Random error analysis of marine $x\text{CO}_2$ measurements in a coastal upwelling region

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Abstract

Quantifying and identifying measurement error is an ongoing challenge for carbon cycle science to constrain measurable uncertainty related to the sources and sinks of CO₂. One source of uncertainty in measurements is derived from random errors (ϵ); thus, it is important to quantify their magnitude and their relationship to environmental variability in order to constrain local-to-global carbon budgets. We applied a paired-observation method to determine ϵ associated with marine x CO₂ in a coastal upwelling zone of an eastern boundary current. Continuous data (3-hr resolution) from a mooring platform during upwelling and non-upwelling seasons was analyzed off of northern Baja California in the California Current. To test the rigor of the algorithm to calculate ϵ we propose a method for determining daily mean time series values that may be affected by ϵ . To do this we used either two or three variables in the function, but no significant differences for ϵ mean values were found due to the large variability in ϵ (-0.088 ± 27 ppm for two variables and -0.057 ± 28 ppm for three variable). Mean ϵ values were centered on zero, with low values of ϵ more frequent than greater values, and follow a double exponential distribution. Random error variability increased with higher magnitudes of x CO₂, and in general, ϵ variability increased in relation to upwelling conditions (up to ~9% of measurements). Increased ϵ during upwelling suggests the importance of meso-scale processes on ϵ variability and could have a large influence seasonal to annual CO₂ estimates. This approach could be extended and modified to other marine carbonate system variables as part of data quality assurance/quality control and to quantify uncertainty (due to ϵ) from a wide variety of continuous oceanographic monitoring platforms.

Index terms *Random error, marine CO₂, upwelling*

1. Introduction

In order to accurately estimate and predict global CO₂ budgets it is essential to determine potential sources of uncertainty that may be due to spatial heterogeneity (Borges, 2009; Reimer et al., 2013), temporal variability (Takahashi et al., 2009), and uncertainty due to measurement errors (Cueva et al., 2015). Most studies of CO₂ sources of variability in the surface ocean have focused on identifying spatial and temporal variations (Bates et al., 2014; Takahashi et al., 2009; Wanninkhof et al., 2013). Determining the magnitude of different sources of errors (i.e., random and systematic) is of critical importance for quality assurance (QA) and quality control (QC) protocols, and leads to a better understanding sources of uncertainty (Raupach et al., 2005). Therefore, an improved understanding of uncertainties may allow us to increase the quality of measurements and modeling efforts of the carbon cycle (Michalak et al., 2011; Raupach et al., 2005).

In the oceans $x\text{CO}_2$ (partially dry mole fraction of CO₂) is measured and used to estimate the partial pressure of CO₂ at saturation ($p\text{CO}_2$); but to date there is no practical approach to estimate uncertainties due to random errors within these important measurements in the oceans. Thus, there seems to be a community need for general improvements of standard of QA/QC for data sets. For example, the Washington State Blue Ribbon Panel Report (2012) and The California Current Acidification Network (C-CAN) Core Monitoring Principles Report (McLaughlin et al., 2013) call for establishing specific guidelines for defining the quality of data sets for marine carbonate system parameters. Presently, a standardized set of protocols established by the Surface Ocean CO₂ Atlas (SOCAT; Bakker et al., 2014) outlines QA/QC and has developed a protocol that requires reporting of accuracy and precision associated with systematic errors, but does not have a method for determining the magnitudes of random errors.

While random errors have received much attention in the terrestrial carbon cycle science community over the last decade (Cueva et al., 2015; Hagen et al., 2006; Menzer et al., 2013; Savage et al., 2008), the quantification and statistical characterization of random error has not been widely examined in the marine science community.

Two possible sources of uncertainty are associated to direct measurements: systematic and random errors (ϵ). Systematic errors, such as system offsets, have a constant value that may be determined during instrument calibration prior to deployment and then corrected for during post-deployment QA/QC. Instrument drift, another systematic error, is a tendency in the measurement value and is also corrected for during traditional QA/QC procedures though may not be a constant value throughout the experimental campaign (Campbell et al., 2013). In contrast, ϵ in experimental measurements are influenced by unknown and unpredictable changes in the experiment, and the values vary across time. An important distinction between systematic and ϵ , is that we cannot correct for ϵ in a time series although we can identify the magnitude and report a range (Hollinger and Richardson, 2005; Richardson et al., 2006; Savage et al., 2008, Cueva et al 2015). Furthermore, ϵ do not affect the mean of the measurements (e.g., daily, seasonal, or annual mean) but they affect the variability around that mean so uncertainty (i.e., standard deviation, 95% confidence intervals of means, standard error) increases (see schematic of this behavior in Figure 1). In this study, we define *uncertainty* as a range of values where an individual measurement is expected to fall, although we recognize that there are slightly different definitions for this term (Billesbach, 2011; Regan et al., 2008).

The use of autonomous moored systems for observing marine CO₂ over time is increasing, and with their ability to auto-calibrate, these systems are often deployed for months to years without system maintenance. Typically, system offsets are assessed pre- and post-

deployment to determine if there has been system drift (i.e., systematic errors), which is then corrected for in post-processing (Sutton et al., 2014). A comprehensive study of *in situ* accuracy and precision of National Oceanographic and Atmospheric Administration (NOAA) MAPCO₂ systems, similar to the sensor used in the present study, determined that their overall precision is 0.7 $\mu\text{mol mol}^{-1}$ (ppm) for sea water and 0.6 $\mu\text{mol mol}^{-1}$ for air (Sutton et al., 2014). These quantities represent <1% of typical marine and atmospheric observations, and are therefore not likely to substantially affect the true value of the measurement.

We propose that quantifying ϵ associated to ocean CO₂ measurements, specifically from moorings, may give insights into sensor function under different environmental conditions, and is an important step in identifying sources of measurement errors in coastal and open ocean estimates of $x\text{CO}_2$, air-sea CO₂ exchange, and therefore carbon budgets. In general, marine studies of $x\text{CO}_2$ and estimations of air-sea CO₂ exchange usually combine all potential errors (i.e., due to natural variations, spatial variability, and ϵ) into one calculation usually represented by the standard deviation (σ) or through error propagation techniques (Lauvset et al., 2013; Omar et al., 2007; Takahashi et al., 2002). These calculations do not provide insights into the sources of errors and how natural environmental variability influences them. For example, a standard deviation value could include diurnal and seasonal variability, depending on the time scale analyzed, whereas, reporting a separate value for ϵ specifically shows that this value is not considered part of the natural variation. In general, quantifying and isolating the contributions of all errors (i.e., systematic and random) is challenging (Schmidt et al., 2012), however, previous attempts have been made. Specifically, 13% of the overall error in the global air-sea CO₂ flux was assigned to ϵ , and another 10% was assigned to ϵ for wind speed in the calculation of the gas transfer velocity but with no systematic or quantitative justification (Takahashi et al., 2009). In

contrast, terrestrial studies on land-atmosphere interactions have been reporting ϵ in measurements of air-land CO₂ fluxes for over a decade (Hollinger and Richardson, 2005). Terrestrial studies report that in some cases systematic error is greater than ϵ (Dragoni et al., 2007; Savage et al., 2008). For example, early analyses of systematic errors in eddy covariance land-atmosphere CO₂ fluxes found that this type of error could range from 10 to 20% of the measured CO₂ flux due to compounding of errors from the various instruments involved (Moncrieff et al., 1996). Whereas Dragoni et al. (2007) and Cueva et al. (2015) found that the relative value of ϵ only accounted for up to 4% of ecosystem scale CO₂ fluxes and 2.4% of soil CO₂ fluxes, respectively. In the present study we show similar results, that systematic error is typically greater than ϵ , however, there are exceptions when ϵ can be higher than systematic error, as measurements are not perfect. The reported systematic error for mooring p CO₂ observations is typically up to 2% (Friederich et al., 1995; Sutton et al., 2014), but calculated p CO₂ includes temperature, salinity, and atmospheric pressure (and associated random and systematic errors). Therefore, a total estimation of 13% by Takahashi et al. (2009) could be an inaccurate representation of ϵ for air-sea CO₂ exchange from mooring derived time series observations. We suggest that the marine community is in need of developing specific methods for direct estimation of magnitudes of uncertainty derived by different sources of errors.

The objective of this study is to characterize ϵ associated with measurements of x CO₂ in the coastal ocean of an eastern boundary current where upwelling is a common occurrence. We study the characteristics and magnitudes of ϵ and propose a method that statistically identifies and isolates ϵ from measurements that is well suited for non-stationarity measurements such as x CO₂. The region under consideration, similar to other eastern boundary currents (e.g., Benguela and Humboldt currents), is characterized by year round upwelling with a strong seasonal

component (Palacios, 2004). We hypothesize that ϵ scales with increased $x\text{CO}_2$; therefore ϵ will be greater during upwelling. Previous studies in terrestrial carbon science have shown that higher land-atmosphere fluxes are associated with higher ϵ values (Savage et al., 2008; Cueva et al., 2015); we expect that this will also be the case for marine measurements. We also hypothesize that different environmental conditions (e.g., upwelling, wind driven turbulence), will affect the magnitude and variability of ϵ , therefore causing the magnitude of ϵ to increase. This hypothesis is supported by the finding that environmental variability influences the concentration of $x\text{CO}_2$; during upwelling $x\text{CO}_2$ is higher than non-upwelling conditions in this region (Reimer et al., 2013) and could also affect the value of ϵ . Finally, we determine which environmental conditions have the greatest effect on ϵ , and how the magnitude of ϵ compares with the determined systematic error of the sensor. The ultimate goal of the manuscript is to inspire the development of alternative ways to calculate ϵ and encourage the refinement of this aspect of QA/QC in ocean measurements.

2. Methods

2.1 Study Site and data collection

Temporal continuous observations ($x\text{CO}_2$, sea surface temperature [SST], and sea surface salinity [SSS]) were collected from a mooring platform off the Baja California Pacific coast outside Todos Santos Bay, Ensenada, Mexico (31.811° N, 116.809° W). This mooring platform is part of FLUCAR, a consortium of scientists interested in quantifying and understanding the controls of carbon fluxes off the coast of Mexico (Vargas et al., 2012). The study site is characterized by year round upwelling (caused by Northwest winds) with stronger more persistent events from February-March through July-August (Palacios, 2004).

The mooring is equipped with an Infrared Gas Analyzer (LI-6252, Li-Cor, Lincoln, NE) to measure $x\text{CO}_2$ in the surface water and in the air (1 m above sea level), as well as SSS and SST sensors (Sea Bird Electronics 37SN Microcat CT, Bellevue, Washington). For a complete description of the mooring, designed and constructed at the Monterey Bay Aquarium Research Institute see *Friederich et al. (1995)* and *Friederich et al. (2002)*. Wind data (discussed below) were collected from a meteorological station on Todos Santos Island, approximately 20 km from the location of the mooring (Reimer et al., 2013). Since the wind speed is measured via a > 10 m tower, we did not adjust the wind speed to that referred to as U_{10} .

2.2 Data processing

We used observations of $x\text{CO}_2$ (partially dry mole fraction) collected at three-hour intervals during 2009, 2010, and 2013. We do not convert $x\text{CO}_2$ to $p\text{CO}_2$, as this requires a calculation using SST, SSS, and atmospheric pressure for two interrelated reasons: 1) there is inherent ϵ associated with SST, SSS, and atmospheric pressure measurements that would add an additional source of ϵ in $p\text{CO}_2$; and 2) since SSS and SST are used to determine ϵ (see below), then using them to calculate another value would skew the statistical results and may result in spurious relationships. The systematic error in the observations was determined and corrected for using a system offset that was calculated periodically (yearly) against the GlobalView atmospheric $x\text{CO}_2$ observations from the closest site (Scripps' La Jolla Pier). The system was calibrated prior to deployment using known concentrations of several CO_2 standards (Friederich et al., 2002; Pierrot et al., 2009). Since deployment may be up to over a year it is necessary to recalculate the offset periodically as atmospheric CO_2 concentrations increase, furthermore, there is inherent measurement drift that is known to occur with these types of systems over time. It

should be pointed out that the mooring used in this study was an earlier design that did not have an onboard standard for calibrating the gas analyzer during deployment; therefore the values for $x\text{CO}_2$ in the air (i.e., marine boundary layer) were used to determine instrument drift during post-deployment QA/QC (Reimer et al., 2013). Instrument drift of our mooring system was up to 6 ppm, and accounted for $< 1\%$ of mean value of measurements over the course of the study period. The pre-deployment systematic error was up to ± 2 ppm; these values are similar to previously reported values for systematic error for similar early systems (Friederich et al., 1995; Pierrot et al., 2009). New systems have been improved by having an onboard standard for calibrating the gas analyzer during deployment (Sutton et al., 2014).

Measurement QA/QC practices were applied to observations prior to determining ϵ which include: first, $x\text{CO}_2$ values were adjusted for the maximum system drift of 4 ppm (determined as the post deployment offset) and second, de-spiking (± 3 standard deviations) removed outliers. A revision of field notes from maintenance visits did not identify periods potentially influenced by biofouling. All outliers were removed, which accounted for $< 1\%$ of observations, leaving us with $\sim 99\%$ of observations from measurements of 2009, 2010, and 2013 after the QA/QC process.

SST and SSS, also measured on the mooring, were used to determine the sea water density at the surface using the definition of sigma t (σ_t); water density at a given temperature. We use the water density to establish boundary conditions for determining ϵ (see explanation below) and for examining physical environmental variability.

2.3 Statistical determination of ϵ and application to oceanographic CO_2 data sets

There are different recognized methodologies to estimate ε , primarily presented in eddy covariance literature. In a first attempt to estimate ε in land-atmosphere carbon fluxes, Hollinger et al. (2004) used a “paired-sensor” approach, where the authors took advantage of having two identical eddy covariance systems located ~775m apart in a commercial forestland. It was assumed that both towers were influenced by similar environmental conditions, and that the difference between simultaneous measurements contains information about the uncertainty of the measurements. A paired-sensor approach to determine ε at the same study site, or nearby sites, could be difficult and costly, particularly in the coastal ocean where there is higher spatial heterogeneity (Bauer et al., 2013; Reimer et al., 2013).

To implement an efficient and cost-effective approach to estimate ε in measurements of carbon and energy fluxes, Hollinger and Richardson (2005) and Richardson and Hollinger (2005) developed the “paired-observation” approach. This approach trades space for time; instead of using measurements from two different instruments at the same time, it uses two measurements from the same instrument at the same place. These measurements are differentiated by 24 hours and the method requires that environmental conditions are the same 24 hours apart (this analysis is discussed further below). This approach has been demonstrated to be versatile by estimating ε across a variety of terrestrial ecosystems (e.g., boreal, temperate, evergreen forests, deciduous forests, cropland fields, and grasslands), as well as using different sensors (e.g., closed and open path infrared gas analyzers, solid state diffusion probes), and measurement techniques (e.g., eddy covariance, soil respiration chambers, gradient method, forced diffusion approach).

The paired-observation approach assumes that ε could be characterized statistically if multiple observations, from a time series, were collected at the same location (Finkelstein and Sims, 2001; Richardson et al., 2006). We assume two paired measurements (M):

$$X_{t=0} = M + \varepsilon_1 \quad (1)$$

$$X_{t=24} = M + \varepsilon_2 \quad (2)$$

where ε_i is a random variable with variance $\sigma^2(\varepsilon)$, then ε in the measured values (i.e., X_1 and X_2 at time t , 24 hours apart) could be quantified by determining the variability of ε [$\sigma(\varepsilon)$]. Thus, the variance of the difference ($X_1 - X_2$) is:

$$\sigma^2(X_{t=0} - X_{t=24}) = \sigma^2(X_{t=0}) + \sigma^2(X_{t=24}) + 2cov(X_{t=0}, X_{t=24}) \quad (3)$$

Assuming that ε_i is independent and identically distributed:

$$\sigma^2(\varepsilon) = \sigma^2(X_{t=0}) = \sigma^2(X_{t=24}) \quad (4)$$

$$cov(X_{t=0}, X_{t=24}) = 0 \quad (5)$$

Then, rearranging Equation 3 and substituting Equation 1 and Equation 2, we obtain:

$$\sigma(\varepsilon) = \frac{\sigma(X_{t=0} - X_{t=24})}{\sqrt{2}} \quad (6)$$

where $\sigma(\varepsilon)$ is the standard deviation, or variability of ε (discussed below), $X_{t=0}$ is the measurement (i.e., *in situ* $x\text{CO}_2$) taken at time (t) zero, and $X_{t=24}$ is the paired-observation taken exactly 24-hours later (see explanation of 24-hour interval below).

To ensure that the difference between the two measurements, $X_{t=0}$ and $X_{t=24}$, were due to ε , and not to otherwise natural variability in environmental factors, only data collected under similar conditions, and with $x\text{CO}_2$ measurements that do not differ by more than ± 1 standard deviation (of the mean for all the observations) were used. “Similar conditions” refers to environmental conditions that are comparable from one day to the next, for each pair of days (e.g., measurements made with a lag of 24 h), the second day (i.e., $d_{t=24} \dots d_{t=47}$ of the day d_{t+1})

must have similar conditions of different independently measured variables (e.g., SST, wind speed, water density) as the first day (i.e., $d_{t=0} \dots d_{t=23}$ of the day d_t). Therefore, the average value of the independent variables of the second day must fall within ± 1 standard deviation of the mean conditions of the first day (i.e., $\mu_{IMV,dt} + 1\sigma_{IMV,dt} > \mu_{IMV,dt+1} > \mu_{IMV,dt} - 1\sigma_{IMV,dt}$). If these conditions were not met then measurements were not considered for the estimation of ε as we assume that there were different environmental conditions between the pair of days, and consequently the independent variables and xCO_2 are not comparable.

When choosing environmental boundary variables to establish similar conditions there are various factors and principles that must be considered. It generally follows that CO_2 variability is a function of air-sea exchange, horizontal and advective mixing, SST, and net biological activity (Takahashi et al., 2002). Physical oceanographic boundary conditions (SST and water density) give insights into upwelling versus relaxed conditions as well as temperature driven thermodynamic changes in xCO_2 . Since rains are highly episodic in the arid climate off of northern Baja California and there are no rivers, we assume that horizontal transport of low salinity water masses from the coastal zone to the near-shore mooring is negligible. Whereas, water density may be used as a measure of vertical transport of dense waters upwelled from depth to the surface. Wind speed represents turbulence-driven gas invasion or evasion at the air-sea interface and therefore gives insights into the potential for differences in xCO_2 due to air-sea exchange. SST and water density represent regional meso-scale water mass movement (tides and upwelling) (Reimer et al., 2013) that transport scalar variables such as all carbonate system parameters (xCO_2 , dissolved inorganic carbon, pH, and total alkalinity) (Nash et al., 2012). At this time we do not have observations that would allow us to define biochemical boundary conditions such as nitrate (NO_3^-), dissolved inorganic carbon (DIC), and/or total alkalinity (TA),

though we suggest that further analyses of ϵ using these variables need to be preformed. Furthermore, while percent oxygen saturation is calculated on this mooring, the estimations necessary to determine net community production (NCP), another potential measure of biologically driven changes, would introduce an additional, and likely relatively high, uncertainty (Shadwick et al., 2015; Xue et al., 2015). Thus, we argue that including NCP (derived from percent oxygen saturation) as a boundary conditions could influence the magnitude of ϵ and result in inaccurate or imprecise results. Another drawback is that neither DIC, nor TA, are measured at the same frequency as $x\text{CO}_2$ time series yet, also hindering the use of a biological boundary condition. While DIC and TA can be calculated from known relationships, these values, similar to NCP, will also carry their own uncertainty (Shadwick et al., 2015; Xue et al., 2015). Therefore, we limit the selection of boundary conditions to variables measured by independent sensors that coincide with $x\text{CO}_2$ measurements rather than adding variables estimated from empirical models that could propagate an unknown uncertainty.

Net biological activity in the California Current has been approximated using estimates of new production (Plattner et al., 2005), yet this method, unfortunately, is not appropriate for generating a boundary condition for ϵ using the paired-observations approach because new production is a calculated value. Plattner et al. (2005), however, address a key issue with respect to decoupling that occurs in upwelling systems between new production and export production due to lateral transport. If we had observations of NO_3^- from an autonomous system (Johnson et al., 2013), then we could potentially use these as a biological boundary in conjunction with density, which could resolve the issue of decoupling between export and net biological activity for the experiment. Changing NO_3^- concentrations could indicate additions via respiration or decreases due to biological uptake. At present, however, due to a lack of a

specific biological boundary condition, we note a few key considerations, specifically, while biological production (uptake of CO₂) in the California Current is largely driven by the availability of upwelled nutrients (Palacios, 2004) and therefore follows SST (already a boundary condition), biological respiration is a factor which should be considered. Changes in DIC will affect the total CO₂ pool considerably during and after bloom periods in the near-shore off Baja California (Feely et al., 2008; Ribas-Ribas et al., 2011). We recognize that organic matter remineralization in any environment is in part dependant on metabolic activity, which is also influenced by temperature; however, this dependence on temperature is also known to decrease at low temperatures during chlorophyll *a* maxima (Azam et al., 1994). For the purpose of this study to suggest an approach to estimate ϵ , we assume that temperature, in addition to the rest of the boundary conditions may explain a large proportion of the biological activity, but we recognize that alternative approaches should be explored.

The paired method requires that observations are only valid if all boundary conditions are satisfied (Hollinger and Richardson, 2005); therefore, the more boundary conditions that are considered in the algorithm, and the lower the allowed difference (defined by the standard deviation threshold) the more rigorous it is. We applied a high level of rigor to select paired observations, thus we preformed the analysis using two (water density and wind speed) and three (water density, SST, and wind speed) boundary conditions within ± 1 standard deviation.

The 24-hour interval was used because of changes in diurnal cycles and the similar period of the regional tidal cycle. Tides are internal nonlinear waves that carry scalar components (Alford et al., 2012), and any differences or similarities based on the tidal cycle will be determined by equation 1 (i.e., changes within 24-hours). Since the frequency of our measurements was every three hours and the tidal period is just over 25 hours, a 24-hour interval

to establish similar conditions is adequate. Furthermore, we are unable to resolve variability on a lower frequency (i.e., using one hour data to resolve for the 25 hour tidal period) due to our resolution of only every three hours. We assume that this interval will capture the diurnal biological cycle, micro-scale wind variability for air-sea exchange and subsequently the $x\text{CO}_2$ concentration, wind-induced wave generated turbulent variability in the surface layer that affects air-sea exchange, an almost full tidal cycle (two high and two low tides), and finally meso-scale variability, such as coastal upwelling (Reimer et al., 2013).

Previous studies, using different techniques to measure carbon fluxes and approaches to estimate ε across a variety of ecosystems, have reported that ε converge into similar statistical characteristics on its probability distributions (Cueva et al., 2015; Richardson and Hollinger, 2005; Savage et al., 2008). The ε is reported as a function of its standard deviation [$\sigma(\varepsilon)$] using a double exponential or Laplace probability density distribution, described by the function:

$$f(x) = e^{-|x|/\beta}/2\beta \quad (7)$$

where β is the double exponential or Laplace function and the standard deviation of distribution is $\sigma = (\sqrt{2}\beta)$, where:

$$\beta = \sum_{i=1}^n |x_i - \bar{x}|/N \quad (8)$$

and N is the sample population. We will show that this is also the case for the present work.

Sensor-specific ε is one of the sources of uncertainty when comparing CO_2 concentrations at the same site (Fratini et al., 2013), therefore for this reason, and because we are limited by instrumentation at the mooring site, we feel that the paired-observation approach is a likely first step in estimating ε in the marine environment. There are ongoing efforts to ground truth mooring observations with underway CO_2 systems, which provide observations from similar sensors (for example underway measurements from closed path Licor-7000 with moored

closed path Licor-820); however, these studies are limited to only several observations within a few hours (Wei-Jun Cai, personal communication) and spatial heterogeneity, especially in coastal regions, could affect these comparisons. Therefore, ground truthing efforts may not be able to give insights into ϵ . Finally, we believe that the statistical method presented here could be a reasonable first attempt at isolating and quantifying ϵ in oceanographic settings.

2.4 Analyses of the variability and seasonality of ϵ

For comparison between the magnitude of $x\text{CO}_2$ and corresponding $\sigma(\epsilon)$, as well as $\sigma(\epsilon)$ with environmental data, we bin the values of $\sigma(\epsilon)$ to remove the effect of non-stationary variability over time, that is the effect of the daily cycles such as wind and thermal heating (Cueva et al., 2015; Hollinger and Richardson, 2005). Furthermore, by separating the data into bins we examine the distributional properties and the effects of the different environmental conditions on $\sigma(\epsilon)$, which gives us insights into the factors that may influence sensors to produce erroneous values. Bins were defined for SST in 1 °C increments for the range of temperatures that satisfy the criteria for similar days. Water density and $x\text{CO}_2$ were divided into 10 bins and wind was divided into eight bins ranging from 0 to 12 m s⁻¹ because there were no ϵ values for the higher wind speeds (12 to 18 m s⁻¹). A weighted least squares regression analysis was used to find relationships of $\sigma(\epsilon)$ with $x\text{CO}_2$ and environmental variables (SST, wind, and water density). A weighted least squares regression reduces the influence of outliers and could be a better estimation of the relationship of ϵ with $x\text{CO}_2$ and environmental variables since we have only a few estimation of ϵ at the high and low ends of the probability distribution (see results section). This regression analysis, with our defined boundary conditions, ignores bins of data that had fewer than 10% of the mean number of observations for all the bins (Table 1). Here, we

considered outliers to be unlikely environmental events that probably do not represent the “normal” variability of $\sigma(\epsilon)$.

Seasonal properties of $\sigma(\epsilon)$ were studied under upwelling and non-upwelling conditions. Seasonality is not limited to upwelling, however, for this region since biological productivity is primarily influenced by upwelling (Palacios, 2004) we consider these two environmental periods as different seasons. We define upwelling using similar criteria as Reimer et al. (2013): positive (gas evasion) changes in $\Delta x\text{CO}_2$ (the air-sea differential) in conjunction with $\text{SST} \leq 15^\circ\text{C}$. $\Delta x\text{CO}_2$ is higher during upwelling and generally results in $x\text{CO}_2$ release from the ocean to the atmosphere in the study region (Reimer et al., 2013). Once upwelling and non-upwelling conditions were defined, we grouped $\sigma(\epsilon)$ $x\text{CO}_2$ by bins of SST (1 $^\circ\text{C}$ bins) and water density (0.5 kg m^{-3} bins) to determine how environmental factors affect $\sigma(\epsilon)$. Seasonality is defined by SST and water density because these two parameters are generally used to distinguish recent upwelled waters. Bins with values that do not fit the criteria for upwelling or non-upwelling conditions are considered to be some “other” condition. For example, if the SST is low, but the $\Delta x\text{CO}_2$ is negative, then it is likely that these characteristics simply represent seasonally low SST. All data analyses were conducted using Matlab 2014a (MathWorks Inc.).

3. Results

3.1 Three boundary conditions: SST, wind, and water density

Of the 6040 observations (755 days) we found 2,448 observations (306 days; 41% of all observations) met our criteria for similar conditions (i.e., similar days) to estimate the value of ϵ (Figure 2A). We report both the mean and median values of ϵ to show that there is influence from the few high values of ϵ (Table 1 and Figure 3A). The median (0.40 ppm) and mean (-

0.057 $\pm$ 28 ppm) ϵ values were centered on zero ($< |1|$ ppm for $x\text{CO}_2$; Table 1) and the frequency distribution is characterized as having long tails and a prominent central peak (Figure 3B). Therefore, this distribution seems to be best approximated by a double exponential distribution rather than a normal or Gaussian distribution (Figure 3A). A Kolmogorov-Smirnov test confirms that the distributions of ϵ are not normal ($p < 0.05$; Table 1), and the strong kurtosis of the distributions (values >4 ; Table 2) suggest a double exponential distribution. The skewness values (<1 ; Table 1) suggest that the distribution of ϵ is symmetrical, and in accordance with the characteristics of a double exponential distribution where 76% of the data points fall within $\pm 1\sigma$.

3.2 Two boundary conditions: wind and water density

Repeating the analysis with two boundary conditions we find that there were 2,592 observations (324 days; 43% of the observations) that met the criteria for similar days (Figure 2B). Figures 2C and 2D are a subsection of the longer time series in Figure 2A and 2B, where it can be seen that two boundary conditions (panel D) result in slightly more similar days than three boundary conditions (panel C), as a result of a less strict selection criteria. Using only two boundary conditions did not generally change the results observed with three boundary conditions, with the kurtosis and skewness showing that the mean value is centered on zero, the distribution is non-Gaussian and better represented by a double exponential distribution (Table 1 and Figure 3B). The mean ϵ value (-0.088 ± 27 ppm) for the two boundary conditions is not statistically different than for the three boundary condition, however, the median is (0.12 ppm).

3.3 Seasonality of ϵ

For all the binned data we found a significant linear relationship (using weighted linear least squares fits) between binned values of the variability of ϵ [$\sigma(\epsilon)$] and environmental variables (SST, wind, and water density) (Figure 4A to F). To highlight the importance of ignoring outliers in this case we summarize the results of simple linear regression analysis in Table 3 and present a more detailed discussion in Supplementary Materials (Supplementary Materials Figure 1). The $\sigma(\epsilon)$ present a negative relationship with SST and a positive relationship to water density and wind (Figure 3). Tables 2 and 3 summarize the criteria for the bins used in the linear weighted least squares regression analysis and equations of the best fit lines. The $\sigma(\epsilon)$ increases with increasing $x\text{CO}_2$ magnitude (Figure 5).

Further seasonal analysis shows that the interquartile range for both upwelling and non-upwelling conditions are not statistically different, however, the spread of the outliers and the standard deviations are greater during upwelling (Figure 6). The remaining “other” observations occurred during physical oceanographic characteristics that may represent transitions periods between upwelling and non-upwelling or some other condition that we cannot identify at this time and will therefore not be discussed further.

4. Discussion

4.1 The magnitude of random errors

The mean values for ϵ determined in this study (Table 1), for both applications of the algorithm, are lower than the determined system offset (± 6 ppm; post deployment processing of this system) as well as the precision (< 0.7 ppm) determined for this system as well as similar systems (Sutton et al., 2014). The standard deviation (up to 28 ppm), however, is higher than the system offset, indicating that in some circumstances ϵ may be very important. The difference in

the mean of the two applications of boundary conditions is likely due to the difference in the number of observations analyzed due to the stricter conditions that must be met. Mean ϵ with three boundary conditions accounts for $\sim 0.02\%$ of the mean $x\text{CO}_2$ (389 ppm) for this study, but could account for up to 4% during upwelling when $x\text{CO}_2$ is highest. Here we discuss a possible framework to calculate ϵ for $x\text{CO}_2$ measurements, and we hope that this method ignites further research and approaches to calculate ϵ by the oceanographic community using larger data sets from a variety of regions.

4.2 Environmental influence on random errors

Our results support the main hypotheses of this study that: 1) higher magnitudes of $x\text{CO}_2$ have higher associated ϵ ; and 2) the variability of ϵ [$\sigma(\epsilon)$] increases with increasing magnitude of $x\text{CO}_2$ and during upwelling (decreasing SST and increasing water density), as well as with increasing wind speed (Figures 4, 5, and 6). Upwelling occurs year round in this region, however, there is a strong seasonal component, with higher $x\text{CO}_2$ from roughly March to September (Palacios, 2004; Reimer et al., 2013). Although, the mean ϵ is not different during upwelling and non-upwelling periods, significantly higher values of $\sigma(\epsilon)$ do occur periodically during upwelling periods (Figure 6). Reimer et al. (2013) identified the response times of air-sea CO_2 flux changes to SST of zero hours (less than the time from one high frequency observation to the next) during upwelling and up to 6 hours (up to two high frequency observations) for relaxed periods. These time periods are well within the inertial period for Ekman transport (between 24 and 27 hours) for the Baja California peninsula (Walsh et al., 1974), as well as the tidal cycle (25 hours) and suggest that physical changes in the water column within this period are influencing the environmentally-associated changes in $\sigma(\epsilon)$.

The better fit of the distribution of ε to a double exponential distribution suggests that high values of ε are less frequent and low values are more frequent than for a normal distribution (Figure 3). The overall frequency of large ε is not common but does exist, and our *in situ* observations are not greatly biased with respect to the mean ε . The mean value of ε accounts for less than 1% of the mean $x\text{CO}_2$ observations. In general ε is less than previously reported systematic errors, which could account for up to 0.5% (Sutton et al., 2014), but could also be higher than the system offset for the sensors used in the present study. Therefore, this 1% of ε , over greater integrated spatio-temporal domains, could have a greater influence on annual CO_2 budgets.

Increased $\sigma(\varepsilon)$ were also influenced by higher wind speeds (Figure 4). Since wind is considered to be an important influence on air-sea CO_2 fluxes, it is likely that further studies will show that higher CO_2 may be influenced by higher magnitudes of ε . On daily time scales wind in this region represents meso-scale (upwelling) as well as micro-scale variability (Reimer et al., 2013). Micro-scale surface turbulence, such as whitecapping and breaking waves release CO_2 from the ocean, therefore it is likely that in regions where waves are breaking or due to time of day (thermal wind), $\sigma(\varepsilon)$ will be higher. We recognize, however, that further research is needed and we hope this study motivates the scientific community to explore uncertainties in $x\text{CO}_2$ as well as air-sea exchange values across the world's oceans.

In this study we focus on the meso-scale processes that influence ε including upwelling, tidal cycles, and daily thermal changes. The three hour interval of the time series is sufficient enough to capture the variability of meso-scale processes, which are the most prominent mechanisms influencing $x\text{CO}_2$ variability at this study site (Reimer et al., 2013). Micro-scale processes, such as breaking waves and bubbles, likely cannot be represented with respect to $\sigma(\varepsilon)$

in the present study due to our relatively low sampling frequency compared with the interval on which micro-scale processes occur (seconds to minutes). To resolve micro-scale processes future work must use a higher sampling frequency. With mooring platforms that have up to one hour frequencies now available, it is likely that we will be able to better estimate ε in time series observations, because with a greater number of observations (higher sampling frequency) the apparent changes from one observation to the next will decrease, though this will still not allow us to resolve micro-scale processes.

4.3 Three versus two boundary conditions

Boundary variables used to define similar conditions allow the user to select independently measured variables to constrain ε , with the more variables that are used, the stricter the method is. Because we do not have a variable that directly represents the biological influence on $x\text{CO}_2$, we believe that using three boundary conditions could better approximate the influence of ε than using only two. Notably, the results from the two analyses (two and three boundary conditions) were similar and mean ε were not statistically different. These results should be tested across different regions and environmental conditions. We found that the number of observations used to calculate ε varies with the number of boundary conditions and therefore could influence ε under rapidly changing environmental conditions.

Future studies of ε in the marine environment should seek to include a variable to represent the biological influence on ε as well as part of a set of boundary conditions. While a biological boundary condition would improve estimations of ε , considerable financial resources must be invested to obtain a direct measurement of this parameter. As mentioned in section 2.3, calculated parameters used to typically estimate biological productivity carry their own

uncertainty, which could influence ϵ . The present study, with currently available resources, provides robust and consistent analyses using the two and three selected conditions (derived from direct measurements), but we call for exploration on how adding direct measurements to determine a biological boundary condition could influence ϵ . If, however, one wished to attempt to include a biological boundary condition, although we are not able to, we suggest that if direct observations are not available, estimating continuous NO_3^- from discrete NO_3^- - SST empirical relationships (Yoder et al., 1985) could be a potentially useful method. Again, we caution that any calculated variable could introduce other uncertainties. Simple experiments with, and without NO_3^- values, as we have implied with testing two and three boundary conditions, could give insights into uncertainties associated with the derived values.

4.4 Considerations for calculation of random errors

There are advantages and disadvantages across approaches to estimate ϵ in observations. Side-by-side sensor comparisons in the field (i.e., paired-sensor approach) should highlight sensor specific differences, but it will be costly and therefore more difficult to implement than the paired-observation approach presented in this study. Another disadvantage for paired-sensor studies is that even with a mobile sensor it could take a long time for a regional-to-national assessment of uncertainty in measurements across a network (e.g., Schmidt et al., 2012). Though, future work in assessing uncertainty and ϵ could include a paired-sensor study of the network of NOAA MAPCO₂ employed to monitor surface ocean $x\text{CO}_2$. We emphasize that assessing errors and uncertainty in controlled laboratory settings, as is carried out pre- and post-deployment, cannot emulate the often rapidly changing environmental conditions that occur during field campaigns and are likely to influence ϵ .

The paired-observation approach offers an alternative method to evaluate the uncertainty in measurements attributable to ϵ . This approach has demonstrated its robustness and applicability to different techniques to measure CO₂ and other variables: 1) carbon and water fluxes at ecosystem level (Kessomkiat et al., 2013; Richardson et al., 2006); 2) soil CO₂ efflux (Savage et al., 2008; Cueva et al., 2015); and 3) x CO₂ measurements from ocean mooring platforms (present study). We recognize, however, that the paired-observation approach also has limitations that should be carefully considered. For example, the time series used to estimate ϵ are shortened at the moment of establishing boundary conditions for similar days; making it impossible to attribute a specific ϵ to every measurement. Moreover, the paired-observation compared with a paired-sensor approach has been found to disagree with other estimates of uncertainty in terrestrial x CO₂ studies by up to 20-25% (Richardson et al., 2006), however, no reason was given for this disagreement. It is unknown yet if there is the potential for this magnitude of disagreement in the marine environment. Therefore, the estimated uncertainty obtained from the paired-observation approach could be taken as an upper limit of confidence intervals until such time that we are able to assign a value to the amount of uncertainty represented by ϵ values.

Estimations of uncertainty are influenced not only by the method used (paired-observation or -sensor), but also by the length of the time series (size of data) (Liu et al., 2009), the magnitude of the variable measured (Richardson et al., 2006), and the frequency and quality of measurements (Billesbach, 2011). We recognize that our proposed method along with the calculated magnitudes and patterns of ϵ should be tested at other marine sites and with different approaches. We postulate that even though ϵ is sensor specific, since it is due to the sensor's

response to environmental variability, we believe that our method is a robust first approach to describe and quantify ε in marine environments.

5. Conclusions

Our results show that ε and $\sigma(\varepsilon)$ increase at higher $x\text{CO}_2$, lower SST and higher σ_t (upwelling), and higher wind speeds (outgassing and upwelling). Since ε , unlike systematic offset values, is not constant, it is higher during upwelling. In this case our upwelling $x\text{CO}_2$ concentrations may be similar to those not only in other upwelling regions (coastal and equatorial), but also in other coastal environments such as estuaries and marshes where CO_2 concentrations are typically higher due to high respiration rates (Cai et al., 2003). Random error is site and sensor specific, and must be calculated for discrete sets of observations across different sites around the world. Because it is expected that $\sigma(\varepsilon)$ increases with higher $x\text{CO}_2$ future studies should focus on regions with higher concentrations. Larger spatial and temporal data sets (that include El Niño versus La Niña conditions), as well as those from different marine environments (specifically net heterotrophic ecosystems such as estuaries, as well as low latitude and equatorial upwelling regions) should be analyzed to further our ability to constrain uncertainty of the global ocean carbon cycle. Accurate and precise measurements are crucial to be able to develop the best models possible, if we are able to identify ε , as we have attempted in this study, then we will be able to account for it in future synthesis studies. Since modeling studies typically have higher associated uncertainty, ε values may not be as important since they are typically very small in comparison to climatological study uncertainty (Takahashi et al., 2009). Distinguishing between natural variability and sources of error is an important step in reducing or understanding uncertainty around CO_2 in all environments and improving modeling

efforts (Michalak et al., 2011). Therefore, random error estimate of 13% of the calculated annual global air-sea CO₂ exchange applied by Takahashi et al. (2009) could be improved or verified if this (or an alternative) method were applied to the various time series across the global oceans as well as to continuous air measurements.

While we acknowledge that ϵ is a small portion of potential values, and generally less than systematic error determined for similar systems, it could be a measure of observational quality as well as an important step in reporting transparency. Furthermore, when using $x\text{CO}_2$ values to calculate $p\text{CO}_2$, all sources of errors will be carried through the calculations. Then $p\text{CO}_2$ in conjunction with other carbonate system variables such as DIC and TA can be used to calculate pH and the saturation state of calcium carbonate minerals; therefore there is a need to determine how ϵ may affect these other calculated values. We suggest that this method be applied to other components of the carbonate system to quantify and constrain error (due to ϵ) from a wide variety of continuous oceanographic monitoring systems.

Regions affected by intrusions of corrosive waters (ocean acidification) are now considered a high priority for resolution of uncertainty and error (Michalak et al., 2011); the method for ϵ analysis presented here may prove to be an important tool for showing statistical certainty and the potential influence of ϵ in these regions. Based on the results presented here, higher concentrations of $x\text{CO}_2$ could have higher associated ϵ and $\sigma(\epsilon)$, and therefore greater measurement error. This approach could be applied to other types of data (e.g., pH, DIC, and TA) to quantify the magnitude of ϵ and identify the environmental conditions that affect it. Future studies should also test how different boundary conditions could be used to define similar biological and physical environmental conditions and consequently their influence on ϵ . We hope

that this work inspires the development of alternative ways to calculate ϵ and ignite the refinement of QA/QC across the oceanographic community and networks.

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Table

Table 1. Statistical analyses of random errors using two (wind and density) or three (wind, SST, and density) boundary conditions. The n -values in parentheses refer to the number of similar days identified in each trial. The last two rows refer to the number of similar days for each condition.

Result	3 boundaries ($n = 2,448$)	2 boundaries ($n = 2,592$)
Mean error (ppm)	-0.057	-0.088
Standard deviation (ppm)	28	27
Median (ppm)	0.40	0.12
Kolmogorov-Smirnov test	$p < 0.05$	$p < 0.05$
Kurtosis	8.13	9.75
Skewness	0.078	-0.053
Upwelling	515	465
Non-upwelling	1,933	2,127

Table 2. Weighted least squares criteria used in the linear regression analyses to determine the relationship of ε to environmental variables. The mean values are the mean number of observations (i.e., random errors) in all the bins for each analysis. 10% of the mean is the number of observations that must be in each bin, otherwise that specific bin is ignored in the regression.

Analysis	Mean observations $\pm$ 1 s.d.	10% of the mean	Value of bin interval	Number of Bins excluded
3 boundary conditions				
SST	216 $\pm$ 183	22	1 °C	3
Water density	245 $\pm$ 180	25	0.5 σ_t	1
Wind	194 $\pm$ 360	19	1.5 m s ⁻¹	3
xCO ₂	245 $\pm$ 368	25	41 ppm	3
2 boundary conditions				
SST	216 $\pm$ 183	22	1 °C	3
Water density	261 $\pm$ 173	26	0.5 σ_t	1
Wind	324 $\pm$ 378	32	1.5 m s ⁻¹	2
xCO ₂	259 $\pm$ 450	26	43 ppm	2

s.d. means standard deviation

Table 3. Linear least squares and weighted least squares fit equations to analyze relationships between random error with environmental conditions for both 2 and 3 boundary conditions. In all equations the variable y is the mean value of the standard deviation of the random error of the bin (x value). “ns” is not significant.

Analysis	Equation	Regression statistics
3 boundary conditions		
Weighted least squares		
SST	$y = -5.6x + 117$	$r^2 = 0.87; p < 0.001$
Water density	$y = 24x - 556$	$r^2 = 0.83; p < 0.001$
Wind	$y = 1.7x + 20$	$r^2 = 0.89; p < 0.01$
$x\text{CO}_2$	$y = 0.21x - 51$	$r^2 = 0.80; p < 0.01$
Least Squares		
SST	$y = -2.9x + 70$	$r^2 = 0.40; p < 0.05$
Water density	$y = 18x - 410$	$r^2 = 0.64; p < 0.01$
Wind	ns	ns
$x\text{CO}_2$	ns	ns
2 boundary conditions		
Weight least squares		
SST	$y = -6.6x + 132$	$r^2 = 0.86; p < 0.001$
Water density	$y = 30x - 699$	$r^2 = 0.89; p < 0.001$
Wind	$y = 2.0x + 17$	$r^2 = 0.84; p < 0.01$
$x\text{CO}_2$	$y = 0.14x - 25$	$r^2 = 0.54; p < 0.05$
Least squares		
SST	ns	ns
Water density	$y = 19x - 424$	$r^2 = 0.62; p < 0.01$
Wind	ns	ns
$x\text{CO}_2$	$y = 0.12x - 14$	$r^2 = 0.42; p < 0.05$

Figure Captions

Figure 1. Conceptual schematic representation of the effect of random error values on a theoretical data set. The grey dashed line represents the mean value of the random error, the dashed black line is the value is the frequency of the occurrence of a theoretical value, and the solid black line is the effect of the random errors on the theoretical data. The mean value does not change, only the distribution around the mean.

Figure 2. Time series of $x\text{CO}_2$ indicating the days that were determined by the algorithm to be similar days (blue squares). The vertical black line indicated a break in the time series where we do not have observations. Panel (A) is the result of the analysis using three boundary conditions (SST, wind, and water density) and panel (B) is the result with only two boundary conditions (wind and water density). Panels (C) and (D), three and two boundary conditions, respectively, are short sections from August, September, and October of 2009 highlighting the different outcomes using the two and three boundary conditions to determine similar days.

Figure 3. Histogram depicting the frequency of the magnitude of ε for the three (panel A) and two (panel B) boundary condition analyses. The solid line is the Gaussian distribution and the dashed line is the double exponential distribution. The double exponential distribution is the best representation for our data with 76% of the data points falling in the range of $\pm 1\sigma$.

Figure 4. Binned values of the $\sigma(\varepsilon)$ and environmental variables for both the two (panels A, C, E; first column) and three (panels B, D, F; second column) boundary condition analyses using a weighted linear least squares approach. Bins are graphically represented by their median value.

For example, SST bins are 1 °C increments from 10 to 23 °C with the tick mark on the x -axis placed in the middle of the bin: the tick for the 11 to 12 °C bin is placed at 11.5 °C. Panels G, I, and K (first column) are the results for the two boundary simple linear regression analysis and panels H, J, and L (second column) are the results for the three boundary simple linear regression analysis. The dashed grey line is the linear fit.

Figure 5. Binned $x\text{CO}_2$ and $\sigma(\varepsilon)$ for two boundary (A) and three boundary (B) conditions with weighted linear least squares. The dashed gray line is the linear fit.

Figure 6. Box plots of ε during upwelling and non-upwelling for the similar days where there are random errors. The black circles represent the outliers for the analysis.

Figure_1

Figure_2

Figure_3

Figure_4

Figure_5

Figure_6