Deep-Sea Research Part II (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Deep–Sea Research II

journal homepage: www.elsevier.com/locate/dsr2

Measurements of pCO_2 and pH from an autonomous surface vehicle in a coastal upwelling system

Francisco P. Chavez*, Jeff Sevadjian, Chris Wahl, Jules Friederich, Gernot E. Friederich

Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039, USA

ARTICLE INFO

Keywords:
Carbon dioxide
pH
Upwelling
Autonomous surface vehicle
Wave Glider
USA
California
Monterey Bay

ABSTRACT

Anthropogenic input of carbon dioxide (CO_2) into the atmosphere and its uptake by the ocean with associated changes in ocean chemistry have created an urgent need to expand coverage of sea surface and atmospheric carbon dioxide observations. Conventional sampling platforms (e.g. ships and moorings) do not provide the spatial and temporal resolution needed to assess the effects of rapidly changing carbon dioxide conditions and are expensive to operate. Through a series of deployments beginning in March 2012, two versions of the Wave Glider autonomous surface vehicles from Liquid Robotics, Inc. have been instrumented with sensors to measure pH, partial pressure of CO_2 (pCO_2) of the atmosphere and sea surface, and wind speed and direction, from which instantaneous sea-air fluxes of CO_2 can be calculated. These deployments, most near Monterey Bay, California, were highly correlated with ΔpCO_2 measurements obtained from the Monterey Bay Aquarium Research Institute's (MBARI) long-term mooring station M1, as well as from shipboard observations. In the central California upwelling system with highly variable pCO_2 levels, the gliders captured large spatial gradients associated with upwelling fronts. Differences in sea surface pCO_2 as large as 470 μatm over $<$ 0.5 km were observed. Unlike traditional ship sampling methods, however, this new generation of sampling platforms is capable of continuous long-term (months) deployments at a fraction of the cost. The vehicles thus have the potential of filling important gaps in present understanding of the effects of global change on ocean chemistry.

1. Introduction

Human activities have increased the concentration of carbon dioxide (CO_2) in the atmosphere from pre-industrial levels of 280 µatm to over 400 µatm in 2014 (Le Quéré et al., 2015). However, anthropogenic CO_2 emissions are over twice as much as what accumulates in the atmosphere with significant uptake by marine and terrestrial environments (Le Quéré et al., 2015). The exact magnitude and variations in the marine sinks remain poorly understood requiring an increase in routine observations over the global ocean. Further, the uptake by the ocean is creating fundamental changes in ocean chemistry, reducing pH and leading to so-called ocean acidification adding to the observation needs. The observations are needed for improved predictions of future atmospheric CO_2 levels, changes in the ocean CO_2 sink, and for improving global carbon budgets (Takahashi et al., 2009). In addition to these overarching large-scale challenges, it is equally important to understand the process-level changes in the carbon cycle that occur over small scales of space and time. These processes are critical to organisms that are sensitive to ocean acidification. Presently, the majority of sea surface pCO_2 observations come from research ships (either by transects or returning regularly to fixed locations), commercial 'ships of opportunity,' or moorings (Takahashi et al., 2009; Monteiro et al., 2009). High operating costs are a critical constraint to improving sampling resolution in both time and space. This lack of resolution has resulted in significant uncertainties in estimates of sea-air CO_2 fluxes over large areas in the Indian, South Atlantic, and South Pacific Oceans (Takahashi et al., 2009) as well as coastal margins (Liu et al., 2000; Pennington et al., 2009; Chen et al., 2013; Takeshita et al., 2015; Bourgeois et al., 2016). At the process level, the high operating costs have also limited understanding of changing pCO_2 on marine communities.

In order to improve sampling over space and time, scientists and engineers have focused over the past decades on the development of relatively small and low-cost autonomous platforms and the sensors that can be deployed on them. The Wave Glider (Liquid Robotics, Inc.) is a self-propelled autonomous surface vehicle (ASV) that uses wave energy for propulsion and solar panels to power the vehicle-control electronics and sensor payload. Although the Wave Glider is a relatively new sensor platform, it has been extensively tested in the field, and has

* Corresponding author.
E-mail address: chfr@mbari.org (F.P. Chavez).

http://dx.doi.org/10.1016/j.dsr2.2017.01.001

0967-0645/ © 2017 Elsevier Ltd. All rights reserved.

proven capable of long-range (> 5000 km) and long-duration (> 500 day) deployments. The vehicle can also run under challenging ocean conditions (6 m seas, 20 m s^{-1} winds) that can make large vessel operations impractical (Hine and McGillivary, 2007; Willcox et al., 2009; Manley and Willcox, 2010; Wiggins et al., 2010). The durability, autonomy, and low operational cost (relative to research ships or oceanographic moorings) of these platforms create tremendous potential for supplementing existing open-ocean and nearshore marine carbon dioxide observing efforts world-wide (Monteiro et al., 2009; Mathis and Feely, 2013). These ASVs could allow for continuous, year-round measurements over large areas of the world's oceans, moving beyond densely-sampled shipping lanes where most carbon dioxide observations are currently obtained.

Wave Gliders operated by the Monterey Bay Aquarium Research Institute (MBARI) have been instrumented with a sensor package to autonomously and continuously sample pH and atmospheric and sea surface pCO_2. Two Wave Glider models (SV2 and SV3) were outfitted with these ocean acidification (OA) sensor packages designed and built at MBARI. Significant engineering was required to adapt earlier designs used in moorings and drifters to fit the package into the Wave Glider body and to ensure quality and reliability of the data with the new platform. A series of over 20 deployments provided the rigorous in situ testing needed to develop and integrate the OA sensor package into the Wave Glider ASV (Table 1). Here, we describe the engineering process, and present data to evaluate the system's performance as well as highlight scientific results.

2. Materials and methods

2.1. Vehicle composition and baseline payload

The Wave Glider ASV consists of three primary components: a buoyant surface float, a submerged diving plane (the glider), and a 4–7-m tether connecting the float and glider. Forward propulsion of the SV2 model is powered entirely by ocean wave energy, utilizing the differential motion of the surface float and submerged glider (Manley and Willcox, 2010). The SV3 model makes use of wave energy as well but is also equipped with a solar-powered thruster for use in calm ocean conditions or strong currents. The vehicle transits at speeds of 0.2–0.8 m s^{-1} depending on the sea state (Manley and Willcox, 2010). Atop the surface float, two solar panels (three on the SV3) power the control electronics and payloads. Energy produced by the solar panels is stored in Lithium-ion rechargeable batteries.

Oceanographic sensors are housed within payload bays at the fore and aft of the surface float. The SV3 model, about 1 m longer than the SV2, can support more payload bays. Between the sensor payload bays, the Command and Control Unit (CCU) dry box houses the primary.

built-in control electronics for the Wave Glider. The Wave Glider Payload Interface Board (PIB) is located in the aft dry box and provides a serial link between on-board sensors and the CCU. An Iridium antenna allows two-way communication between the user and the vehicle and supports data uploads at up to 2-minute intervals. The factory-provided sensor payload for the Wave Glider includes a pumped Glider Payload CTD (GPCTD) from Sea-Bird Electronics (SBE), a dissolved oxygen sensor (SBE 43F), and an Airmar 200-WX weather station. The CTD and oxygen sensors sample every 10 min. The weather station is mounted 1 m above the glider float and provides measurements of wind speed and direction, relative humidity, and air temperature every 10 min.

2.2. Ocean acidification (OA) sensor integration with Wave Glider

The OA package developed at MBARI includes a CO_2 sensor system, a pH sensor, and a control electronic board that acquires data and activates valves, pumps and sensors. The original control and data acquisition system used on the Wave Gliders was a variant of an OASIS (Ocean Acquisition System for Interdisciplinary Science; Chavez et al., 1997) mooring instrument and telemetry controller. OASIS is a general-purpose controller designed for autonomous sensor applications to provide scheduling, sensor control software, data logging, preliminary data processing, and two-way telemetry (Chavez et al., 1997). The present instrument control system for the Wave Glider has been simplified to solely control and log CO_2 and pH. In both cases the control unit provides the Wave Glider Payload Interface Board (PIB) with sensor data once per hour. Liquid Robotics software captures this stream and telemeters the data to shore via Iridium. Independent measurements of pH and pCO_2 allow calculation of dissolved inorganic carbon and total alkalinity. Integrating pCO_2 observations with wind information from the meteorological station allows instantaneous CO_2 fluxes to be calculated.

2.2.1. CO_2 sensor package

The CO_2 sensor package developed for this study evolved from systems designed and built at MBARI for an autonomous pCO_2 device deployed and characterized at mooring Station M1 in Monterey Bay (Friederich et al., 1995). Variations of this initial system are currently deployed on moorings globally by NOAA and other similar institutions (Sutton et al., 2014; Willcox et al., 2009). The present version of the CO_2 sensor package has been redesigned and greatly reduced in size, allowing the CO_2 analyzer, control electronics, valve block and standard to fit within the aft payload dry box of the Wave Glider and to interface with the Wave Glider PIB (Fig. 1a). While improvements to the system have been, and continue to be, made, the basic measurement stages first developed by Friederich et al. (1995), described below, remain.

The components of the CO_2 sensor package include a Licor LI-820 CO_2 analyzer, an equilibrator, air intake, CO_2 standard tank, gas-sampling and valve-switching gas flow circuit, and control board which powers the Licor, acquires data and regulates operation of the valves and pump (Fig. 1; *see also* Supplementary material). With the exception of the equilibrator and air and sea water intakes, all components are housed within the aft dry box. The dimensions of the dry box allow for a more compact arrangement of the sensor components compared to the cylindrical housing design used for moorings and drifters; this additional space was utilized by increasing the size of the CO_2 standard tank to allow for more frequent in situ calibrations. The gas sampling circuit includes a valve block and five valves, which control the flow of gas between the CO_2 analyzer, equilibrator, and standard tank during the different measurement stages. Inside the payload box the air stream is treated to 1) remove moisture and 2) remove CO_2 during the zero stage. A desiccant removes water from the sampled air and prevents moisture in the analyzer. In the zero stage the air is pumped through soda lime, removing the CO_2 and allowing for a zero-reference as part of the measurement cycle.

The Licor LI-820 is an absolute, non-dispersive, infrared gas analyzer, which measures absorption by CO_2 at a wavelength of 4.24 μm over a 14-cm optical path and outputs the mole fraction of CO_2 (xCO_2) in the sample. Licor analyzers are stable, small, and require little power, making them ideal for autonomous operation (Friederich et al., 1995). The accuracy of the LI-820 is quoted as < 3% of the reading, although analysis of data collected during in-house calibrations has suggested the accuracy is more likely < 1%, and the precision is 0.1 μatm. The carbon dioxide measurement cycle consists of seven stages. The instrument control board initiates and ends each of the stages (Friederich et al., 1995; Chavez et al., 1997). A micro diaphragm pump from TCS is used to draw CO_2 samples through the different air circuits; the instrument control board activates the positions of 5 three-way valves based on which of the seven stages is active (Fig. 1). The pump has a 3–6 V DC motor that is run at 5 V through a voltage converter. In the ***equilibrator*** and ***zero stages***, a closed air loop is established with a single input. In the equilibrator stage, air is pumped into the equilibrator tube below the water line (0.2–0.5 m), causing

ARTICLE IN PRESS

Table 1.
Issues and solutions for the Wave Glider ocean acidification payload, by deployment. This table does not include deployments when no issues arose, or when the OA payload was not deployed as part of the sensor package. Data were reviewed to evaluate the OA system performance, and engineering problems were identified and addressed iteratively as a result of trial and error. Totals for vehicle at-sea days and distance travelled are given separately for all deployments, and for the subset of deployments shown here. MB = Monterey Bay, GoM = Gulf of Mexico, St.M = Station M. Station M is located 220 km offshore of San Luis Obispo, California.

Vehicle	Start Date	Location	Days/Distance (km)	Issues	Solutions
SV2	21-May-2012	MB	22.8/825	Equilibrator mast was struck by a ship, no useable CO_2 data following the incident	Newer SV3 model has auto-avoid feature
SV2	29-Aug-2012	MB	24.9/1332	Wave action caused water level in equilibrator to rise, limiting head space at beginning of pump cycle	Water level receded by end of pump cycle, prior to measurement
SV2	15-Oct-2012	GoM	53.0/2260	pH sensor failed	
SV2	23-Jan-2013	GoM	33.0/1263	Wave action caused water level in equilibrator to rise, limiting head space at beginning of pump cycle	Added 'purge' stage in which equilibrator is filled with air, water pumped out
SV2	15-Mar-2013	MB	33.9/1794	Air intake and equilibrator filters plugged over time; pump for CTD flow-path intermittently lost prime, resulting in low pH values	
SV2	6-May-2013	MB	32.9/947	Filters at equilibrator mast plugged over time	Switched from Liquicell membrane filters to Gore-Tex filters
SV2	25-Jun-2013	MB	49.0/1261	Humidity levels in CO_2 sensor flow-path higher than earlier deployments	Installed molecular sieve drying chamber, as part of each sampling cycle
SV2	9-Sep-2013	MB	24.8/1075	Additional deck space required for new Jupiter microscope payload	Components updated with compact versions; allowing for a larger CO_2 standard tank
SV3	21-May-2014	MB	13.8/602	Sea trials; CTD not set up; pH sensor not pumped	
SV3	19-Jun-2014	MB	10.1/256	Sea trials; CTD not set up; pH sensor not pumped	CTD flow-path altered to include pH sensor
SV3	18-Sep-2014	MB	48.8/1777	Intermittent issues venting equilibrator head space	
SV3	12-Feb-2015	MB	33.9/1440	CTD flow-path pump intermittently lost prime, resulting in low O_2 and pH values; Eco-Puck board failed	Eco-Puck board was repaired
SV3	21-Apr-2015	MB	11.7/403	CTD flow-path pump intermittently lost prime, resulting in low O_2 and pH values; Air temp sensor failed	
SV3	1-May-2015	MB	38.4/1433	CTD flow-path pump intermittently lost prime, resulting in low O_2 and pH values	CTD flow-path re-configured; pump was sent to factory for repairs
SV3	11-Jun-2015	MB, St.M	15.5/917	Power board in CCU box failed, causing OA payload to fail	A new power board was purchased and installed
SV3	24-Aug-2015	MB	3.7/236	Atmospheric pressure sensor failed	MET sensor suite was replaced
SV3	21-Sep-2015	MB	23.0/1180	Intermittent low battery charge due to cloud cover	Non-essential sensors manually powered down as necessary
		Total (subset)	473.2/19001		
		Total (all)	583.0/24544		

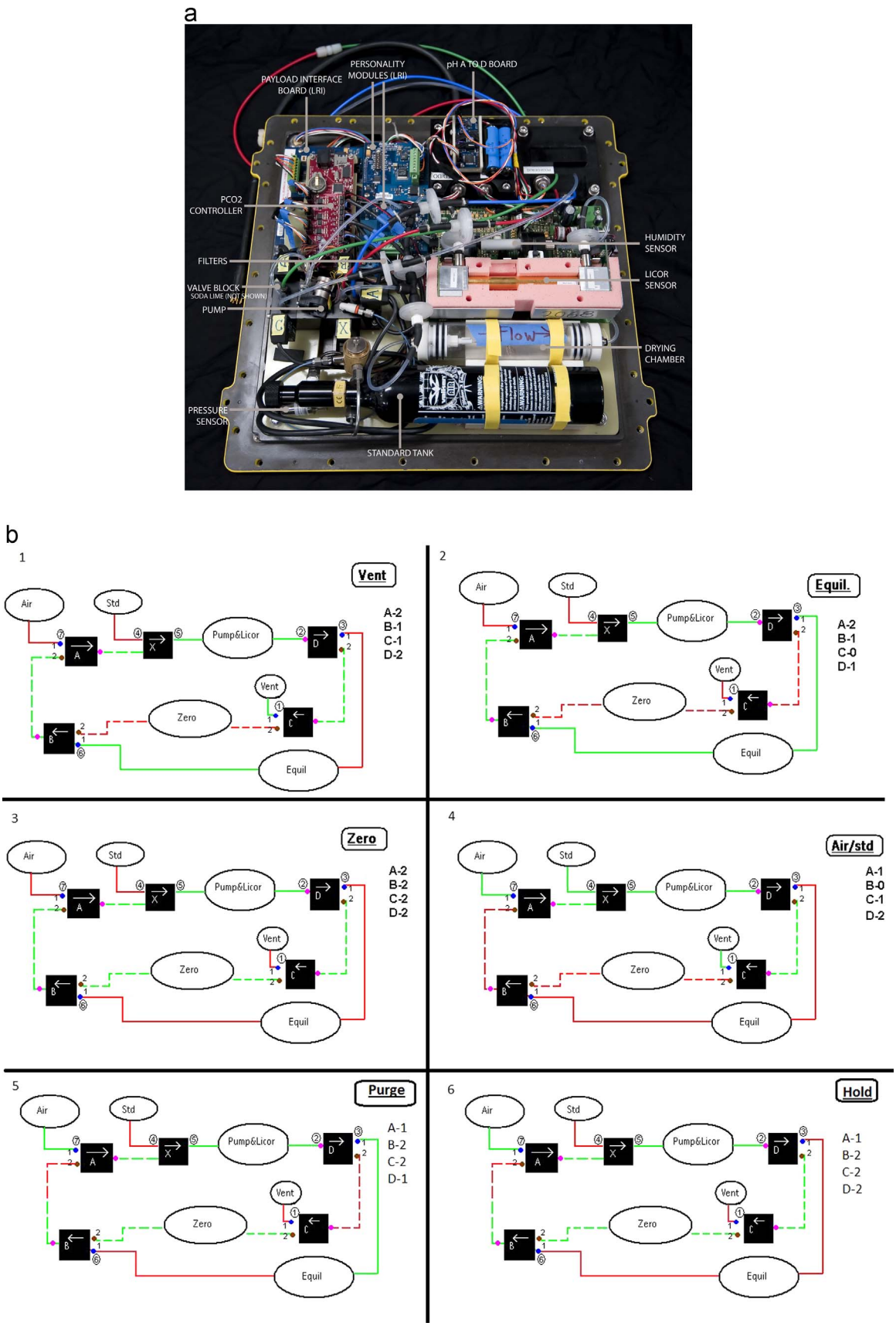

Fig. 1. (a) Layout of CO_2 system components as installed inside a SV2-style dry box for the Wave Glider. The Payload Interface and Personality Module (2) Boards are from Liquid Robotics and are used to log data from the CTD with oxygen and transmit them to shore together with the pCO_2 and pH data. The pCO_2 controller board, with a PIC micro-processor, operates the pCO_2 and pH systems and logs their data. (b) Diagram of gas flow paths showing positions of valves for the various stages in the measurement cycle. Red (green) lines represent closed (open) circuits. Dashed lines represent flow paths within the valve block itself; solid lines represent external tubing.

bubbles to rise and break at the interface of a small air headspace where the pCO_2 quickly reaches levels in the ocean. The equilibrator is mounted on the vehicle hull and reaches the sea water through custom holes drilled into the hull, with plumbing routed to the gas analyzer through a bulkhead. The pump is run for five minutes, then turned off and a CO_2 measurement is taken from air in the headspace. In the zero stage, dry CO_2-free air from the soda lime chamber (located inside the valve block) is circulated through the analyzer and measured. In the ***air stage***, ambient air from an intake on a mast 1.5 m above the waterline is first dried and then pumped through the analyzer before it is vented to the atmosphere. In the ***standard stage***, a measurement is taken from the CO_2 standard tank every 12 hours to allow in situ calibration of the system, and is again vented to the atmosphere. The pCO_2 concentration in the standard tank is between ~350 and 480 µatm, which is typical of the ocean surface. A higher standard concentration would better bracket the expected measurement range in the coastal upwelling environment of Monterey Bay but would result in greater uncertainty within the more commonly observed range of 350–480 µatm. After the air or standard measurement, the valves are opened so that gas from the air block is pumped into the equilibrator (the ***purge stage***) and then the equilibrator is isolated and the pump turned off. This ***hold stage*** is the longest (~50 min) with all power cut to the system, but critical because in this stage the lines to the equilibrator are full of air, preventing sea water from rising into the equilibrator. Before an equilibrator sample is taken there is a ***venting stage***, where the tubing from the equilibrator to the Licor is actively vented. The full measurement cycle takes eight minutes to complete. The sampling interval for CO_2 on these platforms is 1 hour, resulting in a horizontal resolution of 0.7–2.9 km.

The information that is returned via satellite includes variables for quality control, engineering and scientific data. The quality control variables include the pressure in the equilibrator, air, standard and zero gas circuits. Normal operating pressure is approximately equal to atmospheric pressure (101.3 kPa). Deviations from atmospheric pressure > 1–2 kPa suggest a blockage (such as a water droplet) or leak in the plumbing. Pressure is recorded twice over each measurement stage, once at the beginning (with the pump running) and once at the end (with the pump off). Temperature is also recorded twice over each measurement stage to correct for offsets in the Licor measurements as functions of temperature, and to convert pCO_2 at measurement temperature to pCO_2 at in situ water temperature measured by the onboard CTD. Humidity levels are also monitored within the equilibrator, air and standard circuits as well as outside the plumbing (but inside the dry box). The newer LI-840A model has the capability to monitor H_2O in the analysis stream (instead of the humidity sensor used here); the next version will likely use this newer model. An early concern with the original autonomous system was the possibility that water vapor might condense in the gas analyzer during cold nights and generate temporary offsets (Friederich et al., 1995). The most significant technical challenge for the Wave Glider system was preventing moisture within the tubing and gas analyzer, which would render the data useless. Moisture can enter the system either from the air or equilibrator side. The design of the air block, which can become submerged during rough weather, was a key accomplishment. The block uses Gore-Tex filters to keep the air stream dry. A similar design is used above the equilibrator. Finally, blocking off air to the equilibrator during the hold stage prevents water from rising in the equilibrator and potentially ruining the filters and reaching the gas analyzer.

2.2.2. pH sensor

The pH sensor is a Honeywell Durafet II pH electrode. These sensors have proven to be well-suited for ocean measurements (Martz et al., 2010; Bresnahan et al., 2016). The fully submersible electrode incorporates a solid-state, ion-sensitive field-effect transistor (ISFET) sensing element. The sensor is highly stable and provides fast response times. The pH sensor connector and preamplifier cap adaptor (Honeywell) are housed within a Delrin block that is attached to the Wave Glider hull beneath the OA payload box. The pH sensor is plumbed into the same pumped stream as the Sea-Bird CTD and oxygen sensor. The pH sensor is continuously powered by two lithium AA batteries. This removes the need for sensor warm-up time and avoids electrical interference from other power sources or instruments. The voltage signal from the pH sensor is digitized inside the payload box using an isolated high accuracy analog to digital board. The sampling schedule is programmed prior to deployment and data acquisition is controlled internally. Measurements are typically taken at 10-min intervals, resulting in an underway horizontal resolution of 0.1–0.5 km. Data collected by the pH sensor are relayed to the Wave Glider CCU via the control board and are telemetered to shore along with the other sensor data as described above. Calibrations are performed in-house several times per year using certified reference materials for the measurement of oceanic CO_2 parameters (Dickson, 2001). Extensive field experience with these sensors has shown them to be highly stable, reducing the need for frequent calibrations. Raw sensor voltage data are converted to pH (total scale) using in situ temperature data from the onboard CTD.

2.3. Additional modifications

The first critical modification was the plumbing of the CTD system as originally designed by Sea-Bird and implemented by Liquid Robotics. This included removal of an air-bleed valve which was allowing air to enter the plumbing and cause the pump to lose its prime. Second, it was found during initial test runs that the Wave Glider could be up-ended while moving through the waves and, though it would right itself, water could enter the air tower as well as the equilibrator and cause the Licor LI-820 to fail. The initial design of the air tower, modeled after those of stationary moorings, proved to be inadequate when fully submerged. A Liqui-Cel mini membrane contactor was tested before Gore-Tex filters were found to be the best solution for keeping water out of the system. Finally, software changes had to be implemented in order to create the 'purge stage' that prevents sea water from rising into the equilibrator.

2.4. Calibration of gas analyzer and processing of CO_2 data

The Licor CO_2 analyzer is operated without its temperature control, to save power and reduce warmup time. This mode of operation necessitates careful calibration over the entire temperature and xCO_2 range expected during the deployment. During calibration, a temperature-controlled bath is used to continuously adjust calibration temperature in small increments over a range of temperatures typically encountered in the field (~8–25 °C). Five CO_2 standards and a zero are used, covering a range of approximately 0 – 1200 μatm. Analyses of lab calibration data have shown that (1) the T-*vs.*-CO_2 relationship for a given CO_2 standard concentration is generally linear but often better approximated by a 2nd-degree polynomial; (2) the form of this relationship can vary for different CO_2 standard concentrations (e.g. trending downward with increasing T at a lower CO_2 standard concentration, and trending upward with increasing T at a higher CO_2 standard concentration); and (3) each LI-820 gas analyzer behaves slightly differently. By slowly varying the bath temperature while iterating over a set of fixed pCO_2 concentrations, these effects are quantified for each gas analyzer. The result of the calibration is a non-linear curve fit of the form $a + bx + cy + dxy$, where x is temperature, y is offset-corrected xCO_2, and a, b, c and d are the calibration coefficients. Raw xCO_2 field measurements from the equilibrator, air, and standard stages are corrected for zero-offset by subtracting the values obtained in the zero stage. Standard measurements are interpolated to 1-hr intervals and used to scale hourly zero-corrected xCO_2 measurements. The temperature calibration is then applied using

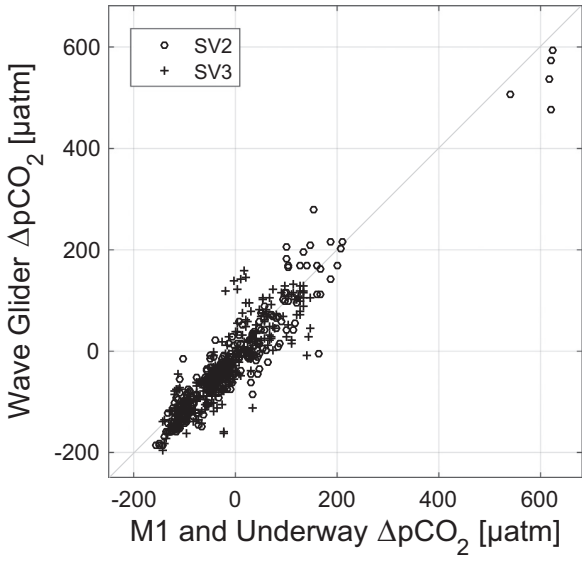

Fig. 2. Comparison of ΔpCO_2 measurements from Wave Gliders SV2 and SV3 (y-axis) with those measured on mooring M1 or from a ship (x-axis). Wave Glider and mooring comparisons are from measurements taken within 4 km and 30 min. The ship comparisons are from transects between stations C1 and M2 (see Fig. 3 for the locations of C1, M1 and M2). The data span 13 Wave Glider deployments between March 2012 and October 2015.

temperature measurements from the CO_2 system during the individual stages. Sea surface pCO_2 is then calculated from these corrected xCO_2 values by saturating the atmosphere with water vapor (assuming 1 atm of pressure) at the temperature and salinity at the time of measurement:

$$pCO_2 = xCO_2(1-pH_2O), \quad (1)$$

where

$$pH_2O = exp(24.4543-67.4509\ (100/T)-4.848\ \log(T/100)-0.000544*S) \quad (2)$$

is the water vapor pressure at equilibrator temperature (Weiss and Price, 1980), and T and S are in situ temperature (K) and salinity from the onboard CTD. Sea-air fluxes of CO_2 are calculated as $FCO_2 = k\ Sol\ \Delta pCO_2$, where k is the gas transfer rate (cm h^{-1}) computed following Wanninkhof (1992), Sol is the solubility of CO_2 in seawater (mol kg^{-1} atm^{-1}) computed following Weiss (1974), and $\Delta pCO_2 = pCO_{2w} - pCO_{2a}$ ($\mu_a$tm) where subscripts w and a refer to water and air, respectively. Thus, positive values for FCO_2 represent a net flux into the ocean, and negative values represent a net flux into the atmosphere. For the calculations of the k and Sol terms, wind and CTD data were linearly interpolated to the sample times of the CO_2 sensor, and wind speed measurements taken 1 m above sea level were normalized to the standard reference height of 10 m following Large and Pond (1981).

2.5. Field deployments

The majority of the Wave Glider deployments were conducted in Monterey Bay, California as part of MBARIs Controlled, Agile, and Novel Observing Network (CANON) project. A broad objective of CANON is to mobilize a new class of autonomous systems in order to study biological processes over their appropriate space and time scales. These processes include phytoplankton blooms, physical perturbations of biogeochemical cycles and the biological carbon pump. The CANON Wave Glider deployments provided the opportunity to evaluate the performance of the integrated OA sensor packages in the SV2 and SV3 vehicles against concurrent data collected from other platforms, while serving the CANON research objectives. The Wave Glider provided spatial maps of hydrography, winds, and carbon variables to guide focused sampling. The Wave Glider surveys were designed to capture variability associated with regional upwelling and to obtain measurements close to Station M1 for validation purposes. Station M1 is located in the mouth of Monterey Bay in about 1000 m of water. Regular pCO_2 measurements at M1 began in 1992 from ships and in 1997 from the mooring, providing perhaps the most comprehensive time-series of carbon dioxide in a coastal system (Friederich et al., 2002). The carbon dioxide time series at M1 has been extensively validated against data from regular shipboard surveys (Chavez et al., 1997; Friederich et al., 2002). The M1 CO_2 system operated in differential mode (ΔpCO_2 only) through 2013, and absolute mode (both pCO_{2a} and pCO_{2w} individually) from 2013 onward.

3. Results

3.1. OA sensor package performance

As of October 2015, MBARI's SV2 and SV3 vehicles have been deployed 22 times, and have logged 583 d at sea, covering a total of 24,544 km, both off the West coast of California and in the Gulf of Mexico (Table 1). For each deployment, Wave Glider sensor data were evaluated for quality using several criteria. All data where the pressure inside the equilibrator, air, standard or zero circuits was < 90 kPa at the end of the measurement stage (indicative of a leak in the CO_2 system plumbing) were removed. Humidity data were inspected in order to identify periods when water vapor entered the flow path. As an internal check of consistency between pH and CO_2 measurements, sea surface pCO_2 was estimated from concurrent pH and salinity measurements by applying an empirical equation derived from archived shipboard bottle data collected near Station M1 which related salinity to total alkalinity (TA; $TA = 2150 + 44\ (S - 31.25)$), and inputting pH and TA into the software package CO2SYS. This helped to identify periods when the pump for the CTD flow path intermittently lost its prime, resulting in low pH and dissolved oxygen values. A summary of these quality control checks is given in Table 1. In general, the OA sensor packages performed well, with most surveys returning > 97% quality data for both pH and pCO_2.

3.2. Comparison of Wave Glider, M1, and underway shipboard pCO_2 field measurements

During 13 of the total 22 Wave Glider deployments, CO_2 data were collected within 4 km of Station M1. Measurements of ΔpCO_2 collected by the SV2 and SV3 Wave Gliders during each of these 13 deployments compared well to measurements taken at Station M1 ($R^2 = 0.86$, $n = 622$) (Fig. 2). Given the large gradients observed in Monterey Bay (see below) and the up to 4 km offset between the Wave Glider and the mooring, these correlations are remarkable. pCO_2 measurements were also compared between the SV3 Wave Glider and the R/V *Rachel Carson* underway pCO_2 system over one shipboard survey (described in more detail in Section 3.4). Measurements from these two platforms also compared very well ($R^2 = 0.96$, $n = 20$) (Fig. 2). Agreement between platforms was strong over a wide range of ΔpCO_2, during both strong upwelling (ΔpCO_2 > 500 µatm) and non-upwelling (ΔpCO_2 < 200 µatm) conditions within the bay. Upwelling and subsequent transport of upwelled water often results in high spatio-temporal variability in carbon parameters near Monterey Bay making direct comparisons between data collected at Station M1 and by the Wave Glider difficult. We used a fixed threshold of 4 km as our criteria for comparison; tighter restrictions resulted in lower errors, but at the expense of fewer observations. These observations represent 'instantaneous' as opposed to time- or space-averaged measurements of ΔpCO_2. Instantaneous measurements allow a more direct comparison of M1 and Wave Glider, and highlight the strong variance in seawater pCO_2 in areas affected by regional upwelling.

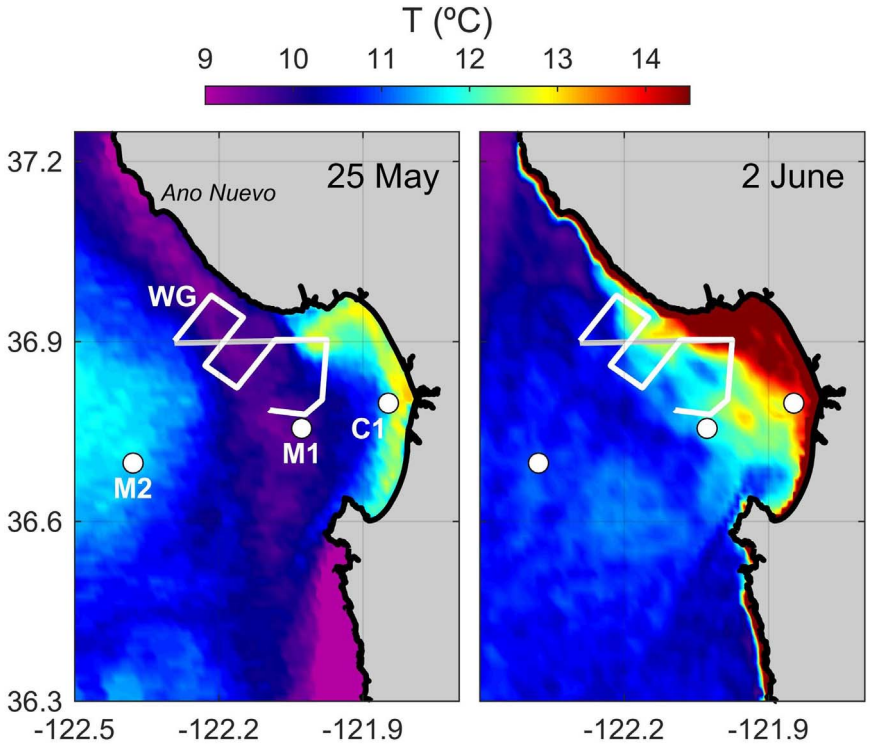

Fig. 3. Satellite-derived surface temperature during the Spring 2012 SV2 Wave Glider survey during upwelling (25 May, left panel) and relaxation (2 June, right panel) conditions near Monterey Bay. Locations of Wave Glider (WG) transects are shown as white and gray lines; mooring locations are shown as white dots. Temperature data are from the 'all-surface' NOAA POES AVHRR product. Data were carefully screened and validated by in situ measurements (Wave Glider; M1).

3.3. Small-spatial scale variability associated with upwelling

During the spring and summer months in Central California, strong northwesterly winds result in upwelling of cool, nutrient-rich, high-pCO_2 water near Point Año Nuevo (Rosenfeld et al., 1994; Friederich et al., 1995, 2002; Pennington et al., 2009; Johnson, 2010). Strong gradients in these properties often form between recently upwelled water ~20–50 km from the coast and warmer waters within the upwelling shadow of northeast Monterey Bay (Friederich et al., 1995, 2002; Pennington et al., 2009). Several Wave Glider surveys coincided with upwelling events near the study area; here we focus on the Spring 2012 SV2 survey because the pre-programmed vehicle trajectory resolved the evolution of an upwelling plume (Fig. 3). For this deployment, the vehicle was programmed to alternate between a grid pattern and a zonal transect along 36.9 °N. Each lap of the grid pattern took about 1.3 d to complete, and each zonal transect took about 0.6 d. A total of 7 grid and 3 zonal transects were completed over 11 d during this deployment.

Winds were consistently upwelling-favorable beginning 15 May 2012 (7 d prior to the beginning of the survey) (Fig. 4). Satellite sea surface temperature data showed a pocket of cool (~10 °C) water near Point Año Nuevo on 20 May; on subsequent days, this upwelled water cooled further and extended southward along a narrow strip across the mouth of Monterey Bay (Fig. 3). Within the bay, near the coast, temperatures remained relatively warm (13–14 °C). The arrival of the upwelled water at Station M1 was seen as a gradual decrease in temperature and increase in pCO_{2w} between 22 and 25 May (Fig. 4). On 28 May, daily-averaged ΔpCO_2 at Station M1 reached 595.7 µatm (sea surface pCO_2 was 1001.7 µatm), the highest value since regular measurements at M1 began in February 1997.

Measurements from the Wave Glider between 24–26 May showed large spatial gradients in sea surface T, S, O_2, pCO_{2w}, and pH associated with the upwelling plume (Fig. 5). The upwelled water had characteristically low temperature (~9 °C), high salinity (~33.9), low dissolved oxygen (~150 µM), high pCO_{2w} (~1000 µatm), and low pH

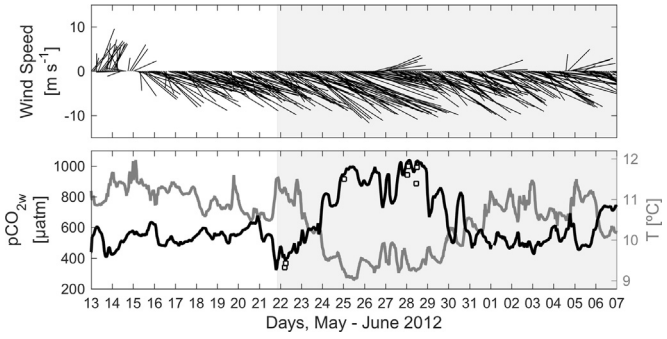

Fig. 4. Time series of wind speed and direction, sea surface pCO_2 (pCO_{2w}, black line), and temperature (gray line) for mooring M1 before and during the Spring 2012 SV2 Wave Glider survey (gray shade). pCO_{2w} at M1 was estimated from ΔpCO_2 measurements by adding the median atmospheric pCO_2 measured by the SV2 Wave Glider during this survey (406 µatm). Measurements of pCO_{2w} from the Wave Glider system within 4 km and 30 min are shown as white squares.

(~7.7). Shoreward of the upwelling front, pCO_{2w} was ~300 µatm. Atmospheric pCO_2 was relatively constant at 406 ± 4 µatm (median ± SD) throughout the survey. Thus, inner bay waters acted as a sink for CO_2 whereas waters just offshore acted as a strong source. Winds were strongest away from the coast, particularly over the cool, high-pCO_{2w} upwelled water (Fig. 5a). Here, the combination of large air-sea differences in pCO_2 and strong winds resulted in enhanced CO_2 fluxes up to 0.6 mmol m^{-2} d^{-1} (Fig. 5f).

To investigate small-scale (sub km) spatial variability in pCO_{2w} associated with the upwelling plume, we used estimated pCO_{2w}, derived from pH and salinity data as described above, to utilize the higher sampling rate of the pH sensor (10 min compared to 60 min for pCO_2). A comparison of measured and estimated pCO_{2w} during this deployment showed that estimated pCO_{2w} from pH was realistic (R^2 = 0.98, n = 195). During the 36.9 °N transect on 30 May, estimated pCO_{2w} was characterized by four discrete ranges of values, corre-

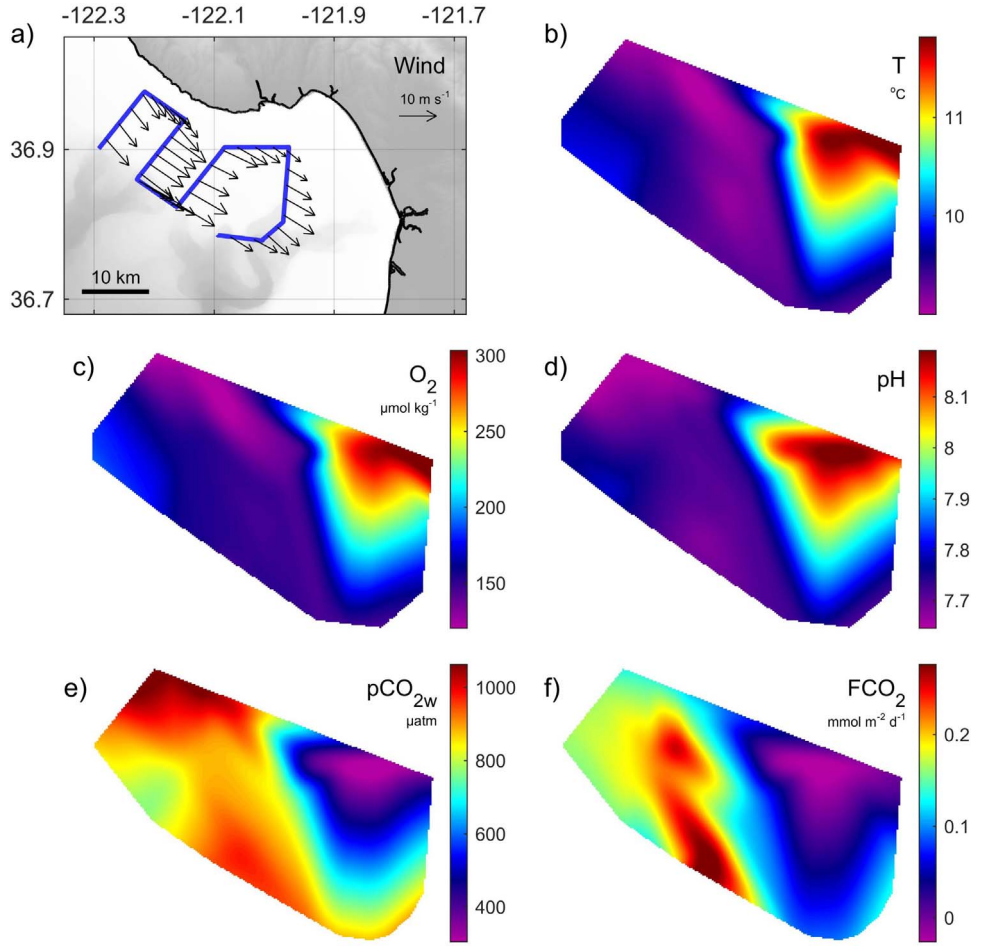

Fig. 5. Distribution of (a) winds, and contoured (b) temperature, (c) dissolved oxygen (O_2), (d) pH, (e) sea surface pCO_2 (pCO_{2w}), and (f) pCO_2 fluxes (FCO_2) in northern Monterey Bay on 24–26 May during the Spring 2012 SV2 Wave Glider survey. Contoured data in panels (b) through (f) are from the same Wave Glider track shown in panel (a).

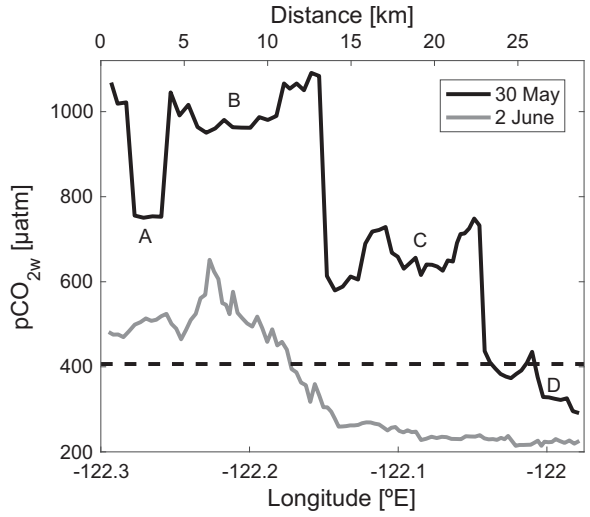

Fig. 6. Sea surface pCO_2 along 36.9 °N during the Spring 2012 SV2 Wave Glider survey (gray line in Fig. 3), during upwelling (30 May) and relaxation (2 June) conditions near Monterey Bay. Dashed line represents the median atmospheric pCO_2 over the deployment (406 µatm).

sponding to different water masses (Fig. 6). These included (from west to east): water offshore of the upwelling plume ("A", mean 753 µatm), water within the upwelling plume ("B", 1012µatm), water inshore of the upwelling plume ("C", 663 μatm), and nearshore water within the upwelling shadow region of northeast Monterey Bay ("D", 366 µatm) (Fig. 6). At the inshore edge of the upwelling plume, estimated pCO_{2w} decreased from 1084 to 614µatm, a difference of 470µatm, over two sequential 10-min samples, a distance of 0.47 km. Sea-air fluxes of CO_2 were positive (into the atmosphere) along the entire transect on 30 May, with the exception of the nearshore 5 km (e.g. within the upwelling shadow region) (Fig. 6). In contrast, by 2 June, sea surface temperature at Station M1 had increased and pCO_{2w} decreased to pre-event levels (Fig. 4). Estimated pCO_{2w} along the 36.9 °N Wave Glider transect decreased such that the net sea-air flux was into the ocean (Fig. 6).

3.4. Comparison of Wave Glider and shipboard pCO_2 field measurements

Regular shipboard carbon dioxide observations in Monterey Bay began in 1992 and to our knowledge are the longest sea surface record of pCO_2 globally. As part of the Fall 2015 CANON project, the SV3 Wave Glider vehicle was programmed to transit between waypoints C1 and M2 (Fig. 3), in tandem with the R/V *Rachel Carson* that collected underway CO_2 measurements along the same line. Friederich et al. (2002) described the underway CO_2 system used by the R/V *Rachel Carson*. The SV3 Wave Glider completed two round-trips of this transect (~1.5 d each) and the R/V *Rachel Carson* one round-trip; here, we present the one shoreward transect leg which was closest in time between the two platforms. The SV3 Wave Glider began the transect leg at M2 at 13:31 on 25 August and ended at 09:31 on 26 August, whereas the R/V *Rachel Carson* began at 19:05 and ended at 22:02 on 25 August. The sampling interval for the underway system on

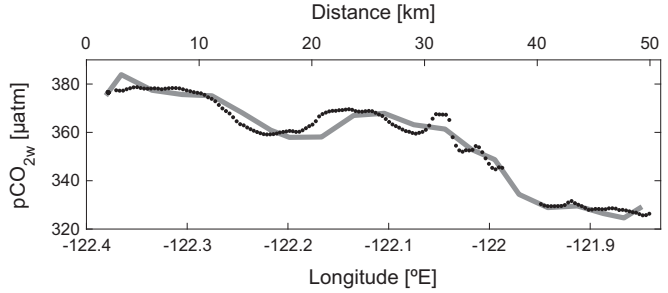

Fig. 7. Comparison of sea surface pCO_2 measurements from the R/V *Rachel Carson* underway system (black dots) and the integrated SV3 Wave Glider system (gray line) during the Fall 2015 deployment. The data are from a single Wave Glider occupation (at ~ 1 knot) versus a single occupation by the ship (at ~10 knots).

the R/V *Rachel Carson* was 1 min.

This survey was conducted during non-upwelling conditions, with negative ΔpCO_2 (sea less than air) throughout the survey. While the range of pCO_2 values was small relative to the 2012 SV2 survey, a clear trend of increasing pCO_2 from inshore to offshore was evident. Smaller scale (km) variability was also observed, and both (trend, variability) of these characteristics were found in the Wave Glider and shipboard systems (Fig. 7). Agreement was strong (R^2 = 0.96, n = 20), with some offset likely due to time-aliasing between the two platforms.

4. Discussion and conclusions

The development and testing of a pCO_2 system on SV2 and SV3 Wave Gliders has been described. We have demonstrated that an integrated instrument package of temperature, salinity, oxygen, pCO_2, pH and wind speed and direction on Wave Gliders, is capable of mapping variability at time (min) and space (km) scales relevant to coastal upwelling processes and the resulting biogeochemical transformations. The Wave Glider allows sea-air fluxes of CO_2 to be estimated over a range of time scales, from individual upwelling or relaxation events to seasonally over the entire upwelling season, and eventually decades, and can be deployed from a small vessel (in this case, the 11-m R/V *Paragon*), eliminating the dependence on a large, costly research vessel. Current assessments of CO_2 fluxes use large bins because of poor time-space density of observations (Takahashi et al., 2009). By maintaining a constant presence, ASVs can capture extreme events and better quantify variance. Long time series like the ones in Monterey Bay are extremely rare, and Wave Gliders or other ASVs with pCO_2 sensors could help fill this void.

The exceptionally high ΔpCO_2 (highest in the close to 20-year record at M1) and low pH values measured during the Fall 2012 SV2 survey are illustrative of increasingly acidic waters observed in the California Current coastal upwelling system. Surface waters in coastal upwelling systems have two sources for higher pCO_2 and lower pH: 1) the slow uptake of anthropogenic atmospheric CO_2, the so-called ocean acidification; and 2) the coastal upwelling process that brings higher pCO_2 and lower pH waters to the surface. Steady decreases of oxygen at depth in coastal California waters have been reported (Bograd et al., 2008) and linked to increased degradation of organic matter (Deutsch et al., 2014). Degradation of organic matter leads to further increases in CO_2 compounding the ocean acidification problem. Reducing oxygen to low (hypoxic) levels creates a separate and additive threat to west coast marine ecosystems. The aragonite saturation horizon in the northeastern Pacific Ocean is already among the shallowest in the global ocean at < 250 m (Feely et al., 2004), and upwelling brings this acidified water onto the shelf and occasionally to the surface (Feely et al., 2008; Booth et al., 2012). Undersaturation of aragonite within upwelled waters off California affects shell size and strength in animals that precipitate calcium carbonate from seawater such as pteropods, an important food source for salmon (Hofmann et al., 2010). These observations of increasingly acidic source waters in upwelling systems speak to the urgent need for more comprehensive pCO_2 and pH observation strategies.

In summary, Wave Gliders have proven to be robust platforms and the integrated OA sensor package has provided quality datasets that compare favorably to traditional moored and shipboard systems. The lower cost of Wave Glider operation allows for greater spatio-temporal coverage and demonstrates their potential to bolster existing observing efforts worldwide.

Acknowledgements

This research was supported by a small grant from Google to purchase a Wave Glider payload box and a Command and Control unit and by the David and Lucile Packard Foundation. Two MBARI summer interns contributed to the mechanical integration (Brendan Tougher) and to data analysis (Michael Fong). Gabriela Chavez and Tim Pennington provided constructive editorial comments on the paper. Numerous members of the staff at both MBARI and Liquid Robotics graciously supported the at-sea deployment, recovery and operation of Wave Gliders.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.dsr2.2017.01.001.

References

Bograd, S.J., Castro, C.G., Di Lorenzo, E., Palacios, D.M., Bailey, H., Gilly, W., Chavez, F.P., 2008. Oxygen declines and the shoaling of the hypoxic boundary in the California Current. Geophys. Res. Lett. 35. http://dx.doi.org/10.1029/2008GL034185.

Booth, J.A.T., McPhee-Shaw, E.E., Chua, P., Kingsley, E., Denny, M., Phillips, R., Bograd, S.J., Zeidberg, L.D., Gilly, W.F., 2012. Natural intrusions of hypoxic, low pH water into nearshore marine environments on the California coast. Cont. Shelf Res. 45, 108–115. http://dx.doi.org/10.1016/j.csr.2012.06.009.

Bourgeois, T., Orr, J.C., Resplandy, L., Terhaar, J., Ethé, C., Gehlen, M., Bopp, L., 2016. Coastal-ocean uptake of anthropogenic carbon. Biogeosciences 13, 4167–4185. http://dx.doi.org/10.5194/bg-13-4167-2016.

Bresnahan, P.J., Wirth, T., Martz, T.R., Andersson, A.J., Cyronak, T., D'Angelo, S., Pennise, J., Melville, W.K., Lenain, L., Statom, N., 2016. A sensor package for mapping pH and oxygen from mobile platforms. Methods Oceanogr. 17, 1–13. http://dx.doi.org/10.1016/j.mio.2016.04.004.

Chavez, F.P., Pennington, J.T., Herlien, R., Jannasch, H., Thurmond, G., Friederich, G.E., 1997. Moorings and drifters for real-time interdisciplinary oceanography. J. Atmos. Ocean. Technol. 14, 1199–1211. http://dx.doi.org/10.1175/1520-0426(1997)014 < 1199:MADFRT > 2.0.CO;2.

Chen, C.-T.A., Huang, T.-H., Chen, Y.-C., Bai, Y., He, X., Kang, Y., 2013. Air–sea exchanges of CO_2 should be subscript 2 in the world's coastal seas. Biogeosciences 10, 6509–6544. http://dx.doi.org/10.5194/bg-10-6509-2013.

Deutsch, C., Berelson, W., Thunell, R., Weber, T., Tems, C., McManus, J., Crusius, J., Ito, T., Baumgartner, T., Ferreira, V., Mey, J., van Geen, A., 2014. Centennial changes in North Pacific anoxia linked to tropical trade winds. Science 345, 665–668. http://dx.doi.org/10.1126/science.1252332.

Dickson, A.G., 2001. Reference materials for oceanic CO_2 measurements. Oceanography 14, 21–22.

Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., Millero, F.J., 2004. Impact of anthropogenic CO_2 on the $CaCO_3$ system in the oceans. Science 305, 362–366. http://dx.doi.org/10.1126/science.1097329.

Feely, R.A., Sabine, C.L., Hernandez-Ayon, J.M., Ianson, D., Hales, B., 2008. Evidence for upwelling of corrosive "acidified" water onto the continental shelf. Science 320, 1490–1492. http://dx.doi.org/10.1126/science.1155676.

Friederich, G., Walz, P., Burczynski, M., Chavez, F., 2002. Inorganic carbon in the central California upwelling system during the 1997–1999 El Niño–La Niña event. Prog. Oceanogr. 54, 185–203. http://dx.doi.org/10.1016/S0079-6611(02)00049-6.

Friederich, G.E., Brewer, P.G., Herlien, R., Chavez, F.P., 1995. Measurement of sea surface partial pressure of CO_2 from a moored buoy. Deep Sea Res. Part I 42, 1175–1186. http://dx.doi.org/10.1016/0967-0637(95)00044-7.

Hine, R., McGillivary, P., 2007. Wave powered autonomous surface vessels as components of ocean observing systems. In: Proceedings of Pacific Congress on Marine Science and Technology (PACON), Honolulu, HI, June 2007, p. A-3.

Hofmann, G.E., Barry, J.P., Edmunds, P.J., Gates, R.D., Hutchins, D.A., Klinger, T., Sewell, M.A., 2010. The effect of ocean acidification on calcifying organisms in marine ecosystems: an organism-to-ecosystem perspective. Annu. Rev. Ecol. Evol. Syst. 41, 127–147.

Johnson, K.S., 2010. Simultaneous measurements of nitrate, oxygen, and carbon dioxide

on oceanographic moorings: observing the Redfield ratio in real time. Limnol. Oceanogr. 55, 615–627.

Large, W.G., Pond, S., 1981. Open ocean momentum flux measurements in moderate to strong winds. J. Phys. Oceanogr. 11, 324–336.

Le Quéré, C., Moriarty, R., Andrew, R.M., Canadell, J.G., Sitch, S., Korsbakken, J.I., Friedlingstein, P., Peters, G.P., Andres, R.J., Boden, T.A., Houghton, R.A., House, J.I., Keeling, R.F., Tans, P., Arneth, A., Bakker, D.C.E., Barbero, L., Bopp, L., Chang, J., Chevallier, F., Chini, L.P., Ciais, P., Fader, M., Feely, R.A., Gkritzalis, T., Harris, I., Hauck, J., Ilyina, T., Jain, A.K., Kato, E., Kitidis, V., Klein Goldewijk, K., Koven, C., Landschützer, P., Lauvset, S.K., Lefèvre, N., Lenton, A., Lima, I.D., Metzl, N., Millero, F., Munro, D.R., Murata, A., Nabel, J.E.M.S., Nakaoka, S., Nojiri, Y., O'Brien, K., Olsen, A., Ono, T., Pérez, F.F., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Rödenbeck, C., Saito, S., Schuster, U., Schwinger, J., Séférian, R., Steinhoff, T., Stocker, B.D., Sutton, A.J., Takahashi, T., Tilbrook, B., van der Laan-Luijkx, I.T., van der Werf, G.R., van Heuven, S., Vandemark, D., Viovy, N., Wiltshire, A., Zaehle, S., Zeng, N., 2015. Global carbon budget 2015. Earth Syst. Sci. Data 7, 349–396. http://dx.doi.org/10.5194/essd-7-349-2015.

Liu, K.-K., Atkinson, L., Chen, C.T.A., Gao, S., Hall, J., MacDonald, R.W., McManus, L.T., Quiñones, R., 2000. Exploring continental margin carbon fluxes on a global scaleEos Trans. 81. AGU, 641–644. http://dx.doi.org/10.1029/EO081i052p00641-01.

Manley, J., Willcox, S., 2010. The Wave Glider: a new concept for deploying ocean instrumentation. IEEE Instrum. Meas. Mag. 13, 8–13.

Martz, T.R., Connery, J.G., Johnson, K.S., 2010. Testing the Honeywell Durafet for seawater pH applications. Limnol. Oceanogr.-Meth. 8, 172–184.

Monteiro, P.M.S., Schuster, U., Hood, M., Lenton, A., Metzl, N., Olsen, A., Rogers, K., Sabine, C., Takahashi, T., Tilbrook, B., Yoder, J., Wanninkhof, R., Watson, A.J., 2009. A global sea surface carbon observing system: assessment of changing sea surface CO_2 and air-sea CO_2 fluxes. Proc. OceanObs'09: Sustain. Ocean Obs. Inf. Soc. 2, 702–714. http://dx.doi.org/10.5270/OceanObs09.cwp.64.

Pennington, J.T., Friederich, G.E., Castro, C.A., Evans, W.W.I., Michisaki, R.P., Chavez, F.P., 2009. The northern and central California coastal upwelling system. In: Carbon and Nutrient Fluxes in Continental Margins, Global Change, The IGBP Series. Springer-Verlag, Berlin Heidelberg, 29–44.

Rosenfeld, L.K., Schwing, F.B., Garfield, N., Tracy, D.E., 1994. Bifurcated flow from an upwelling center: a cold water source for Monterey Bay. Cont. Shelf Res. 14, 931–964. http://dx.doi.org/10.1016/0278-4343(94)90058-2.

Sutton, A.J., Sabine, C.L., Maenner-Jones, S., Lawrence-Slavas, N., Meinig, C., Feely, R.A., Mathis, J.T., Musielewicz, S., Bott, R., McLain, P.D., Fought, H.J., Kozyr, A., 2014. A high-frequency atmospheric and seawater pCO_2 data set from 14 open-ocean sites using a moored autonomous system. Earth Syst. Sci. Data 6, 353–366. http://dx.doi.org/10.5194/essd-6-353-2014.

Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D.C.E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T.S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C.S., Delille, B., Bates, N.R., de Baar, H.J.W., 2009. Climatological mean and decadal change in surface ocean pCO_2, and net sea–air CO_2 flux over the global oceans. Deep Sea Res. Part II 56, 554–577. http://dx.doi.org/10.1016/j.dsr2.2008.12.009.

Takeshita, Y., Frieder, C.A., Martz, T.R., Ballard, J.R., Feely, R.A., Kram, S., Nam, S., Navarro, M.O., Price, N.N., Smith, J.E., 2015. Including high-frequency variability in coastal ocean acidification projections. Biogeosciences 12, 5853–5870. http://dx.doi.org/10.5194/bg-12-5853-2015.

Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. J. Geophys. Res. C: Ocean. 97, 7373–7382. http://dx.doi.org/10.1029/92JC00188.

Weiss, R.F., 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Mar. Chem. 2, 203–215. http://dx.doi.org/10.1016/0304-4203(74)90015-2.

Weiss, R.F., Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Mar. Chem. 8, 347–359.

Wiggins, S., Manley, J., Brager, E., Woolhiser, B., 2010. Monitoring marine mammal acoustics using Wave Glider. In: Proc. MTS/IEEE OCEANS, Seattle, WA.

Willcox, S., Meinig, C., Sabine, C.L., Lawrence-Slavas, N., Richardson, T., Hine, R., Manley, J., 2009. An autonomous mobile platform for underway surface carbon measurements in open-ocean and coastal waters. In: Proc. MTS/IEEE OCEANS, Biloxi, MS.