

🔗 Evaluation of a New Carbon Dioxide System for Autonomous Surface Vehicles

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ABSTRACT

Current carbon measurement strategies leave spatiotemporal gaps that hinder the scientific understanding of the oceanic carbon biogeochemical cycle. Data products and models are subject to bias because they rely on data that inadequately capture mesoscale spatiotemporal (kilometers and days to weeks) changes. High-resolution measurement strategies need to be implemented to adequately evaluate the global ocean carbon cycle. To augment the spatial and temporal coverage of ocean-atmosphere carbon measurements, an Autonomous Surface Vehicle CO₂ (ASVCO₂) system was developed. From 2011 to 2018, ASVCO₂ systems were deployed on seven Wave Glider and Saildrone missions along the U.S. Pacific and Australia's Tasmanian coastlines and in the tropical Pacific Ocean to evaluate the viability of the sensors and their applicability to carbon cycle research. Here we illustrate that the ASVCO₂ systems are capable of long-term oceanic deployment and robust collection of air and seawater *p*CO₂ within $\pm 2 \mu\text{atm}$ based on comparisons with established shipboard underway systems, with previously described Moored Autonomous *p*CO₂ (MAPCO₂) systems, and with companion ASVCO₂ systems deployed side by side.

1. Introduction

As a carbon sink, the oceans have helped buffer climate change during the Anthropocene by absorbing approximately one-quarter of the carbon dioxide (CO₂) emitted to the atmosphere from human activity (Friedlingstein et al. 2019; Gruber et al. 2019; Sabine et al. 2004). Indeed, measurements of surface waters are documenting the fact that although much more variable than the atmosphere, over long time and space scales the ocean CO₂ levels are increasing at about the same rate as the atmospheric CO₂ concentrations (Bates et al. 2014; Landschützer et al. 2014; Takahashi et al. 2009; Wanninkhof et al. 2013a). The oceanic removal of CO₂ from the atmosphere is

reducing the effects of climate change but in turn it is acidifying surface seawater.

The ocean removes carbon from the atmosphere via gas equilibration and moves it into the ocean interior at deep and intermediate water formation regions, in a process known as the solubility pump. Atmospheric carbon dioxide is also moved into the ocean interior via the biological pump, when the carbon that is taken up by phytoplankton during photosynthesis is transported down as organisms die or are eaten and repackaged into fecal pellets. Much of this biologically fixed organic carbon sinks to the subsurface ocean, where it is rapidly remineralized or respired back to dissolved CO₂. Because both of the solubility and biological pumps vary by region and season, there is tremendous spatial and temporal variations in surface ocean CO₂ concentrations (Bates et al. 2014; Landschützer et al. 2014; Takahashi et al. 2009; Wanninkhof et al. 2013a).

Coastal regions are particularly vulnerable to changes in ocean carbon chemistry and its biological impacts.

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Changes in tides, temperature, salinity, and primary production expose coastal regions to seasonal and spatial variations in surface ocean dissolved CO₂ concentrations (Bauer et al. 2013; Damm et al. 2010; Fassbender et al. 2018). For example, along the Pacific coast of the United States, seasonal (late spring to early fall) strengthening of the northwesterly winds transport dense, CO₂-rich water from the subsurface up onto the continental shelf, exposing coastal ecosystems to potential acidification from both natural and anthropogenic sources (Fassbender et al. 2018; Feely et al. 2016). Changes in the frequency, duration, and intensity of acidified conditions will affect marine ecosystems in ways that we are only starting to understand (Barton et al. 2012; Bednarssek et al. 2012, 2014a,b, 2017; Fabry et al. 2008; Kleypas et al. 2006; Reum et al. 2015). The fate of these economically important regions is still largely unknown due to the limitations of applying results of laboratory experiments to the complexity of real-world ecosystems, as well as a paucity in current biological and carbon system monitoring approaches.

Underway systems on research ships and commercial volunteer observing ships as well as autonomous systems on mooring platforms have documented substantial variations in the oceanic partial pressure of CO₂ (*p*CO₂) and subsequent carbonate chemistry of coastal waters (Fassbender et al. 2018; Feely et al. 2016; Sutton et al. 2019; Wanninkhof et al. 2015). While research expeditions can gather data over vast spatial scales, large-scale coastal expeditions occur infrequently. This fails to capture mesoscale temporal (days to weeks) variations in the carbon cycle. Mooring deployments compensate for the temporal gaps by capturing high-frequency time series, but the sparsity of moorings that measure CO₂ leaves large spatial gaps. Spatiotemporal gaps left by current measurement strategies hinder the scientific understanding of the oceanic carbon cycle, especially in coastal regions that are exposed to mesoscale physical and biogeochemical forcing.

Much of the carbon data collected from ships (bottle measurements and underway *p*CO₂ systems) and moored platforms have been synthesized into data products. Data products such as the Lamont Doherty Earth Observatory surface ocean *p*CO₂ database (Takahashi et al. 2009), the Surface Ocean CO₂ Atlas (SOCAT) (Bakker et al. 2016) and the Global Data Analysis Project (GLODAP) (Olsen et al. 2019) provide the basis for ocean uptake calculations and validation of model simulations (Gruber et al. 2019; Wanninkhof et al. 2013b). Together, large-scale carbon data products and modeling efforts have improved our understanding of oceanic carbon cycling and allowed for better climate predictions. Unfortunately, large-scale and global data products and models are

subject to regional bias because they rely on data that inadequately capture mesoscale spatiotemporal (kilometers and days to weeks) changes. High-resolution spatiotemporal measurement strategies need to be implemented in order to adequately evaluate the regional aspects of the global ocean carbon cycle.

To augment the spatial and temporal coverage of ocean-atmosphere carbon measurements, the National Oceanic and Atmospheric Administration (NOAA) Pacific Marine Environmental Laboratory (PMEL) developed an Autonomous Surface Vehicle CO₂ (ASVCO₂) system for deployment on remotely operated autonomous platforms. In collaboration with Liquid Robotics Inc. (liquid-robotics.com) and Saildrone Inc. (saildrone.com), PMEL integrated ASVCO₂ systems (Fig. 1) on two types of autonomous surface vehicles, a Wave Glider and Saildrone. Similar *p*CO₂ instruments have been deployed on Wave Gliders recently (Chavez et al. 2018; Northcott et al. 2019), but the ASVCO₂ system has the advantage of being directly comparable to a network of moored CO₂ systems deployed in all the major ocean basins. The ASVCO₂ systems described here were deployed on four Wave Glider and three Saildrone missions along the U.S. Pacific coast, Australia's Tasmanian coastline, and in the tropical Pacific between 2011 and 2018 in order to evaluate the performance of the sensors, and the utility of these systems in carbon cycle research.

2. Methods

a. ASVCO₂ system

The ASVCO₂ system is a modified version of the Moored Autonomous *p*CO₂ (MAPCO₂) system developed by PMEL and Monterey Bay Aquarium Research Institute, which has been used for over a decade on dozens of moored surface buoys around the world (Sutton et al. 2014). The details of the ASVCO₂ design, components (including equilibrator design), gas flow paths, and analysis sequences/timing are all identical to the MAPCO₂ except as noted here, so they will not be repeated. The modifications primarily involved a repackaging of the components and the development of small, high pressure gas bottles for the reference gas (Luxfer M22A high pressure carbon wrapped, aluminum-lined cylinder) for deployment on the Liquid Robotics, Inc., Wave Glider (Willcox et al. 2010) and Saildrone, Inc. (Meinig et al. 2015), surface vehicles. The new cylinders were extensively tested at NOAA's Earth System Research Laboratory for more than a year to ensure the concentrations did not significantly drift (<0.1 ppm over six months) before they were implemented. A manifold linking three small bottles together along with a lower flow rate (from 0.25 LPM on MAPCO₂ to

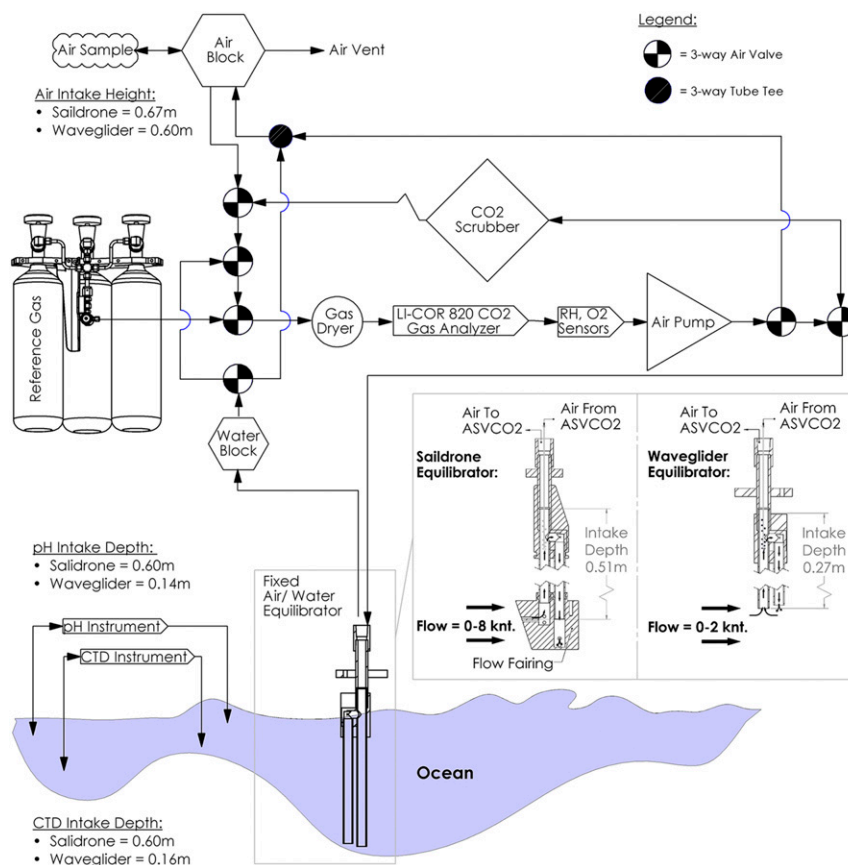


FIG. 1. ASVCO₂ system components and sampling paths.

0.13 LPM on ASVCO₂) was used for long deployments (Fig. 1). The equilibrator was shortened and placed at a fixed depth compared to the floating equilibrators used on the buoy-based MAPCO₂ systems, with the Wave Glider and Saildrone acting as the float. The equilibrator operated on the same bubble equilibration principles as described by Sutton et al. (2014). A fairing was added on the equilibrator water inlet and exit of the Saildrone system to prevent both sucking all the water out of the equilibrator and filling the equilibrator with water when moving at higher speeds of 4+ kt ($1 \text{ kt} \approx 0.51 \text{ m s}^{-1}$).

Like the MAPCO₂ system, the primary measurement was made using a nondispersive infrared (NDIR) detector (Li-Cor-820) either on air drawn from the atmosphere above the vehicle (0.6 m above sea level for Wave Glider or 0.7 m for Saildrone) or on air equilibrated with surface seawater. The gas streams were partially dried by passing through a 0.14 m Nafion tube packed in silica desiccant. The Li-Cor was calibrated before every set of atmospheric and seawater-equilibrated air measurements using a closed loop of air drawn through a soda lime column (~35 g) to scrub out all CO₂ to zero the

instrument, then using a gas with a known CO₂ concentration (traceable to the World Meteorological Organization and supplied by NOAA's Earth System Research Laboratory) to span it. Detector calibration shows a precision and accuracy comparable to the mooring-based systems (<0.7 and $<1.5 \mu\text{atm}$, respectively; Sutton et al. 2014). Measurements can be made on approximately 30-min intervals; however, measurements were typically made at hourly intervals on field deployments. The mole fraction of air CO₂ ($x\text{CO}_2$) equilibrated with surface seawater was determined using temperature and relative humidity, and $p\text{CO}_2$ was subsequently calculated by multiplying the $x\text{CO}_2$ by total pressure (Sutton et al. 2014). An internal GPS recorded the position and time of each measurement.

A Honeywell Durafet III ion-sensitive field-effect transistor (ISFET) pH sensor (Martz et al. 2010) was also fixed within the ASVCO₂ waterproof enclosure (Fig. 1). The Durafet response time is milliseconds, but readings were averaged over the same time period that the CO₂ measurements were collected. For deployment on the Wave Glider, the sensor was directly exposed to the surrounding water. On the Saildrone, the instrument

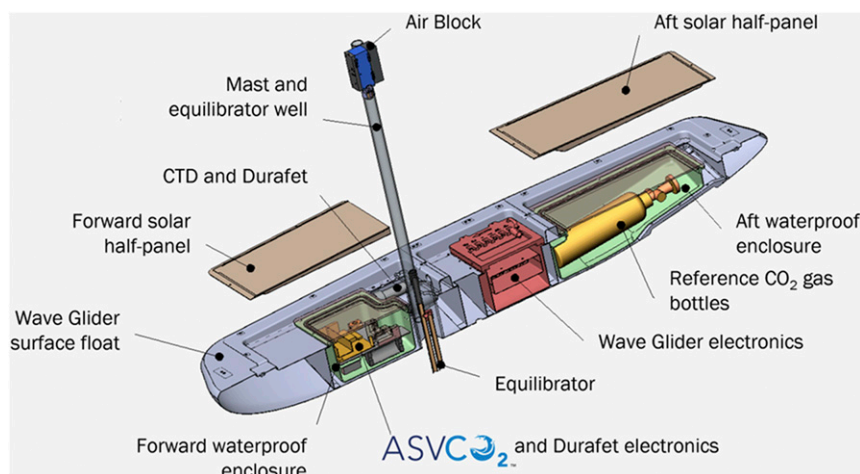


FIG. 2. Cross section of the Liquid Robotics, Inc., Wave Glider surface float with the ASVCO₂ system. Various configurations of reference CO₂ gas bottles have been tested; here we show one gas cylinder, and Fig. 1 shows three.

was inside a housing with surface water pumped through antifoulant to reduce biofouling. The Durafet has a laboratory-based reported short-term (order of hours) precision of ± 0.0005 pH units that weakens to approximately ± 0.005 pH units over longer periods (order from weeks to months) (Martz et al. 2010). Accuracy was assessed in situ using independent validation data (Bresnahan et al. 2014).

A Sea-Bird Scientific Prawler CTD (SBE37 variant) measured sea surface temperature (SST) and sea surface salinity (SSS) simultaneously with the pair of carbon parameters, $p\text{CO}_2$ and pH. In addition, an SBE63 dissolved oxygen sensor was used on the Wave Glider. For the Sairdrone, an Aandera 4831 dissolved oxygen sensor was located in the pumped and poisoned housing with the pH. An oxygen sensor is also part of ASVCO₂ gas analysis, but that is primarily for diagnostics and does not replace the in situ sensor. All measurements were recorded on approximately 30-min or hourly intervals and saved to the internal memory card. While integration of pH and dissolved oxygen sensors into the ASVs are introduced here, the field evaluation of data quality focuses on air-sea CO₂ measurements made by the PMEL-built ASVCO₂.

b. Autonomous vehicle platforms

The ASVCO₂ system was integrated into both the Wave Glider and Sairdrone autonomous surface vehicles. The Liquid Robotics Inc. Wave Glider SV2 float is 210 cm \times 60 cm ($L \times W$). The float joins submerged articulated fins (191 cm \times 40 cm) with a 4-m tether. The articulated fins harness wave energy below the float to propel the platform forward through the water with an average speed of 1.1 kt (Willcox et al. 2010). Two solar

panels sit atop the float and harvest sunlight (a maximum of 112 W) to charge the battery (maximum payload of 40 W) that powers the sensors. The Wave Glider's ability to harness solar and wave energy as well as the programmable course feature allows it to operate at sea for several months at a time without servicing. The programmable course can be modified by a land-based pilot through an Iridium satellite communication link. Other mobility features include targeted station keeping and repetitive course holding. Averaged data were returned to shore in real time via the Iridium satellite communication link and raw data saved on the memory flash card.

The ASVCO₂ electronics and pH sensor were modified to fit in a custom form waterproof box that was secured near the front of the float. The equilibrators and air block were mounted in the center of the float. The span gas bottles were located in the rear end of the float (Fig. 2). The CTD was mounted just aft of the equilibrators at 0.3-m depth. Although the ASVCO₂ system was tested on the Liquid Robotics, Inc., Wave Glider SV2 model, introduced in 2008, the ASVCO₂ system's versatile design can easily be integrated onto the new, larger, faster SV3 model introduced in 2013 and the variants added in 2017 and 2019.

The Sairdrone is a wind-powered autonomous surface vehicle with a 7-m hull, 5-m wing sail, and 2.5-m keel (Fig. 3). It has an average speed of ~ 3 kt but can reach speeds of up to 8 kt. Solar panels and batteries provide power to the onboard electronics and instruments. A number of scientific instruments have been integrated into the vehicle over the last decade, including the ASVCO₂ system (Meinig et al. 2015, 2019). The ASVCO₂ system was packaged in a manner similar to

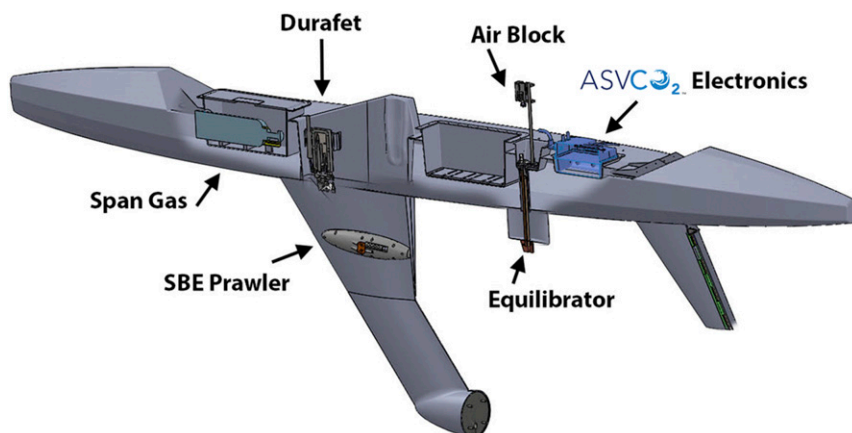


FIG. 3. Cross section of the Saildrone with the integrated ASVCO₂ system and associated components.

the Wave Glider, except for the air and water intake levels, pH mounting, and dissolved oxygen sensor used as noted in section 2a. The CTD was mounted in a tunnel inside the keel at 0.5-m depth. The pH sensor was housed in the hull near the ASVCO₂ system in a channel pumped through antifoulant.

As with the Wave Glider, the Saildrone can be autonomously controlled from shore via Iridium satellite communications. To ensure safe operations at sea, both the Wave Glider and Saildrone carry automated

identification system (AIS) transceivers, enabling them to see surrounding commercial traffic. Raw data were stored on board, and averaged data were transmitted to shore in near-real time. To assess data quality, the ASVCO₂ systems integrated on both carbon Wave Gliders and Saildrones were deployed off the U.S. Pacific coast from 2011 to 2018 and on Saildrones deployed off Australia's Tasmanian coast in 2018 (see Fig. 4). All data are available through the National Centers for Environmental Information (www.ncei.noaa.gov) and

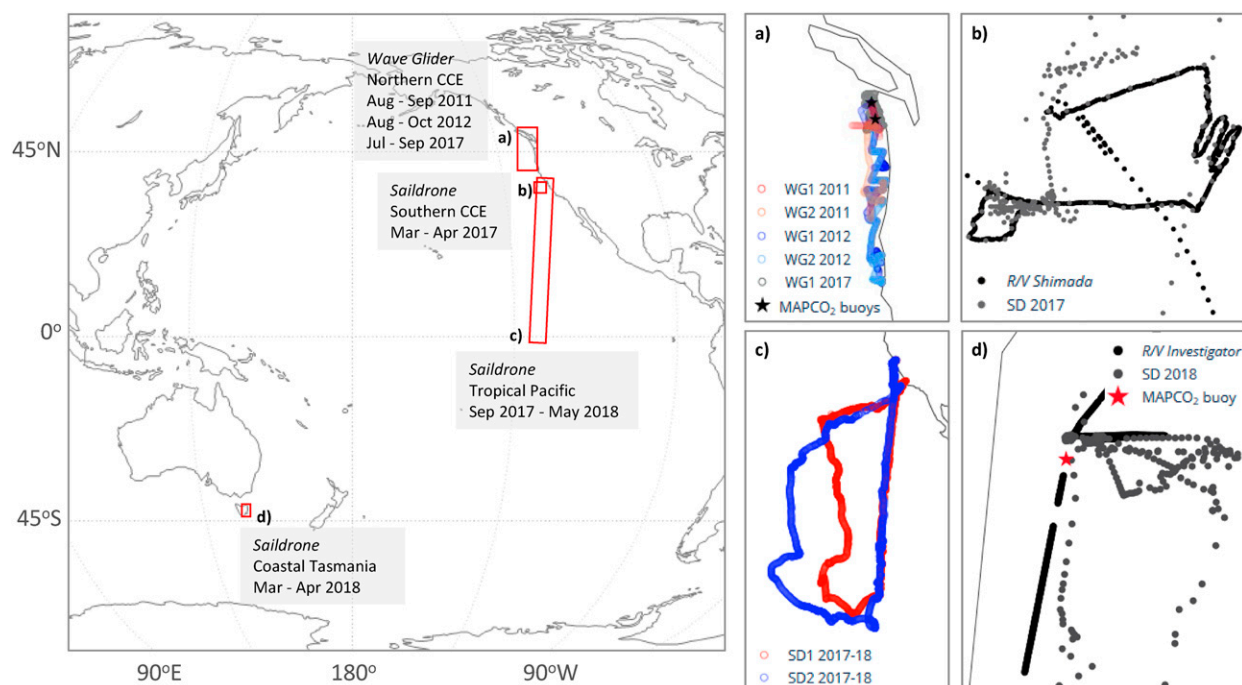


FIG. 4. (left) Locations and mission dates for the Wave Glider and the Saildrone ASVCO₂ deployments. Insets show (a) Wave Glider deployments in the northern California Current ecosystem (CCE), (b) ship and Saildrone intercomparison in the southern CCE, (c) Saildrone deployment to the tropical Pacific, and (d) Saildrone intercomparison in coastal Tasmania.

SOCAT (www.socat.info), except for the data collected in Tasmanian coastal waters, which are available through the Integrated Marine Observing System (<http://imos.org.au/>) and SOCAT.

c. Deployments

1) WAVE GLIDER

The locations and mission dates for all ASVCO₂ deployments presented here are shown in Fig. 4. On 4 August 2011 two Wave Glider vehicles were deployed off of Washington State using the 10-m Washington Department of Fish and Wildlife (WDFW) vessel, R/V *Corliss* (Fig. 4a). One Wave Glider occupied a zonal track along 47.1°N between 125.2° and 124.7°W. The National Data Buoy Center's Cape Elizabeth mooring, which was outfitted with a MAPCO₂ system, was on the primary zonal line. The Wave Glider made 14 passes around the mooring. It also made one excursion to the north to make a pass around the University of Washington's La Push/Čhá7ba (Quileute for "whale tail") mooring, which was also outfitted with a MAPCO₂ system, before it was recovered on 29 September 2011.

The second Wave Glider traveled along the same zonal path for a week before transitioning south to transit longitudinally along the Washington and Oregon coastlines. Both Wave Gliders were brought back together off the Washington coast for recovery after nearly two months of operation. The following year the same two Wave Glider/ASVCO₂ systems were deployed off of Washington State with a mission of surveying the coastal upwelling system along the U.S. West Coast. They were deployed on 23 August 2012 from the WDFW vessel, the R/V *Corliss*, just west of the harbor off of Westport, Washington. Both Wave Gliders traveled south in a zigzag pattern down to Eureka, California (~25°W from 48° to 40.8°N), with one vehicle leading and the second following the same path eight days later. Once the Wave Gliders reached Eureka, they were recovered, shipped back to Washington, and deployed again 6 days later to repeat the track. The final recovery was on 18 October 2012.

In 2017, one Wave Glider with an ASVCO₂ system was deployed again off the Washington State coast to survey coastal waters in the northern California Current System during the upwelling season (Fig. 4a). This deployment started earlier in the season compared to the 2012 mission and surveyed a coastal area north of the region surveyed during the 2012 mission. The full 2017 mission was from 27 July to 27 September 2017. The Wave Glider was deployed and recovered from the Olympic Coast National Marine Sanctuary vessel the R/V *Tatoosh* near the La Push/Čhá7ba buoy at 48.0°N,

125°W. After deployment, the Wave Glider traveled south in a zigzag pattern down to 46.9°N just west of Westport, then returned north following the same pattern. ASVCO₂ systems have also been deployed on Wave Gliders in the Bering Sea, Chukchi Sea, Gulf of Alaska, South Central Pacific, and Southern Ocean; however, quality-controlled data are not yet available for high-quality intercomparisons.

2) SAILDRONE

A couple of months before the last Wave Glider mission, the first field intercomparison of the ASVCO₂ system on a Saildrone was conducted (Fig. 4b). The intercomparison period had a duration of approximately 24 h from 21 to 22 March 2017 and was carried out in coastal waters just south of San Francisco Bay and approximately 20 n mi (1 n mi = 1.852 km) offshore. The Saildrone sailed from Saildrone Inc. headquarters in Alameda, California to the testing site where it rendezvoused with the R/V *Shimada*. The purpose of the deployment was to allow for a field intercomparison between instruments deployed on the Saildrone to those aboard the R/V *Shimada*, including a General Oceanics 8050 underway pCO₂ system (Pierrot et al. 2009). The first activity was a box grid, followed by a straight-leg transit headed east from the box grid, then a series of transects set out in a zigzag pattern, and finally another transect with an L shape headed first north and then west (Fig. 4b). The R/V *Shimada* was generally within about 600 m of the Saildrone and at times less than 200 m, especially for the straight transect headed west. After the intercomparison with the ship, the Saildrone headed south to the CCE1 buoy located at 33.5°N, 122.5°W for an intercomparison with the MAPCO₂ system. From 19 to 25 April, the Saildrone sailed a box around the buoy generally within less than 1 km of the buoy. After this intercomparison, the Saildrone returned to Alameda.

On 1 September 2017, two Saildrones with ASVCO₂ systems departed Alameda for the tropical Pacific (Fig. 4c). While intercomparisons with MAPCO₂ systems on buoys were planned, low wind conditions prevented the Saildrone from safely navigating near the buoys. However, during the three months that both Saildrone ASVCO₂ systems made CO₂ measurements, the vehicles sailed together to allow for comparisons between the two systems. After traveling as far south as 3°S, both Saildrones returned north and were recovered off the central California coast in early May 2018.

On 28 March 2018 three Saildrones with ASVCO₂ systems departed Hobart, Tasmania, Australia, for a field intercomparison with air and surface water measurements made on the R/V *Investigator* and a MAPCO₂ system on the mooring on located at 42.7°S, 148.2°E to the

TABLE 1. Statistical comparison of ASVCO₂ xCO₂ ($\mu\text{mol mol}^{-1}$) measurements minus concurrent measurements made by moored MAPCO₂ systems, ship underway CO₂ systems, and another ASVCO₂ system. Comparisons include all data when both platforms were within 1 km and measurements were within 20 min. Sample size n , mean, and 1 standard deviation of the mean are shown for each platform–platform comparison and all comparisons combined for air and seawater xCO₂.

	Atmospheric xCO ₂ ($\mu\text{mol mol}^{-1}$)			Seawater xCO ₂ ($\mu\text{mol mol}^{-1}$)		
	n	Mean	Std dev	n	Mean	Std dev
MAPCO ₂ vs ASVCO ₂	83	0.4	2.7	82	1.2	6.9
Underway vs ASVCO ₂	23	1.1	0.9	56	−1.2	3.0
ASVCO ₂ vs ASVCO ₂	209	0.1	1.3	112	−1.4	3.4
All comparison data	315	0.3	2.0	250	−0.5	4.9

east of Maria Island, Tasmania (Fig. 4d). Air measurements on the R/V *Investigator* were recorded as 1-min averages of 22 readings using a Picarro 2301 cavity ring-down spectrometer (Humphries et al. 2019) as part of the Global Atmosphere Watch program of the World Meteorological Organization. Surface water measurements were made using a General Oceanics 8050 underway $p\text{CO}_2$ system. Starting on 3 April, the Saildrones spent 36 h navigating a box grid around the Maria Island buoy, then transited east to meet the R/V *Investigator* for an intercomparison starting on 5 April. The Saildrones held a steady course for about 6 h separated from each other by about 300 m and the ship trailing behind the Saildrones by about 300–600 m. After this intercomparison, two Saildrones returned to the Maria Island buoy, while one continued south to test Saildrone performance in Southern Ocean conditions. ASVCO₂ systems have also been deployed on Saildrones in the Bering Sea, Chukchi Sea, and Southern Ocean; however, quality-controlled data are not yet available for high-quality intercomparisons.

d. Data quality assurance and control

Prior to all deployments, the ASVCO₂ systems were run in a laboratory test tank and compared with MAPCO₂ and a General Oceanics 8050 underway CO₂ systems as described in more detail by Sutton et al. (2014). The test tank was used to ensure that the systems were running properly and CO₂ values were within specifications (± 2 ppm) of the comparison systems with known data quality.

During the field deployment, the systems sent back summary data, including a range of diagnostic information, once per day so the system operation could be evaluated. Diagnostic information (e.g., internal pressures with air pumps on and off, calibration flags, and relative humidity) provide information on any flow restrictions or mechanical problems with the air handling and Li-Cor operation.

Once the vehicles were recovered, the raw data were downloaded from the systems and processed in the same

manner described by Sutton et al. (2014) for the MAPCO₂ systems. Quality control program flags were assigned following WOCE guidelines: flag of 2 (good), 3 (questionable), and 4 (bad). Any data flagged as bad were excluded from the plots and intercomparisons shown here. Questionable flags, often caused by diagnostic issues, were individually evaluated. If the data were flagged because of a non-CO₂ related issue, then they were included in the analyses.

Data quality was evaluated from the diagnostic information collected with the measurements, through a comparison of air CO₂ values with the NOAA Greenhouse Gas Marine Boundary Layer Reference (Dlugokencky et al. 2016) from the same time period and latitude, and through comparisons of CO₂ values against MAPCO₂ moorings or shipboard underway measurements (Table 1).

One difficulty with water $p\text{CO}_2$ comparisons is the small time and space scales of variability. In the field it is difficult to determine if differences between systems reflect errors in the measurements or real variations between the sampling times and locations. Comparisons between systems were generally restricted to times within 20 min and 1 km of each. As the differences generally increased with separation distance, the comparisons clearly include both the analytical errors and real variability.

3. Results and discussion

a. Carbon sensor verification

One way to evaluate the system performance while deployed is to look at the calibration results. The system calibrates itself before every set of measurements, but readings of the zero air and the span gas are made immediately before the calibration. By comparing the zero reading before and after the calibration, a sense of the instrumental stability can be determined. The standard deviation of all zero air calibrations during the deployments described here was $0.7 \mu\text{mol mol}^{-1}$, the same as the reported xCO₂ precision determined in the laboratory

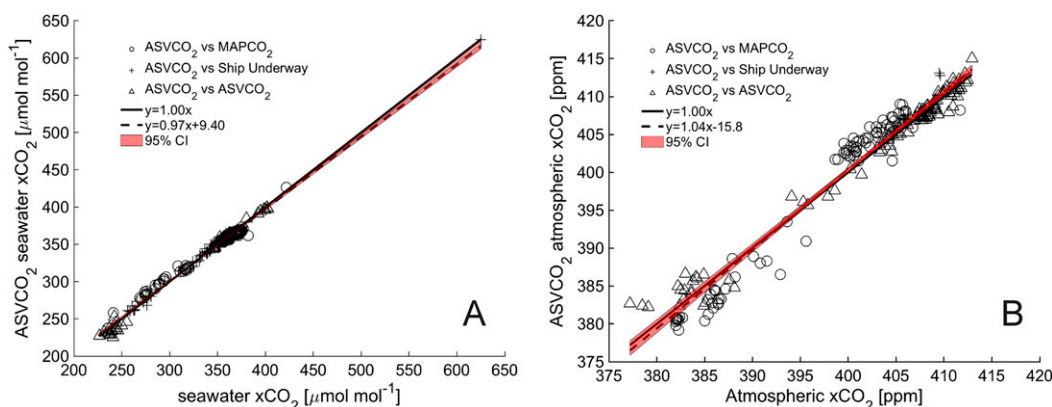


FIG. 5. Comparison of ASVCO₂ (a) seawater and (b) atmospheric measurements with concurrent measurements (within 20 min) made on a ship's underway CO₂ system (crosses), from moored buoys (circles), or from another ASVCO₂ system (triangles) while within 1 km of an ASVCO₂ system. The ASVCO₂ seawater measurements are in good agreement with both of the other platform measurements over the range of measured values as shown by the strong (both $R^2 = 0.99$; RMSE = 4.82 and 4.66, respectively) positive $\sim 1:1$ linear (both slopes ~ 1) relationship. The atmospheric CO₂ comparison data show a similar strong (both $R^2 = 0.96$; RMSE = 1.97 and 1.94, respectively) positive linear relationship (both slopes ~ 1). These results further support the accuracy and precision of the ASVCO₂ system detailed in Table 1.

and consistent with the reported MAPCO₂ precision (Sutton et al. 2014).

The span gas adjustments before and after calibration were up to two orders of magnitude larger than the zero adjustments. This is not surprising because the NDIR CO₂ signal is a strong function of temperature and pressure. Thus, the environmental effects are much more prevalent at higher CO₂ concentrations. Although temperature and pressure are measured in the NDIR detector, small variations in environmental conditions can impact the calibration. This is exactly why the system is calibrated immediately before every measurement, so the calibration is at the same environmental conditions as the in situ measurements.

1) ATMOSPHERIC CARBON DIOXIDE

Atmospheric CO₂ comparisons in offshore conditions provide a good test of system performance because the atmosphere is relatively well mixed and variations in time and space are significantly smaller than in the ocean. Average atmospheric xCO₂ (xCO_{2,atm}) concentrations recorded along the U.S. West Coast of 384.6 ± 6.7 ppm (or μmol mol⁻¹) from August to September 2011, 390.0 ± 5.3 ppm from July to October 2012, and 402.7 ± 8.6 ppm from July to September 2017 agree with the Mauna Loa Observatory Northern Hemisphere monthly in situ pCO_{2,atm} mean values of 389.6, 392.3, and 406.6 ppm, respectively (Dlugokencky et al. 2019; Keeling et al. 2005). The average xCO_{2,atm} concentration recorded along Australia's Tasmanian coast in 2018 of 404.3 ± 2.0 ppm compares well with the flask pCO_{2,atm} monthly average of 403.3 ppm measured at

Baring Head, New Zealand (Dlugokencky et al. 2019; Keeling et al. 2005).

Comparisons of xCO_{2,atm} with underway and mooring systems (within 20 min, and within 1 km) showed more variability than the xCO_{2,atm} comparisons with the flask sampling, with values spiking as high as 415 ppm (Fig. 5b). Part of that variability may be explained by the proximity to shore or another local source of elevated atmospheric CO₂. Many of these measurements were made in coastal regions where offshore winds can introduce elevated CO₂ (Lindquist et al. 2018).

To reduce as much variability between the comparison platforms as possible, Table 1 shows comparisons when platforms measured within 20 min and 1 km. Based on 83 comparisons between the ASVCO₂ system and buoy-mounted MAPCO₂ systems, there was no significant bias in atmospheric xCO₂ and a mean difference of 0.4 ± 2.7 ppm (mean ± 1 standard deviation). There were 23 comparisons between shipboard underway measurements and the ASVCO₂ system. The ASVCO₂ measurements were on average 1.1 ppm higher than the underway system with a mean difference of 1.1 ± 0.9 ppm. Comparisons with shipboard measurements can be a challenge because the ship's air intake can be higher than the ASVCO₂ system, there can be contamination from the ship as the air is transported to the underway system, and the ship's engines are a large local source of CO₂, that either the underway or the autonomous systems may detect.

Because both the autonomous platforms and the instrumental systems are new technologies, they were typically deployed in pairs. This allowed a more thorough

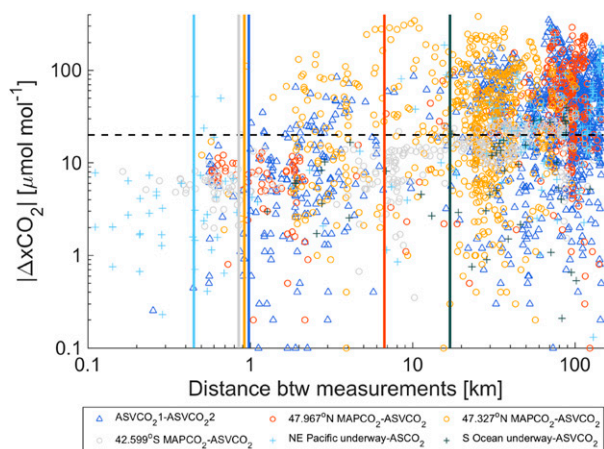


FIG. 6. The absolute difference between ASVCO₂ seawater measurements and concurrent seawater measurements (within 20 min) made by ship underway systems (light blue and gray crosses), moored buoys (orange, yellow, and light-gray circles) or another ASVCO₂ system (blue triangles) as a function of distance between the two platforms.

evaluation of total system performance as the two systems could be compared with each other under a variety of conditions. There were 209 opportunities to compare simultaneous atmospheric CO₂ measurements made from two independent ASVCO₂ systems within 1 km of each other. These comparisons showed a mean difference of 0.1 ± 1.3 ppm.

The comparison for all deployments and platforms showed an overall mean difference of 0.3 ± 2.0 ppm (Table 1). Figure 5b further shows the agreement between $x\text{CO}_{2,\text{atm}}$ measured on the new ASVCO₂ system and other platforms (slope ≈ 1 ; $R^2 > 0.96$; RMSE < 2). The data were carefully examined to look for biases associated with a particular platform, time of year, or geographical location. No significant trends or biases were found.

2) SURFACE WATER CARBON DIOXIDE

As noted previously, comparisons of the surface seawater $x\text{CO}_2$ measurements can be more difficult to interpret given the greater dynamic range and slower mixing. Figure 6 shows the absolute difference between an ASVCO₂ system and either another ASVCO₂ system, a buoy based MAPCO₂ system, or a shipboard underway CO₂ system as a function of distance between the two platforms. The differences generally increase as the separation distance increases. The acceptable distance between platforms seems to vary depending on the platform and the location. Note that the two are usually convoluted so it is difficult to separate whether the difference is platform dependent or location dependent. For example, if a difference of $20 \mu\text{mol mol}^{-1}$ ($10 \times$ the

ideal accuracy of the systems) were set as the limit for comparison (black dashed line in Fig. 6), the acceptable separation distance would range from only half a kilometer for the underway system to nearly 7 km for one of the moorings (vertical lines in Fig. 6, colors correspond with type of system comparison). Closer examination of the comparison data between the moorings at 47.967° and 47.327°N suggest daily variations in physical forcing (i.e., winds) drive the variability in correlation length scale rather than intrinsic site or instrument differences; however, all of these variables are extremely convoluted and difficult to isolate.

Despite the variations in correlation length scale, seawater $x\text{CO}_2$ comparisons between ASVCO₂ systems and other platforms were constrained to measurements taken within 20 min and 1 km of one another. The difference in the paired sea surface temperature (difference $< 0.5^\circ\text{C}$) and salinity (difference < 0.5) measurements from the onboard CTD confirmed the validity of these comparison constraints. Under these constraints, ASVCO₂ seawater $x\text{CO}_2$ measurements are in good agreement with concurrent measurements by other platforms, as seen in Fig. 5a (slope ≈ 1 ; $R^2 > 0.99$; RMSE < 5). One must be careful with fitting data like these with linear functions as the values at the extremes of the data range are disproportionately weighted, but these are encouraging results nonetheless. The mean differences between ASVCO₂ seawater $x\text{CO}_2$ measurements minus concurrent measurements (within 20 min and 1 km) made by moored MAPCO₂ systems, ship underway CO₂ systems, and another ASVCO₂ system equated to $1.2 \pm 6.9 \mu\text{mol mol}^{-1}$, $-1.2 \pm 3.0 \mu\text{mol mol}^{-1}$, and $-1.4 \pm 3.4 \mu\text{mol mol}^{-1}$, respectively (Table 1). Combined, these seawater $x\text{CO}_2$ comparisons show a mean difference of $-0.5 \pm 4.9 \mu\text{mol mol}^{-1}$ ($n = 250$). While the absolute mean difference for all seawater comparison data is similar to the atmospheric $x\text{CO}_2$ results ($0.3 \mu\text{mol mol}^{-1}$), the standard deviations are much higher than the atmospheric comparisons ($2.0 \mu\text{mol mol}^{-1}$). A portion of this variation is likely due to enhanced natural variability in seawater relative to air (Fig. 6).

These $x\text{CO}_2$ field intercomparison results are very similar to previous analysis of the MAPCO₂ technology that the ASVCO₂ is based on, and in this case, the statistics are more robust with 65% more seawater $x\text{CO}_2$ comparisons available for the ASVCO₂ than there were for the MAPCO₂ (Table 5 in Sutton et al. 2014). Laboratory testing of the ASVCO₂ system shows these systems have a precision of less than $0.7 \mu\text{mol mol}^{-1}$ and an accuracy of less than $1.5 \mu\text{mol mol}^{-1}$ for $x\text{CO}_2$ values between 100 and $600 \mu\text{mol mol}^{-1}$. Other sources of error, such as the water vapor correction, results in a total uncertainty of calculated air and seawater $p\text{CO}_2$ of less

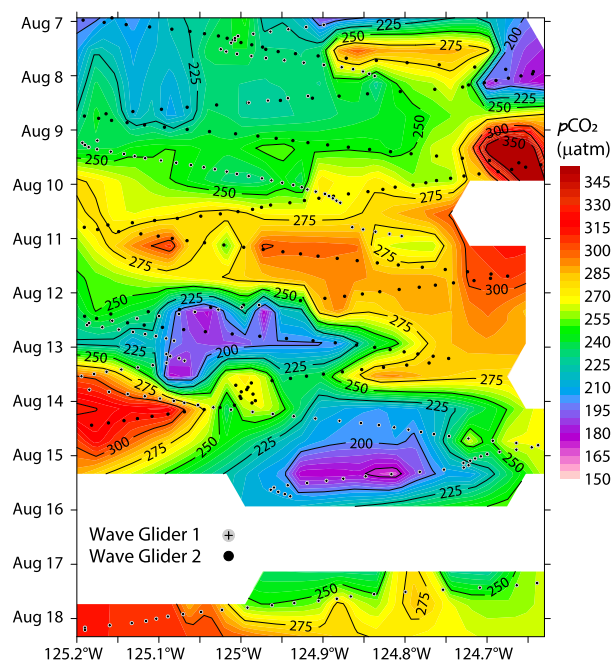


FIG. 7. Hovmöller diagram of surface seawater $p\text{CO}_2$ data (μatm) along the 47°N line in August 2011. Black and gray dots represent measurement locations.

than $2 \mu\text{atm}$ (Table 3 in Sutton et al. 2014). Given the laboratory testing results and the consistency of the resulting statistics for the ASV CO_2 comparisons with MAP CO_2 and shipboard underway systems, this suggests a similar air and seawater $p\text{CO}_2$ uncertainty of less than $2 \mu\text{atm}$ for the ASV CO_2 on Wave Glider and Saildrone platforms.

b. Design and operation

The goal of the ASV CO_2 development was to design a robust and accurate surface CO_2 system that could be used in a range of autonomous surface vehicles. The system has been tested on two very different platforms, the Wave Glider and the Saildrone. Each platform has a unique set of capabilities, but it can be useful to have the same instrumentation on these different platforms so that the data are comparable. The ASV CO_2 system is modified from the MAP CO_2 design, so very similar systems can now be deployed on fixed moorings and autonomous surface vehicles.

Each of the missions described here used the system in a different manner. In one deployment the system occupied a transect off the Washington coast for multiple days. This time series application of the platform-sensor combination is useful for demonstrating the variability of the area over time in more detail than a single mooring can provide (Fig. 7).

Figure 7 shows a Hovmöller diagram of surface seawater $p\text{CO}_2$ data along the 47°N line. This plot clearly

shows the large variability observed during the survey period. The variability is driven by a dynamic interaction between high summertime productivity and coastal upwelling driven by upwelling-favorable winds during 8–12 August and again after 16 August. A ship-based survey aboard the R/V *Wecoma* sampled this line on 13 August, a period of relaxed winds that allowed the upwelling to subside and the local phytoplankton to draw down the surface $p\text{CO}_2$. These preliminary results show that the ship survey happened to sample during a period of low surface values. The ASV CO_2 systems on the Wave Gliders were able to characterize the conditions before and after the ship passed through to put that survey data in a temporal context.

The U.S. West Coast deployment of the Wave Gliders the following year, 2012, used a different approach to evaluate variability. Rather than focus on one transect, the two Wave Gliders were sent down the coast following the same path, but one Wave Glider was approximately 1 week behind the other. This approach characterized both spatial variability along the ASV track, but also temporal variability when comparing between the tracks of the two Wave Gliders (Fig. 8). This work clearly illustrates the temporal variability in $p\text{CO}_2$ resulting from changes in wind and upwelling regimes on time scales of a few days.

Although this manuscript has focused on the adaptation and evaluation of the MAP CO_2 for use on autonomous surface vehicles, these vehicles were also outfitted with a suite of other sensors (e.g., temperature, salinity, chlorophyll, dissolved oxygen, wind speed, and pH) that can provide a very rich context through which to interpret biogeochemical signals along the ASV track. For example, low salinity values (not shown) at 46°N indicate a plume of water from the Columbia River that resulted in low CO_2 values observed by both Wave Gliders (Fig. 8). Relatively cold sea surface temperatures confirmed a strong upwelling of high CO_2 waters at 42°N for the first Wave Glider, but had relaxed by the time the second Wave Glider passed through the area (Fig. 8). Measurements of pH using the Durafet sensors along these tracks provide a completely independent measurement and had a nearly identical pattern of variability to the CO_2 . These measurements not only provide a useful check on the CO_2 , but also provide the second parameter needed to evaluate ocean acidification along the West Coast.

The Saildrone is faster than the Wave Glider and can cover more ground. These vehicles have been used in a manner more similar to underway systems on research ships yet do not require a ship for deployment and recovery. Saildrones also have the advantage that they can transit into waters that are typically shallower than some large vessels are willing to enter. This potentially offers

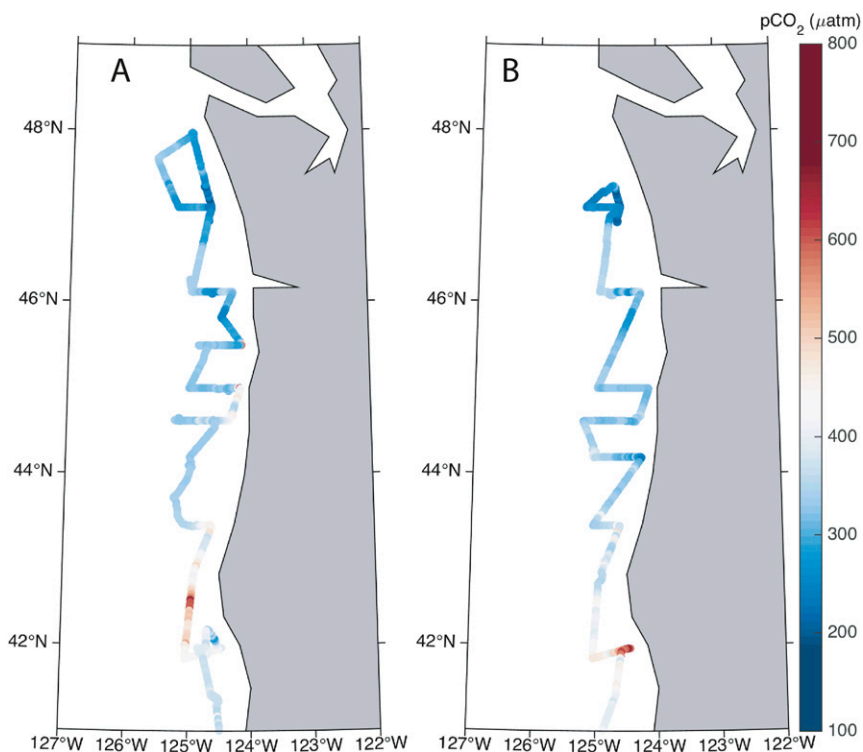


FIG. 8. Plots of surface seawater $p\text{CO}_2$ (μatm) along the U.S. West Coast (23 Aug–18 Oct 2012). Two Wave Gliders were deployed off Westport together. Both vehicles traveled north together for a day, and then (b) one vehicle was sent south to California. (a) The second Wave Glider went to 48°N and then turned south following behind the first Wave Glider on the same track about a week later.

the opportunity to map areas closer to the coast than one typically can get.

The viability of the Sailer ASVCO₂ to make basin-scale surface $p\text{CO}_2$ observations was demonstrated during the 260-day mission from San Francisco Bay south to the Equator (Fig. 9). The ASVCO₂ observed a range of seawater $p\text{CO}_2$ of 350–550 μatm from the coastal shelf to the upwelling region of the tropical Pacific. In the equatorial region, the Sailer crossed sharp fronts in seawater $p\text{CO}_2$ (e.g., Fig. 9 at 2°S, 125°W), SST, and SSS associated with tropical instability waves. While Sailer navigation in low wind conditions was a challenge in this early mission to the tropical Pacific, subsequent ASV development has improved control under such conditions.

Thermodynamic and biological influences cause mesoscale temporal (from days to months) and spatial (km) variability in seawater carbon concentrations. Sparse measurements from instrumented survey expeditions and moorings can lead to biases in the characterization of these mesoscale dynamics within the carbon system, particularly in coastal regions. The new ASVCO₂ technology can be used to supplement current carbon measurement techniques, particularly with its cost-effective

and energy-efficient design. The Wave Glider and Sailer have the ability to accurately measure air–sea CO₂ with an overall uncertainty of $\pm 2 \mu\text{atm}$ paired with sea surface pH, SSS, and SST every 30 min. The short measurement interval provides carbon measurements that can capture small-scale spatiotemporal variability in the carbon system near the air–sea interface along the measurement

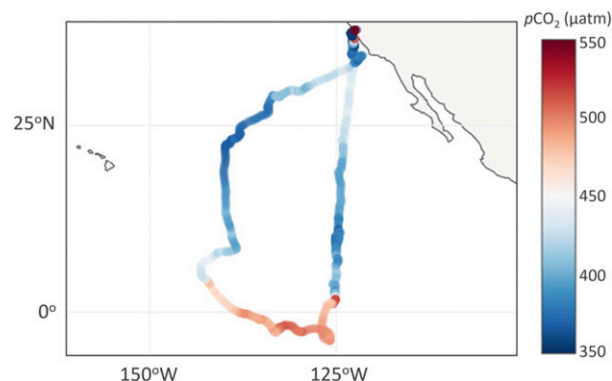


FIG. 9. Surface seawater $p\text{CO}_2$ (μatm) measured by a Sailer ASVCO₂ during the 260-day mission to the tropical Pacific in 2017–18.

path. Wave Glider and Saildrone ASVCO₂ deployments combined with mooring and shipboard carbon measurements can contribute to a better understanding of past, present, and future carbon dynamics. In particular, with long transit capabilities and autonomous operation, Saildrone and Wave Glider ASVCO₂ systems have the potential to fill large observing gaps in the surface seawater pCO₂ network.

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Data availability statement. Data presented in this paper are publicly available through the National Oceanic and Atmospheric Administration (NOAA) Ocean Carbon Data System repository located within the National Centers for Environmental Information (<https://www.nodc.noaa.gov/ocads/>).

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