.001 per mil for $\delta(\text{O}_2/\text{N}_2)$ and $\delta(\text{O}_2/\text{Ar})$,

Figure 1: Custom mass spectrometer inlet system, with nitrogen gas added into the sample line. This N_2 addition forced the sample O_2/N_2 ratio to match the reference ratio. A version of this figure, without the lines for nitrogen addition, appeared in Rafelski et al. (2013).

and ± 0.005 per mil for $\delta^{18}\text{O}$. A “working tank,” with composition close to ambient air, was run for 30 minutes every 2 hours to verify the stability of the reference gas, which was used as the ultimate reference for our measurements.

Even with the N_2 gas addition, variations in O_2/N_2 were not completely eliminated. However, the feedback loop reduced the variations by at least a factor of 10, such that the uncertainty in the residual interference was small. This interference was quantified by interpolating the data with the N_2 gas addition to the time periods without the N_2 gas addition, and calculating the change in $\delta(34/32)$ and $\delta(32/28)$ due to the N_2 gas addition. The ratio of the change in $\delta(34/32)$ to the change in $\delta(32/28)$ gave the interference. The interference was calculated hourly, but the correction did not show a trend over time, so we used the mean value. The mean interference (n_{18} in Equation 3) was 0.0022 ± 0.0003 , in units of per mil in $\delta^{18}\text{O}$ for a 1 per mil change in $\delta(32/28)$.

To measure the interference due to CO_2 (c_{18} in Equation 3), a test was conducted where CO_2 was removed from the sample stream of gas using a glass trap filled with Ascarite II (2/3 of trap length), followed by magnesium perchlorate (1/3 of trap length) to remove any water produced by the reaction of CO_2 with Ascarite II. The trap was switched in or out of the sample line every 90 minutes. The sample was run for two 90 minute periods with the trap, and two 90 minute periods without the trap. The mean value of $\delta(34/32)$ for each of these periods was plotted against $\delta(44/28)$. The slope gave a CO_2 interference in $\delta^{18}\text{O}$ of $(7.2 \pm 0.4) \times 10^{-5}$, in units of per mil in $\delta^{18}\text{O}$ for a 1 per mil change in $\delta(44/28)$. The trap could have been introduced regularly to obtain quasi-continuous measurements of the CO_2 interference,

but for this study, the test was only conducted once.

2.2. Equilibrator system

The equilibrator used was a counterflow-type, as described in Rafelski et al. (2013). The equilibrator was made of a 5.2 cm I.D., 53.3 cm long PVC pipe filled with 12 mm glass Raschig rings. Water entered the equilibrator at a flow rate of 5.6-5.8 L min⁻¹, and dissolved gas exchanged with headspace gas on the surfaces of water droplets, bubbles, and Raschig rings. Gas circulated through the equilibrator in a pressure-controlled loop, and was sampled from the equilibrator loop at a flow rate of 3 mL min⁻¹.

A unique aspect of the equilibrator is that the headspace gas pressure was adjusted to match the total gas tension of the water, thus reducing corrections due to incomplete equilibration of total gas pressure in the equilibrator. The total gas tension was measured using a gas tension device made of a Liquicel MicroModule Membrane Contactor interfaced to a pressure transducer, as described in Rafelski et al. (2013).

Corrections were applied for incomplete equilibration, which were based on a model of equilibrator performance as described in Rafelski et al. (2013). The model required measurements of equilibrator headspace pressure, gas sample flow rate, and the gas exchange coefficient, and allowed for uncertainty in these parameters. Under typical operating conditions, the uncertainty due to the equilibrator system was 2.2 per mil for $\delta(\text{O}_2/\text{N}_2)$, 1.5 per mil for $\delta(\text{O}_2/\text{Ar})$, and 0.059 per mil for $\delta^{18}\text{O}$ (Rafelski et al., 2013).

2.3. Field deployment

Dissolved gases were measured in seawater at the Scripps Institution of Oceanography (SIO) pier in La Jolla, CA from June 22 to August 1, 2011. The SIO pier is located at $32^{\circ} 52.52'N$, $117^{\circ} 15.30' W$. It extends 330.4 m from shore and is 10.2 m above the ocean surface, which we define as the mean lower low water (MLLW) level. The bottom depth at this location is around 5 m below MLLW, but can vary with sand movement. As described in Rafelski et al. (2013), seawater was pumped into an air-conditioned lab on the pier approximately 35 m east of the end of the pier, from a fixed location 2 m below MLLW. With this configuration, the sampling depth, measured relative to the instantaneous water surface, varied with waves and tides. Water was pumped at a flow rate of 40 L min^{-1} using a submersible effluent pump (Little Giant). Some of the water flowed through a line that filtered the water before it flowed into the equilibrator and the gas tension device. The rest of the water flowed into a 95-L insulated tank (Igloo Products Corp.), in which the gas tension device and an optode O_2 sensor (Aanderaa) were submerged. The optode was calibrated using Winkler titrations to measure the dissolved O_2 concentration in seawater taken from the sampling line. The optode oxygen concentration was multiplied by 1.012 to match the optode data to the Winkler titrations.

Measurements of salinity, chlorophyll, and water pressure at depth were obtained from the Southern California Coastal Ocean Observing System (SCCOOS), which has a station at the SIO pier at 5 m depth (relative to MLLW), which is near the ocean floor. Chlorophyll data were adjusted using surface chlorophyll concentration measurements from the SCCOOS Harmful Algal

Bloom program, which measures chlorophyll concentration every few days by extracting chlorophyll from bottle samples. The 5 m depth chlorophyll data were multiplied by 2.15 to bring the values into agreement with the surface measurements. Measurements of photosynthetically active radiation (PAR) and wind speed were obtained from the SIO pier weather station. Water temperature was measured using 9 temperature sensors mounted to a pier piling (a “temperature chain”), with vertical resolution of approximately 1 m (provided by Eric Terrill, Coastal Observing R&D Center, Scripps Institution of Oceanography).

2.4. *Biological oxygen*

Changes in dissolved oxygen saturation are caused by both physical processes (such as water temperature changes), and biological processes (photosynthesis and respiration). Craig and Hayward (1987) showed that, because Ar and O₂ have similar responses to physical processes, but Ar is not affected by biological processes, the saturation of Ar can be used to resolve the physical component of the O₂ saturation. The residual biological component is known as the “biological oxygen saturation,” %O_{2(bio)}, and can be defined as (Hendricks et al., 2004):

$$\%O_{2(bio)} = \frac{([O_2]/[Ar])}{([O_2]_{sat}/[Ar]_{sat})} \quad (4)$$

where [O₂] and [Ar] are the concentrations of oxygen and argon dissolved in water, and the subscript *sat* is the concentration at saturation. Here we apply this same formula, instead using [O₂]/[Ar] from the equilibrated air stream and replacing [O₂]_{sat}/[Ar]_{sat} with the molar abundance ratio of these gases in background air. This approach yields an equivalent estimate of %O_{2(bio)}

because the ratios of dissolved gases versus equilibrated air are related by solubility coefficients, which cancel in the numerator and denominator. As in Luz and Barkan (2009), we calculate the gas ratios using observed delta values, yielding the relation:

$$\%O_{2(bio)} = \frac{\delta(O_2/Ar) + 1}{\delta(O_2/Ar)_{air} + 1} \quad (5)$$

The quantity $\delta(O_2/Ar)$ is measured in the equilibrated air stream, and $\delta(O_2/Ar)_{air}$ is the atmospheric value. Here, $\delta(O_2/Ar)_{air}$ is close to zero because our reference gas was very close to atmospheric composition.

We then convert the biological saturation to concentration units:

$$\Delta[O_2]_{bio} = (\%O_{2(bio)} - 1)[O_2]_{sat} \quad (6)$$

where $[O_2]_{sat}$ is calculated using the measured temperature and salinity and the equations in Weiss (1970). By this definition, a positive value of $\Delta[O_2]_{bio}$ means net photosynthesis has occurred, and a negative value means net respiration has occurred. We similarly express the optode measurements in terms of the deviation from saturation ($\Delta[O_2]$) by subtracting the O_2 concentration at saturation from the O_2 concentration measured by the optode.

3. O_2 and $\delta^{18}O$ model

Simple models of biological O_2 saturation and $\delta^{18}O$ can be used to determine rates of primary productivity. Models used previously have ranged in complexity from box models that include only photosynthesis, respiration, and air-sea gas exchange (Venkiteswaran et al., 2007; Quiñones-Rivera et al.,

2007, 2009), to more complex models that also include advection and diffusion terms (Quay et al., 1993; Levine et al., 2009). We use a one-box model that includes photosynthesis, respiration, air-sea gas exchange, and mixing:

$$h \frac{dC}{dt} = P - R + k(C_{sat} - C) + M(C_m - C) \quad (7)$$

where h is the box depth, C is the oxygen concentration, P is the gross oxygen production from photosynthesis, R is autotrophic and heterotrophic respiration, k is the gas exchange coefficient, M is the mixing rate, C_{sat} is the oxygen concentration at saturation, and C_m is the oxygen concentration of water in a hypothesized subsurface box, with which surface waters are constantly exchanging. P , R , M , h , and C_m are free parameters in the model. C_{sat} is determined from the mean water temperature and salinity using the equations in Weiss (1970).

We define k using the wind-speed parameterization of Ho et al. (2006), and the measured mean squared wind speed of $7.88 \text{ m}^2 \text{ s}^{-2}$. In our model, k has a value of 0.4 m day^{-1} for oxygen. Although air-sea gas exchange may be enhanced at the coast due to increased turbulence and bubble entrainment from breaking waves (Melville, 1996; Upstill-Goddard, 2006), it may also be diminished due to the presence of surfactants from phytoplankton (Upstill-Goddard, 2006). In the absence of parameterizations that take into account these and other variables, we use the Ho et al. (2006) parameterization for simplicity.

Similarly, the equation describing the evolution of $\delta^{18}\text{O}$ is:

$$\begin{aligned} h \frac{d}{dt}(CX^{18}) = & PX_w^{18}\alpha_p - RX^{18}\alpha_r + k\alpha_k(C_{sat}X_{sat}^{18} - CX^{18}) \\ & + M(C_mX_m^{18} - CX^{18}) \end{aligned} \quad (8)$$

The term X^{18} is the ratio of $^{18}\text{O}^{16}\text{O}$ to $^{16}\text{O}^{16}\text{O}$, and can be substituted with $(1+\delta^{18}\text{O}/1000)$, where $\delta^{18}\text{O}$ is in units of per mil. The subscripts w , sat , and m represent oxygen in H_2O , dissolved O_2 in water at saturation with air, and dissolved O_2 in the subsurface box, respectively. We use atmospheric O_2 as the reference value for $\delta^{18}\text{O}$. The parameters α_p , α_r , and α_k are the fractionation factors of photosynthesis, respiration, and kinetic gas exchange, respectively. To compare the model with observations, the value of $\delta^{18}\text{O}_{sat}$ is subtracted from the computed $\delta^{18}\text{O}$ because our measured O_2 is in equilibrium with dissolved O_2 , and therefore offset from dissolved $\delta^{18}\text{O}$ by the equilibrium fractionation.

The model requires as inputs estimates of $\delta^{18}\text{O}_w$, $\delta^{18}\text{O}_{sat}$, and $\delta^{18}\text{O}_m$. Measurements of $\delta^{18}\text{O}_w$ of the seawater at the SIO pier give a mean value of -0.5 per mil on the SMOW scale (Chun-Ta Lai and Lisa Welp, personal communication), or -23.46 per mil relative to atmospheric O_2 (Hendricks et al., 2004). The value of $\delta^{18}\text{O}_{sat}$ is 0.73039 per mil at the mean measured water temperature of 19.24°C , relative to atmospheric O_2 (Benson and Krause, 1980). The parameter $\delta^{18}\text{O}_m$ is left as a free parameter, which is fit using $\delta^{18}\text{O}$ data.

The model also requires estimates of α_k , α_r , and α_p . For α_k we use a value of 0.9972 (Knox et al., 1992). For α_r and α_p we adopt two alternate sets of values, the first based on Luz and Barkan (2011) of $\alpha_r = 0.9803$, $\alpha_p = 1.004$, and the second based on Hendricks et al. (2004) of $\alpha_r = 0.978$, $\alpha_p = 1$. These choices are rationalized as follows: Based on the long-held assumption that photosynthesis does not fractionate oxygen (Guy et al., 1993), the fractionation factor of respiration has been found to be 0.978-

0.979 (Quay et al., 1993; Hendricks et al., 2004, 2005). However, recent work suggests that photosynthesis does fractionate oxygen (Eisenstadt et al., 2010). Based on this finding, Luz and Barkan (2011) suggest a global average α_r of 0.9803, and α_p of 1.004 for the surface ocean.

Equations 7 and 8 are solved with forward time stepping with prescribed variations in P . Studies have shown that photosynthesis rates are a function of irradiance (e.g. Platt and Jassby, 1976; Marra et al., 1985), and will increase with irradiance until a saturation level is reached, and then either stabilize or decrease (photoinhibition) with increasing irradiance. In the absence of measurements of the photosynthesis-to-irradiance relationship during sampling, we choose a saturation level of $500 \mu\text{mol photons m}^{-2}\text{s}^{-1}$, which is within the range of observed values (e.g. Gilstad et al., 1993; Meyer cordt et al., 1999; Yoshie et al., 2010), and we assume that there is no photoinhibition. Therefore, P is modeled as:

$$P = \begin{cases} xPAR & \text{if } PAR < 500 \\ x \times 500 = P_{max} & \text{if } PAR \geq 500 \end{cases} \quad (9)$$

where PAR is the photosynthetically active radiation and is in units of $\mu\text{mol photons m}^{-2}\text{s}^{-1}$, x is a conversion factor between PAR and the rate of photosynthesis, and P_{max} is the maximum daily photosynthesis rate. As shown in Equation 9, P at any time during the day can be determined if PAR and P_{max} or x are known. The timing of P_{max} is influenced by the cycle in PAR, but the value of P_{max} is also influenced by other factors such as the availability of nutrients in the water. These other factors are implicitly included in the scaling term x . PAR is prescribed using the average diurnal cycle in

measured PAR. The parameter P_{max} (or equivalently, x) is a free parameter in the model. In the model, R is replaced with $\bar{P}/R$, where $\bar{P}$ is the mean photosynthesis rate over 24 hours. Overall, there are 6 free parameters: h , P_{max} , M , C_m , $\bar{P}/R$, and $\delta^{18}\text{O}_m$, which we assume are constant with time, except for special cases discussed in Section 5.3. These parameters are adjusted to fit observations.

4. Experimental results

4.1. Timeseries of $\Delta[\text{O}_2]_{bio}$ and $\delta^{18}\text{O}$

The timeseries of measurements from the SIO pier are shown in Figure 2. Except for brief gaps due to instrument maintenance, we obtained nearly continuous measurements from June 22 to August 1, 2011. Biological O_2 was supersaturated for most of the record, with concentrations as high as 55 mmol m^{-3} (125% saturation), but during the first week, there were periods when the concentration dropped as low as -18 mmol m^{-3} (92% saturation). Values of $\delta^{18}\text{O}$ were nearly all negative relative to the atmosphere, which is consistent with enhanced O_2 due to photosynthesis. Both biological O_2 concentration and $\delta^{18}\text{O}$ showed strong diurnal variability.

A “regime change” in the biological O_2 concentration, $\delta^{18}\text{O}$, chlorophyll concentration, salinity, and water temperature occurred around July 12. Compared to the period before July 12, the period after was characterized by less variability in biological O_2 concentration, $\delta^{18}\text{O}$, temperature, and salinity, and by lower chlorophyll concentrations. Temperature profile data showed that until July 12, temperatures below 14.5°C were seen at depths between 2.3 and 5 m (Figure 3). After July 12, temperatures this low were not ob-

Figure 2: Data from the SIO pier. Times are in Pacific Standard Time. Biological O_2 concentration ($\Delta[\text{O}_2]_{\text{bio}}$) and $\delta^{18}\text{O}$ were measured using the mass spectrometer. $\delta^{18}\text{O}$ here and in all other figures is relative to air. $\Delta[\text{O}_2]$ was measured using the optode. Chlorophyll, pressure, and salinity are from the SIO pier SCCOOS station, at 5 m depth. Chlorophyll concentration was adjusted using surface bottle measurements, as described in the Section 2.3. Water temperature was interpolated to 2 m depth from the temperature chain data. Photosynthetically active radiation (PAR) and wind speed (u) are from the SIO pier weather station. The dashed vertical line at July 12 marks a regime change, as described in the text.

Figure 3: Temperature profile from the SIO pier. Times are in Pacific Standard Time. The depth is relative to MLLW. The tidal height (from the NOAA La Jolla, CA station) is shown in black. When the water level was lower than a sensor on the temperature chain, the temperature at that sensor is not shown. The dashed vertical line at July 12 marks a regime change, as described in the text.

served. In the Southern California Bight, water with a temperature above 14.5°C has a nitrate concentration below the detection limit of approximately $1\ \mu\text{mol L}^{-1}$ (Lucas et al., 2011). These data suggest that around July 12, there was a reduction in the nutrient availability, which caused a decrease in production.

4.2. Observed diurnal cycle

To assess the spectral characteristics of the biological O_2 concentration and $\delta^{18}\text{O}$, we used the Lomb-Scargle periodogram technique, a frequency analysis method for unevenly spaced data (Lomb, 1976; Scargle, 1982). The results show a peak at a frequency of 1/day, supporting the presence of a regular diurnal cycle, and no peaks at higher frequencies, suggesting that tidal variations contributed little to the observed variability. The data were

bin-averaged by hour of the day to determine the mean diurnal cycles, shown in Figure 4 along with the standard error of the mean. Biological O_2 and $\delta^{18}O$ were strongly anti-correlated, and stabilized late at night. The amplitude of the cycle in $\Delta[O_2]_{bio}$, calculated using the mean values from 4:30-7:30 and 16:30-19:30, was 19 mmol m^{-3} , which agrees well with the amplitude of the O_2 concentration measured by the optode, 22 mmol m^{-3} . The amplitude of the $\delta^{18}O$ cycle was 1.1 per mil. Previous measurements of daily variations in oxygen in the nearby La Jolla Kelp Forest showed an amplitude of 63 mmol m^{-3} , with a standard deviation of 39 mmol m^{-3} (Frieder et al., 2012). Diurnal variability in $\delta^{18}O$ has not previously been observed for this length of time, but a shorter study in Sagami Bay, Japan, showed a diurnal cycle in $\delta^{18}O$ with an amplitude of around 0.6 per mil (Sarma et al., 2005).

The peak in $\Delta[O_2]_{bio}$ was shifted from the peak in PAR by around 6 hours, which is consistent with observations of dissolved O_2 in the Chesapeake Bay (Sanford et al., 1990). Because PAR is correlated with instantaneous production, and biological O_2 concentration gives a measure of production integrated over time, this lag is consistent with photosynthesis driving the observed cycle in O_2 .

Temperature and salinity both showed semi-diurnal variability. As illustrated in Figure 3, colder periods occurred during both high and low tides, indicating that this variability was not due to changes in the absolute depth of the pump intake. Instead, these variations could have been due to internal tides bringing in sub-thermocline water, which would be consistent with other observations in the Southern California coastal ocean described in Lucas et al. (2011). The variability in temperature and salinity did not

Figure 4: Mean diurnal cycle in biological O₂ concentration, $\delta^{18}\text{O}$, O₂ concentration measured by the optode, chlorophyll concentration, temperature at 2 m depth, squared wind speed, salinity, and photosynthetically active radiation. The same 24-hour period is shown twice.

correlate with the variability in O_2 or $\delta^{18}O$, suggesting that internal tides were not a primary driver of oxygen variability.

The amplitude of the biological O_2 cycle can be used to estimate a lower bound on the photosynthesis rate. A rise in $\Delta[O_2]_{bio}$ of 19 mmol m^{-3} over 12 hours suggests a minimum mean photosynthesis rate of $1.6 \text{ mmol } O_2 \text{ m}^{-3} \text{ hr}^{-1}$ during the day, in the limiting case where no processes compensate for the photosynthetic O_2 buildup. The true rate of photosynthesis must be higher than this, because some compensation due to respiration, gas exchange, and mixing must have occurred.

4.3. Observed relationship between biological O_2 concentration and $\delta^{18}O$

The anti-correlation between $\Delta[O_2]_{bio}$ and $\delta^{18}O$ is consistent with previous measurements in subsurface water showing that as O_2 decreases with depth, $\delta^{18}O$ tends to increase, as expected from fractionation during respiration (Kroopnick and Craig, 1976; Bender and Grande, 1987; Quay et al., 1993). When $\delta^{18}O$ is plotted against $\Delta[O_2]_{bio}$, the subsurface data from Kroopnick and Craig (1976) fall along a relatively tight line, whereas our data have a sharp upper limit, but fan out below the line (Figure 5A). The deviations from the upper limit in our data were closely tied to temperature, as shown in Figure 5B. Colder water tended to have lower $\delta^{18}O$ values for a given biological O_2 concentration, compared to warmer water. The cold water data are explored more in Section 5.4.

4.4. Nocturnal O_2 decrease

An important constraint on the processes is the nighttime decrease in biological O_2 (Figure 4). The decrease was most rapid between 18:00 and

Figure 5: (A) Data from this study shown with data from Kroopnick and Craig (1976), for which we calculated the deviation from oxygen saturation using their reported values of percent saturation and oxygen concentration. The isotopic composition of dissolved oxygen in equilibrium with the atmosphere (0.73039 per mil) was subtracted from the Kroopnick and Craig data to put it on the same scale as our data. The line is a fit to the Kroopnick and Craig data that fall between -65 and 0 mmol m^{-3} . (B) Data from this study. The color of the point corresponds to the water temperature when that measurement was taken. The mean diurnal cycle is shown in black.

0:00, with a much slower decrease the remainder of the night, and with O_2 remaining supersaturated even though photosynthesis does not occur at night. If air-sea gas exchange or respiration were the primary driver of the nighttime decrease, the biological O_2 concentration would not be expected to remain supersaturated, because air-sea gas exchange would drive the O_2 concentration to saturation, and respiration would be expected to continue to decrease the O_2 concentration throughout the night. As discussed further below, we hypothesize that this decrease is driven primarily by mixing with a subsurface or offshore reservoir with a lower, but still supersaturated, O_2 concentration.

5. Model results and discussion

5.1. Diurnal cycle

We now use the box model described in Section 3 to account for the regular diurnal cycles in biological O_2 and $\delta^{18}O$. A Levenberg-Marquardt algorithm was used to fit the model to the O_2 cycle. Prior to optimization, the model was run with specified parameter values to assess the relationships among the parameters and determine the key control parameters. From these runs we found that P_{max}/h and M/h were insensitive to both h and C_m , with P_{max}/h constrained to be $4.7 \text{ mmol } O_2 \text{ m}^{-3} \text{ hr}^{-1}$ and M/h constrained to be around 2.7 day^{-1} based on the rate of decrease in O_2 supersaturation after sunset. $\bar{P}/R$ was sensitive to changes in C_m . Because h is effectively arbitrary, we set h to 2.5 m, just below the depth of the pump in the water. We set C_m to a series of fixed values so that a range of best-fit values for $\bar{P}/R$ could be found. We left P_{max} , $\bar{P}/R$, and M to be determined by

the optimization. Then, using these best-fit values, $\delta^{18}\text{O}$ data were used to determine $\delta^{18}\text{O}_m$.

Table 1 and Figure 6 show results of the optimizations. For C_m between 100% and 112% saturated, P_{max}/h was $4.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$, M was 6.8-6.9 m day^{-1} and $\bar{P}/R$ was 0.6-4.4. For C_m below 99%, the model failed to reproduce the stabilization of O_2 late at night. The C_m values used are supported by CalCOFI oxygen profiles taken in August 2011 from a station located around 10 km north of the SIO pier and 4 km offshore, and a station 26 km west of the pier. At these stations, water is supersaturated in oxygen down to around 17 km or 28 km depth, with supersaturations in oxygen up to around 112%.

Because we observed a regime shift in the data starting July 12, we also calculated mean diurnal cycles for the data before July 12 and after July 12, and fit our model to these observations (Table 1, Cases 7 and 8). P_{max}/h was $6.0 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ before July 12, and $3.5 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ after July 12. The modeled mixing rate was 8.1 m day^{-1} before July 12 and 6.1 m day^{-1} after July 12. $\bar{P}/R$ for both of these time periods was similar to the modeled $\bar{P}/R$ for the entire set of observations.

Other measurements provide independent support for some parameter values. P_{max}/h is consistent with chlorophyll measurements from the SIO pier, as explained in Section 5.2. P/R values of 0.6-4.4 are supported by a survey of coastal ocean measurements showing an average P/R ratio of 1.17, with a range of 0.03 to 34.3 (Duarte and Agustí, 1998). M was 6.8 to 6.9 m day^{-1} for a depth of 2.5 m. One hypothesis is that this mixing rate is a measure of upwelling offshore, where the mixed layer is deeper, and that

this offshore mixed layer is also mixed horizontally with water at the pier. In terms of the model construction, this can be thought of as expanding the size of the box, so that it includes the offshore, deeper mixed layer. In this case, h would be much greater than 2.5 m, which would require a greater M in order to fit the O_2 decrease rate after sunset. For example, a mixed layer depth of 20 m would require a mixing rate of 54-83 m day⁻¹. Because upwelling in Southern California has a rate of only 6-12 m day⁻¹ (King and Barbeau, 2011), it is unlikely that the mixing we observed is primarily due to upwelling. Instead, the water we observed could have been part of a diurnal surface layer, which mixed with slightly deeper water above the thermocline (Lynn and Svejksky, 1984).

Our model analysis suggests the following conclusions. We find that the cycle in O_2 and $\delta^{18}O$ is primarily a balance between photosynthesis, respiration, and mixing; air-sea gas exchange is a very small contribution (1-6% of the sum of respiration and mixing fluxes). The rapid drawdown in O_2 after sunset is explained by mixing, while the subsequent slowing is caused by the surface water and the subsurface water becoming well mixed by around midnight.

5.2. *Photosynthesis rate*

The photosynthesis rate is constrained independently by the amplitudes of the diurnal cycles in biological O_2 and $\delta^{18}O$. Fitting to O_2 yields a daily maximum photosynthesis rate of 4.7 mmol O_2 m⁻³ hr⁻¹ (Table 1, Cases 1-4). Fitting to the cycle in $\delta^{18}O$ instead of O_2 yields a P_{max}/h of 3.7-4.5 mmol O_2 m⁻³ hr⁻¹ depending on the values of α_r and α_p used (Table 1, Cases 5-6). Given the structural constraints of the model, P_{max} doesn't vary by more

Figure 6: Mean measured diurnal cycle, as shown in Figure 4, and the modeled diurnal cycle of biological O₂ concentration and $\delta^{18}\text{O}$, using four of the cases described in Table 1. The bottom panel shows how the photosynthesis rate varied over 24 hours, for Cases 1-4.

Table 1: Best-fit parameters for the O₂ and $\delta^{18}\text{O}$ diurnal cycle model. Bolded numbers were set for that run, and non-bolded numbers were fit using the model.

Variable	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7 ^a	Case 8 ^b	Case 9 ^c	Case 10 ^d
h (m)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
P_{max}/h (mmol O ₂ m ⁻³ hr ⁻¹)	4.7	4.7	4.7	4.7	4.5	3.7	6.0	3.5	3.8	4.9
M (m day ⁻¹)	6.8	6.9	6.8	6.9	10.3	10.4	8.1	6.1	7.0	6.8
$\bar{P}/R$	4.4	1.0	0.6	1.0	1.0	0.9	1.1	0.9	1.0	1.0
C_m (mmol m ⁻³) ^e	0	14.2	28.3	14.2	13.9	14.8	14.2	14.2	14.2	14.2
$\delta^{18}\text{O}_m$ (per mil)	-0.4	-1.6	-2.6	-1.5	-1.5	-1.5	-1.9	-1.3	-1.6	-1.6
α_r	0.9803	0.9803	0.9803	0.978	0.9803	0.978	0.9803	0.9803	0.9803	0.9803
α_p	1.004	1.004	1.004	1	1.004	1	1.004	1.004	1.004	1.004
Data used for fit	O ₂	O ₂	O ₂	O ₂	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$	O ₂	O ₂	O ₂	O ₂

^a Model was fit to data before July 12.

^b Model was fit to data after July 12.

^c Respiration rates were twice as high at night as during the day.

^d Air-sea gas exchange was varied based on the measured diurnal cycle in the mean squared wind speed.

^e Expressed as the deviation from saturation, $\Delta[\text{O}_2]$.

than 25%.

The modeled peak photosynthesis rate of $3.7\text{--}4.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ can be reconciled with the observed chlorophyll concentration of $2.55 \mu\text{g L}^{-1}$ assuming a conversion factor of $1.5\text{--}1.8 \text{ mmol O}_2 (\text{mg Chl a})^{-1} \text{ hr}^{-1}$. Assimilation numbers, which are typically measured using ^{14}C incubations, relate chlorophyll concentration to carbon production at light-saturation. During our study, the mean observed light levels of $500\text{--}1400 \mu\text{mol photons m}^{-2}\text{s}^{-1}$ were presumably at or near saturation based on photosynthesis versus irradiance curves (e.g. Gilstad et al., 1993; Meyercordt et al., 1999; Yoshie et al., 2010). Using the modeled peak photosynthesis rate, the measured chlorophyll concentration, and a ratio of O_2 production to ^{14}C production of $2.7\text{--}3.5$ (measured isotopically or via O_2/Ar ratios; Bender et al., 1999; Laws et al., 2000; Hamme et al., 2012), we calculate an assimilation number of $5.1\text{--}8.0 \text{ mg C (mg Chl a)}^{-1} \text{ hr}^{-1}$. This is well within the typical assimilation number range of $2\text{--}10 \text{ mg C (mg Chl a)}^{-1} \text{ hr}^{-1}$ (Laws et al., 2002).

5.3. Sensitivity to model assumptions

To assess how changes in the model structure would change the results, we also carried out runs that allowed for diurnal variations in respiration and air-sea gas exchange. In one run, respiration was increased at night, as possibly supported by Duval and Geen (1976) and Pavlova (1994) (Table 1, Case 9). A doubling of the respiration rate at night relative to the day decreased P_{max}/h from 4.7 to $3.8 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$, and did not significantly change M or $\bar{P}/R$.

In another run, we allowed the gas exchange to vary with the time of day based on the measured variations in wind speed and the Ho et al. (2006) wind-

speed parameterization (Table 1, Case 10). The mean squared wind speed varied between $3.5 \text{ m}^2\text{s}^{-2}$ at night and $16.0 \text{ m}^2\text{s}^{-2}$ at midday (Figure 4). The model showed a slight increase in P_{max} from 4.7 to 4.9 $\text{mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$, and no significant change in M or $\bar{P}/R$.

5.4. Relationship between O_2 and $\delta^{18}\text{O}$

In Section 5.1, we showed that the mean diurnal cycle, which represents part of the upper envelope of the relationship between O_2 and $\delta^{18}\text{O}$ (Figure 5B) can be explained by photosynthesis, respiration, and mixing. If the model is run with a higher photosynthesis rate, the full range of the upper envelope can be reproduced. However, this model does not explain the low oxygen, low $\delta^{18}\text{O}$ values observed. Because these data correspond with lower water temperatures, it is possible that this water came from greater depth than the rest of the data. One hypothesis is that these points are explained by incursions of thermocline water that has been exposed to sunlight, but has not had significant contact with the atmosphere.

To test this hypothesis, we used only photosynthesis and respiration in our model to drive changes in thermocline water. We used initial values, C_i and $\delta^{18}\text{O}_i$, that fall along a linear fit to the Kroopnick and Craig data shown in Figure 5. Consistent with Bender and Grande (1987), the properties evolve along a series of curves depending on the P/R ratio, as shown in Figure 7. We find that, using either set of fractionation factors ($\alpha_r = 0.978$ and $\alpha_p = 1$ or $\alpha_r = 0.9803$ and $\alpha_p = 1.004$), the model can explain the anomalous cold water data (Figure 7). The results shown are examples of conditions that can describe the data, but other combinations of starting values and P/R ratios could also be used.

Figure 7: A) Time evolution of a water parcel starting at 85% or 90% oxygen saturation ($\Delta[\text{O}_2]_{\text{bio}} = -35.4$ or -23.6 mmol m⁻³), with different P/R ratios, for $\alpha_r = 0.978$ and $\alpha_p = 1$. Points show data from this study, as also shown in Figure 5. Stars show the gross O_2 production in increments of 50 mmol O_2 m⁻³. The dot-dash line shows the fit to the Kroopnick and Craig (1976) data shown in Figure 5. (B) Time evolution of a water parcel starting at 70% or 75% oxygen saturation ($\Delta[\text{O}_2]_{\text{bio}} = -59.0$ or -70.8 mmol m⁻³), with different P/R ratios, for $\alpha_r = 0.9803$ and $\alpha_p = 1.004$.

6. Conclusions

Using an equilibrator interfaced with a mass spectrometer, we observed dissolved O_2/N_2 , O_2/Ar , and $\delta^{18}\text{O}$ in the coastal ocean over a period of 5 weeks, obtaining the first continuous measurements of $\delta^{18}\text{O}$. We observed diurnal cycles in biological O_2 concentration and $\delta^{18}\text{O}$, and showed that these cycles can be explained primarily by photosynthesis, respiration, and mixing with a subsurface region of supersaturated water. The average peak daily photosynthesis rate of $3.7\text{--}4.7 \text{ mmol O}_2 \text{ m}^{-3} \text{ hr}^{-1}$ is consistent with the chlorophyll-based light-saturated photosynthesis rate, using a ratio of O_2 -based production to ^{14}C -based production of 2.7–3.5. We used the measurements in biological O_2 concentration and $\delta^{18}\text{O}$ to identify intrusions of thermocline water which was previously exposed to light but not to gas exchange during upwelling.

The narrow spatial extent of our observations limited the conclusions that could be drawn from our model. P/R in the model depended on the $\delta(\text{O}_2/\text{Ar})$ and $\delta^{18}\text{O}$ of water offshore and at depth. Vertical profiles of $\delta(\text{O}_2/\text{Ar})$ and $\delta^{18}\text{O}$ offshore would have helped us to better constrain P/R . Although we were able to use CalCOFI oxygen profiles from a similar time period, simultaneous measurements of $\delta^{18}\text{O}$ would have provided an independent constraint on P/R . These measurements would also have helped constrain the P/R that led to the low O_2 , low $\delta^{18}\text{O}$ observations described in Section 5.4. Furthermore, continuous measurements of $\delta(\text{O}_2/\text{Ar})$ and $\delta^{18}\text{O}$ at depth offshore would have given us a better understanding of how these properties changed over time. In the future, continuous measurements of $\delta^{18}\text{O}$ and O_2 at a range of depths could allow for a better calculation of P/R , or the use of

more complex 1-D models.

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