

An inter-comparison of autonomous *in situ* instruments for ocean CO₂ measurements under laboratory-controlled conditions

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ARTICLE INFO

Keywords:

Marine CO₂ system
Autonomous sensors
Sensor inter-comparison
Ocean acidification
Internal consistency

ABSTRACT

Observations of the marine CO₂ system are important for understanding ocean acidification, air-sea CO₂ fluxes and the marine carbon cycle in general. A variety of autonomous *in situ* instruments have been developed and used towards this end. There is, however, a lack of inter-comparison studies of currently available sensor technologies. In this study, a total of 10 instruments including commercially available pH, partial pressure of CO₂ (pCO₂), and total alkalinity (A_T) sensors were tested and compared in a 5000 L seawater tank located at Scripps Institution of Oceanography (SIO), California, USA. The test took place over ~12 days (August 16 to 28, 2016) where conditions in the tank were artificially varied to encompass a wide range of A_T, pH and pCO₂ as well as temperature and salinity. To assess accuracy, independent measurements of pH, pCO₂, dissolved inorganic carbon (DIC) and A_T were made using benchtop instrumentation. We also evaluated internal consistency, comparing the measured parameter from the sensors with the calculated parameter, e.g. pCO₂ calculated from A_T and pH compared with directly measured pCO₂. DIC can be precisely derived (within ±5 μmol/kg) over a wide range of conditions from measured pH or pCO₂ paired with A_T. Sensor accuracy established by discrete samples is sufficient for short-term and seasonal dynamical studies, but their ability in determining long-term (e.g. climate) variability could not be evaluated because of the brevity of the study. These results provide insights into sensor performance and strategies for data quality control for future studies of ocean acidification and carbon cycling.

1. Introduction

The oceans currently act as a sink for atmospheric CO₂, and are absorbing 25% of modern anthropogenic emissions (Sabine et al., 2004; Watson et al., 2020). This uptake of CO₂ has decreased seawater pH and calcium carbonate (CaCO₃) mineral saturation state (Ω), a process known as ocean acidification (OA). Sustained observations of CO₂ chemistry provide critically needed data for understanding not only OA, but spatiotemporal variability and magnitudes of air-sea CO₂ fluxes for use in regional and global carbon budgets (Sutton et al., 2017; Takahashi et al., 2002). The temporal resolution of ship-based measurement programs, such as the Hawaii Ocean Time-series (Karl and Lukas, 1996) and the Bermuda Atlantic Time-series (Michaels and Knapp, 1996) are limited by high capital and labor investments. Such programs are useful for characterizing long-term trends in the open ocean, but cannot capture episodic events, such as phytoplankton blooms (Westberry et al., 2016)

and storms (Wu et al., 2020) that influence seasonal and interannual CO₂ levels. Hourly to monthly variability on local scales cannot be resolved using surface inorganic carbon data based on sparse sampling. For example, coastal environments have rapid fluctuations in the CO₂ system through biological production and short-term physical influences such as upwelling (Cai et al., 2020; Gac et al., 2020; Harris et al., 2013; Takeshita et al., 2015). Ecosystems such as kelp forests and coral reefs often exhibit significant short-term dynamics (Cyronak et al., 2020; Hofmann et al., 2011; Pezner et al., 2021), requiring high-frequency measurements to decipher. Compared to ship-based measurements, ocean datasets collected using autonomous, *in situ* instruments have significant advantages for characterizing these complex systems (Islam et al., 2017; Wang et al., 2019; Claustre et al., 2020).

The inorganic carbon system can be fully characterized by quantifying two of the four commonly measured inorganic carbon parameters along with peripheral variables (e.g. temperature and salinity): total

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<https://doi.org/10.1016/j.marchem.2022.104085>

Received 29 August 2021; Received in revised form 19 November 2021; Accepted 5 January 2022

Available online 7 January 2022

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alkalinity (A_T), pH, the partial pressure of CO_2 (pCO_2), and dissolved inorganic carbon (DIC) (Millero, 2007; Orr et al., 2018). Ideally, we would have autonomous sensors for each of the four parameters, but some of the measurement techniques are challenging to adapt for autonomous measurements because of their complexity, power consumption, and other limitations such as reagent consumption. Instruments are commercially available for measurements of pH (e.g. Seidel et al., 2008; Martz et al., 2010), pCO_2 (e.g. DeGrandpre et al., 1995; Friederich et al., 1995; Clarke et al., 2017) and A_T (Spaulding et al., 2014; Shangguan et al., 2021). There are also new technologies that potentially further extend our *in situ* observational capabilities, such as DIC (Liu et al., 2013; Fassbender et al., 2015; Wang et al., 2015) and A_T sensors (Briggs et al., 2017), but they have not been commercialized and are not yet widely available.

The assessment of biological and biogeochemical responses to small changes in the CO_2 system requires accurate, precise and stable *in situ* measurements (Williams et al., 2017). Thus, it is important to rigorously evaluate instrument performance under controlled conditions rather than on a remote mooring or other platform where access is limited. The quality of data from varying instruments can be assessed through comparison with bottle samples, over-determinations of the CO_2 system, as well as measuring the same parameter with multiple instruments. Past inorganic carbon inter-comparison studies have focused on shipboard underway pCO_2 (Arruda et al., 2020; Körtzinger et al., 2000; Macovei et al., 2021) and underway pH measurements (Rérolle et al., 2016), *in situ* pH sensors (Okazaki et al., 2017), and simultaneous measurements of pCO_2 , pH and/or DIC (Wang et al., 2007; Ribas-Ribas et al., 2014; Gray et al., 2011). The Alliance for Coastal Technologies (ACT) has also documented performance evaluations of *in situ* pH and pCO_2 sensors (Tamburri et al., 2011). With the increased use and availability of autonomous instruments since most of these past inter-comparisons were completed, there is a continued need for inter-comparison studies of the variety of autonomous inorganic carbon instruments now available.

The goal of this research is to extensively evaluate a suite of *in situ* CO_2 system sensors in a controlled environment. To accomplish this, a subset of commercially available autonomous A_T , pH, and pCO_2 instruments were tested in a 5000 L seawater tank (Fig. 1) at Scripps Institution of Oceanography (SIO). The pH and pCO_2 instruments have been widely used for autonomous *in situ* seawater measurements (e.g. Gray et al., 2018; DeGrandpre et al., 2020; McLaughlin et al., 2017; Sutton et al., 2019), while A_T instruments have only recently become available (Spaulding et al., 2014; Pezner et al., 2021). The tank chemistry was artificially varied to encompass a wide range of conditions (temperature, salinity, and inorganic carbon species). The 12-day test provides valuable insights into the sensor performance, data quality

control, and strategies for using the sensors in studies of inorganic carbon cycling.

2. Materials

2.1. Instrumentation

As shown in Table 1, this study used two SAMI-pHs (Sunburst Sensors, LLC; p66 and p87) (Seidel et al., 2008), two SeapHOx sensors (SP020 and SP032) (Bresnahan et al., 2014) along with an *in situ* sensor for pCO_2 (Sunburst Sensors, LLC; SAMI- CO_2) (DeGrandpre et al., 1995). The SAMI-pH is based on the spectrophotometric pH method using meta-cresol purple (mCP) indicator (Clayton and Byrne, 1993). A pump and a valve draw in seawater and mix with indicator before spectrophotometric detection. The SeapHOx uses a potentiometric pH sensor, the Honeywell Durafet (Martz et al., 2010). The SAMI- CO_2 uses a gas-permeable membrane where a colorimetric pH indicator equilibrates with ambient seawater pCO_2 . The equilibrated solution is pumped into a fiber-optic cell for detection. A benchtop analyzer, the Super CO_2 (Sunburst Sensors, LLC), was used as a pCO_2 reference measurement (Hales et al., 2004). The Super CO_2 is based on non-dispersive infrared (NDIR) gas detection (model LI-850, Li-COR, Inc.) after the seawater stream equilibrates with a gas stream in a showerhead equilibrator. Three identical A_T instruments (SAMI-alk) were also tested (Sunburst Sensors, LLC, alk00, 01, and 03) (Martz et al., 2006; Spaulding et al., 2014). The SAMI-alk was developed based on Tracer Monitored Titration (TMT), where an acidified indicator solution is incrementally pumped into a mixed fiber-optic flow cell and used to simultaneously quantify pH and dilution factor (volumetric ratio between indicator solution and sample). A_T can then be solved by nonlinear least-square analysis (NLLS) from a sequence of titration points. A CTD (Conductivity, Temperature, and Depth) (Sea-Bird Scientific; SBE 37-SI) recorded temperature and salinity in the tank.

The 10 instruments were placed in the SIO test tank (Fig. 1). The tank is 305 cm in diameter and 84 cm in height and contains ~5000 L of seawater. The tank was filled with seawater pumped from the Scripps Pier one week prior to the experiment. Tank water is first run through

Table 1

A list of instruments used in this study.

Parameters	Instruments
pH	SAMI-pH (p66 and p87), SeapHOx (SP020 and SP032)
pCO_2	SAMI- CO_2 , Super CO_2
A_T	SAMI-alk (00, 01, and 03)
Temperature and salinity	CTD (SBE 37-SI)

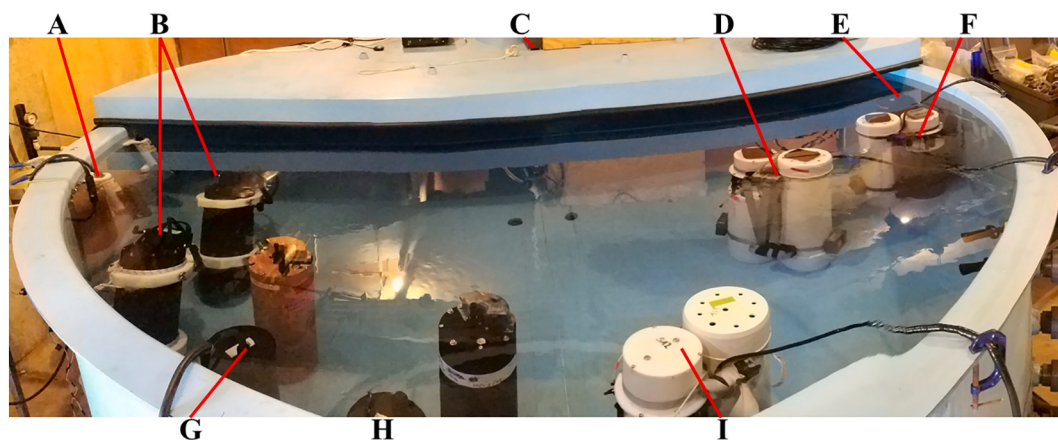


Fig. 1. Test tank at Scripps Institution of Oceanography with letters showing instrument locations and identities. The 5000 L test tank is 305 cm across. A: CTD (SBE 37-SI) B: SeapHOx (SP020, SP032) C: Super CO_2 intake point D: SAMI-alk00 E: SAMI-pH (p87) F: SAMI-alk01 G: SAMI-pH (p66) H: SAMI- CO_2 I: SAMI-alk02.

sand filters at the pier. Once in the tank, seawater is sterilized with a DEL Ozone Generator for 3 h and then continuously filtered through a 1 μm bag filter (Part Number F3AB00013, Eaton). Seawater is internally circulated through the tank with a pumping rate of ~ 170 L/min (model DB7P-M227, Finish Thompson, Inc.). Although tank temperature is not under precise control, a manually-operated heat exchange unit allows rapid tank temperature changes on-demand. The tank was open to the atmosphere allowing gas exchange and evaporation. Instruments were deployed close to the edge of the tank for easy-access (Fig. 1).

2.2. Chemicals

Nanopure water (17.9 M Ω -cm specific resistance) was obtained from a Barnstead water purification system (Thermo Scientific) and used for all solutions. Chemicals used to modify the CO₂ chemistry for the tank seawater included 0.1 N HCl (Fischer Scientific) and a solution with A_T ~ 0.23 mol/kg and DIC ~ 0.17 mol/kg prepared from dried NaHCO₃ and Na₂CO₃ powder (analytical grade, Fischer Scientific). This carbonate solution was used to increase A_T for the tank seawater (see *Seawater CO₂ chemistry in the tank*).

Bromocresol purple sodium salt (BCP) (indicator grade, Sigma-Aldrich), NaCl powder (analytical grade, Fischer Scientific), and 0.1 N HCl were used to prepare titrant solutions for the SAMI-alks (Spaulding et al., 2014). The titrant solution contained approximately 6.5×10^{-5} mol/kg BCP, 8.3×10^{-4} mol/kg HCl and 0.68 mol/kg NaCl. Salty carbonate standards for SAMI-alks were made from Na₂CO₃ (ACS primary standard grade, Alfa Aesar) and 0.1 N HCl with 0.68 mol/kg NaCl solution. Alkaline bromothymol blue (BTB) solutions for SAMI-CO₂ contained 5.6×10^{-5} mol/kg BTB and 8.5×10^{-5} mol/kg NaOH prepared from BTB powder (ACS Reagent grade, Sigma-Aldrich) and certified 0.1 N NaOH (Fischer Scientific) (DeGrandpre et al., 1995). The SAMI-pH used purified mCP (original powder from Sigma-Aldrich, indicator grade mCP). Indicator purification procedures are described in DeGrandpre et al. (2014). The mCP concentration was $\sim 3.8 \times 10^{-4}$ mol/kg with a pH of 7.8 adjusted by using 0.1 N NaOH and HCl. Indicator and carbonate standard solutions were stored in gas-impermeable bags.

3. Procedure

3.1. Instrument calibration

Calibration of the SAMI-alks was performed as described in Spaulding et al. (2014) using certified reference materials (CRMs) (Batch 158, A_T = 2226.6 $\mu\text{mol/kg}$) (Dickson et al., 2003). A calibration factor was obtained by comparing the A_T output from SAMI-alks to the certified A_T. Calibration factors vary among three SAMI-alks and depend on the combined uncertainties of the optical pathlength and molar absorptivities, as discussed below. In addition to the CRM calibration, synthetic carbonate standards were measured *in situ* twice per day during the deployment through a three-way selection valve in the SAMI-alk.

Calibration and pre-deployment preparation of the SAMI-CO₂, SAMI-pH, and SeapHOx were performed as described in DeGrandpre et al. (1995), Seidel et al. (2008), and Bresnahan et al., 2014, respectively. All SAMI instrument calibrations (pCO₂) and validations (pH) were performed in the DeGrandpre lab before shipment to the SIO test facility. Specifically, the SAMI-CO₂ was calibrated by determining its response over variable CO₂ concentrations in a water-filled temperature-controlled tank while CO₂ was simultaneously monitored by an NDIR CO₂ analyzer (model LI-840, Li-COR, Inc.) with a membrane equilibrator (Hales et al., 2004). The SAMI-pH accuracy was validated to within 0.004 pH units using tris buffer (DelValls and Dickson, 1998). Calibrations of the SeapHOx systems were performed by the Martz lab group before testing began by applying a single calibration point with reference to spectrophotometric pH (see *Seawater CO₂ chemistry in the*

tank). SuperCO₂ periodically measured standard CO₂ gas at three different concentrations (202.7, 800.0, and 1503.0 ppm), which were used to correct for drift following the descriptions in Dickson et al. (2007).

3.2. Seawater CO₂ chemistry in the tank

The experiment was designed to reduce temporal and spatial mismatch to minimize errors from non-sensor sources. All instruments were configured to start measurements on the hour. The SeapHOx, CTD, SAMI-pH, and SAMI-CO₂ instruments were set to 15 min measurement intervals. The SAMI-alks were set to 1-h intervals due to reagent and power limitations. The SuperCO₂ recorded pCO₂ every four seconds. All data are reported at Universal Time (UTC) throughout this paper.

Three replicate discrete samples (0.5 L each) were drawn from the tank on the hour for benchtop analyses $\sim$ four times per day. A total of 52 samples for pH, 50 samples for A_T and 43 samples for DIC were collected. The pH samples were analyzed by spectrophotometry immediately after collection using purified mCP. The A_T and DIC samples were poisoned and stored following standard protocol (Dickson et al., 2007), and were analyzed within three days using CRMs for quality assurance (Batch 156). A_T was determined by open-cell potentiometric titration (Gran, 1952) and a nonlinear least squares approach (Dickson et al., 2007). DIC was determined by acidifying samples and quantifying the extracted CO₂ gas by infrared detection (Goyet and Snover, 1993). Bottle sample results were compared to measurements from the autonomous instruments.

Seven different tests were run during the 12-day experiment listed here in chronological order and labeled in the time-series data in Fig. 2a:

1. Static environment (August 16, 21:00): this test was to determine the stability of the instruments keeping conditions as constant as possible. All instruments operated without any purposeful changes in conditions over a 72 h period.
2. Increase A_T and DIC (August 19 at 22:00): this test was to determine instrument performance at higher A_T and DIC. The A_T was raised by adding a 2 L carbonate solution with A_T ~ 0.23 mol/kg and DIC ~ 0.17 mol/kg. The solution was used to simulate a natural A_T increase of ~ 90 $\mu\text{mol/kg}$ and ~ 70 $\mu\text{mol/kg}$ increase in DIC and was prepared based on a mass balance calculation. Measurements were made for 24 h after addition of the carbonate solution.
3. Decrease A_T with constant DIC (August 20 at 22:00): this test continued to evaluate the instruments' performance over a range of A_T, pH, and pCO₂. The A_T was lowered using 1 L of a 0.1 N HCl solution. These conditions were observed for 48 h.
4. Decrease pCO₂ with constant A_T (August 22 at 22:00): this test was performed to evaluate instrument response to changes of lowered pCO₂ and elevated pH with constant A_T. The pCO₂ was lowered without changing A_T by bubbling compressed air through an air stone into the tank. The test was observed for 24 h.
5. Increase pCO₂ with constant A_T (August 23 at 22:00): this test was used to evaluate instrument response to elevated pCO₂ and lowered pH changes by dissolving small amounts of dry ice in the tank. The test was observed for 24 h.
6. Temperature change (August 24 at 22:00): this test was performed to evaluate instruments' response with varying temperature. Temperature was decreased by $\sim 7^\circ\text{C}$ from ambient (24°C) using a closed loop cooling tower attached to the test tank. The cooling tower maintained the lower temperature for 24 h, and was shut off thereafter allowing the tank to warm naturally for another 24 h.
7. Salinity change (dilution) (August 26 at 22:00): this period evaluated the instruments' response to changes in salinity by adding 480 L of deionized water to dilute the tank by $\sim 10\%$. Due to the tank's maximum capacity, ~ 500 L of seawater was drained from the tank to allow addition of the deionized water. This test was observed for 24 h.

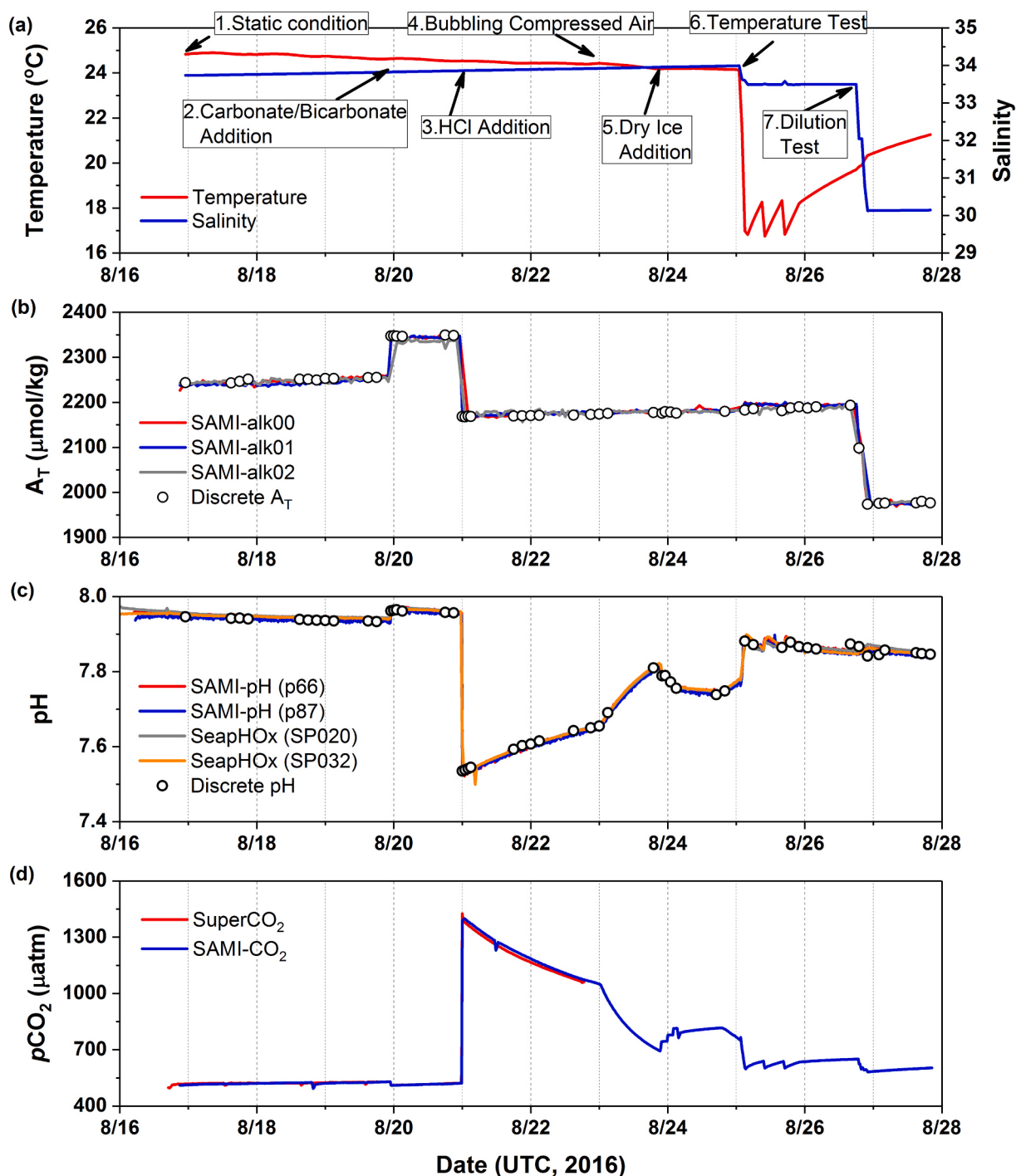


Fig. 2. The 12-day time-series measured in the SIO test tank (Fig. 1) with a suite of autonomous CO_2 system instruments, as well as temperature and salinity. (a) Temperature and salinity in different phases of the tank conditions; (b) data from three SAMI-alks and discrete samples; (c) data from 4 pH sensors (two SAMI-pH and two SeapHOx) and discrete samples; (d) data from Super CO_2 and SAMI- CO_2 . Super CO_2 data after August 22 22:00 are not shown (see $p\text{CO}_2$ data assessment). Note that traces overlie each other and are not distinguishable.

3.3. Data analysis

To assess sensor performance, we used accuracy defined as the difference between results obtained by sensor and bottle measurements (sensor values – bottle values). For internal consistency comparisons, the differences are expressed as mean difference (measured – calculated) $\pm$ one standard deviation (SD). All pH were determined on the total hydrogen ion concentration scale. $p\text{CO}_2$ was directly used without converting to carbon dioxide fugacity ($f\text{CO}_2$). All CO_2 calculations were

made using CO2SYS version 2.1 (Pierrot et al., 2006) and also the more recent version in Orr et al. (2018) that allows assessment of uncertainties in CO_2 calculations. The carbonic acid dissociation constants of Lueker et al. (2000), the total-boron-to-salinity ratio from Lee et al. (2010), and K_{HSO_4} from Dickson (1990) were used. The choice of Lueker et al. (2000) was to be consistent with recent evaluations of CO_2 system calculations (Fong and Dickson, 2019; Patsavas et al., 2015; Raimondi et al., 2019). Phosphate and silicate concentrations were assumed to be zero. Some data sets were averaged or interpolated for internal

consistency comparisons. SuperCO₂ data was averaged to 15-min intervals to be in sync with the SAMI-CO₂ and other instruments. SAMI-alk data were interpolated to 15-min intervals. Based on the rapid changes in temperature and salinity, 95% mixing time for the tank was estimated to be 1.5 h and 1.9 h from temperature and salinity data, respectively, by using a first-order reaction model. Sensor and bottle measurements immediately after the addition of the NaHCO₃/H₂CO₃ and HCl solutions were excluded from the accuracy assessment because the tank was not fully homogeneous.

4. Results and discussion

4.1. Tank conditions

The tank was exposed to the air during the 12-day experiment, allowing for natural CO₂ air-water exchange, temperature fluctuations and evaporation. From August 16–24 temperature slowly decreased from 24.8°C to 24.0°C while salinity increased from 33.7 to 34.0 due to evaporation (Fig. 2a). As indicated above and in Fig. 2a, temperature and salinity tests were performed after August 24 at 22:00, artificially altering these parameters. The sawtooth pattern on August 25 is due to the unstable cooling tower temperature regulation with a resolution of ~1–2°C. The temperature test was accompanied by a salinity drop of ~0.5 because the seawater stored in the heat exchanger and associated piping remained at a salinity of ~33.5 while the tank water had evaporated to a higher salinity before the test began. This inflow was later found to produce negligible effects on A_T (Fig. 2b), but a temporary increase of ~40 μmol/kg in DIC (discussed in *Internal Consistency* section). Dilution (August 26 at 22:00) led to a further salinity decrease of ~3.2.

The initial measured A_T (2238 μmol/kg) (Fig. 2b) is typical of the range of 2200–2250 μmol/kg reported by Bockmon et al. (2013) for this area. The A_T then increased by ~10 μmol/kg due to evaporation during the 3-day static conditions. After the addition of carbonate/bicarbonate solution (August 19 at 22:00), A_T increased from ~2250 to 2350 μmol/kg, followed by a ~190 μmol/kg decrease due to acid addition (August 20 at 22:00). The final step of dilution (August 26 at 22:00) led to another ~190 μmol/kg decrease of A_T.

The pH and pCO₂ ranged from ~7.50 to 7.97 (Fig. 2c) and ~500 to 1430 μatm (Fig. 2d), respectively, using the approximate range measured by each sensor. They were relatively stable during the static period with a ~0.01 unit decrease in pH and ~15 μatm increase in pCO₂ caused by slow gas exchange with the high indoor air pCO₂. Adding carbonate/bicarbonate solution (August 19 at 22:00) did not dramatically change pH and pCO₂ because they are not strongly affected by simultaneous increase of A_T and DIC due to buffering. The largest variation was observed by HCl addition (August 20 at 22:00) which caused a ~0.47 unit decrease in pH and ~960 μatm increase in pCO₂. After addition of the acid, the CO₂ chemistry evolved by CO₂ degassing into the air, evidenced by gradually increased pH and decreased pCO₂ from August 21 to 22 until more rapid changes were created by bubbling with compressed air (August 22 at 22:00). The dry ice addition (August 23 at 22:00) led to a decrease of pH of ~0.05 pH units and an increase of pCO₂ of ~110 μatm. On August 24 at 22:00, as the temperature dropped by ~7°C, pH increased by ~0.12 unit and pCO₂ decreased by ~190 μatm. By using CO₂sys with bottle A_T (2180 μmol/kg) and DIC (2032 μmol/kg) at this time, we determined that the temperature change from 24°C to 17°C would increase pH by 0.10 units and decrease pCO₂ by 188 μatm, close to the observed changes indicating that the seawater inflow from the cooling system did not strongly affect pCO₂. The effect of dilution (August 26 at 22:00) on pH and pCO₂ is small, similar to the test of increased A_T.

To summarize, A_T, pH, and pCO₂ encompassed a large range characteristic of coastal to open ocean surface waters and deep open ocean waters (Cai et al., 2010; Carter et al., 2016; Jiang et al., 2008; Millero, 2007; Takahashi et al., 2002). A detailed analysis of sensor performance

is presented in the following sections.

4.2. SAMI-alk data

SAMI-alk accuracy depends on accuracy of parameters that form its theoretical basis and calculations, which are titrant acidity (C_{a,i}), combined optical pathlength (b) – molar absorption (ε) coefficients (εb), and indicator and carbonate thermodynamic constants (Martz et al., 2006). Of these variables, εb is an instrument-dependent property that requires careful experimental determinations for each SAMI-alk. The parameter was only measured on SAMI-alk00 for this experiment, however, and the other instruments' optical cells were disassembled before we realized its variability. With recent evaluations and A_T modeling (Shangguan et al., 2021), we found that errors in εb create concentration dependent A_T errors that are not corrected by the single point CRM calibration. These errors were evident in the raw SAMI-alk data where values were close to the CRM (2226.6 μmol/kg), but increased away from the lower A_T level (~20 μmol/kg on August 27). Adjustment of εb was found to reduce these concentration dependent errors; consequently, we used the initial discrete sample A_T and final A_T (August 27) to determine the optimal εb and this reduced the sensor errors for the entire data set. Optimized εb varied by 1.6% for three SAMI-alks and are within the manufacturing tolerance (~5%) controlled by placement of the optical fibers in the flow cell. Each εb can be precisely determined to ~0.3% based on replicate measurements of known concentrations of indicator species (n = 5 typically). These results highlight the importance of εb determination for SAMI-alk calibration if a wide range of A_T is encountered. After εb optimization, the SAMI-alk accuracies relative to discrete samples are 0.9 ± 4.8, 0.0 ± 5.8 and -0.5 ± 6.0 μmol/kg (n = 45) for SAMI-alk00, alk01 and alk02, respectively (Fig. 3a). Using SAMI-alk01 as a reference (SAMI-alk00 or alk02 – alk01), the differences for SAMI-alk00 and SAMI-alk02 are -1.4 ± 4.2 μmol/kg and -0.2 ± 6.6 μmol/kg (n = 240) (Fig. 3b). The difference between SAMI-alk00 and SAMI-alk02 is 1.3 ± 6.7 μmol/kg (n = 240, not shown).

Instrument performance can also be evaluated by examining the twice daily measurements of *in situ* standards (22 total for each SAMI, Fig. 3c). The mean values and standard deviations are 2209.7 ± 5.4 μmol/kg for SAMI-alk00, 2216.4 ± 6.9 μmol/kg for SAMI-alk01, and 2214.1 ± 4.0 μmol/kg for SAMI-alk02. Upon further inspection, the first 4 standard measurements of SAMI-alk01 were affected by poor optical blanks likely due to bubbles temporarily entrained in the optical cell. Replacing measured blanks with accurate blanks from other subsequent measurements recover these four standards and improve the results to 2213.8 ± 4.1 μmol/kg. Consequently, the *in situ* standards provide an independent validation of the accuracy and stability of the SAMI-alks during the experiment.

4.3. pH sensor inter-comparison

All four pH sensors (Table 1) exhibited excellent accuracy (mean errors <0.004 with one standard deviation < ±0.008) compared with discrete pH samples, n = 48 (Figs. 2c and 4a). These comparisons are also included in Tables 2 and 3 for clarity. The errors for all pH sensors are significantly correlated (p < 0.05, not shown). Around August 21 at the time of high pCO₂ (Fig. 2), consistent negative pH errors may have resulted from degassing during sampling and analysis that increased the discrete bottle pH (Bockmon and Dickson, 2015). Therefore, the standard deviation of accuracy was at least partially due to the quality of discrete samples (Table 2). We also noted positive A_T errors over the same period (Fig. 3a) possibly because of loss of CO₂ in the SAMI-alk titration cell for the higher temperature measurements affecting non-linear least squares algorithm in its data processing (Spaulding et al., 2014). Larger errors after the dilution test (August 26 at 22:00) were found for all pH sensors possibly caused by inadequate mixing in the tank. Samples were taken through a spigot located near the bottom of

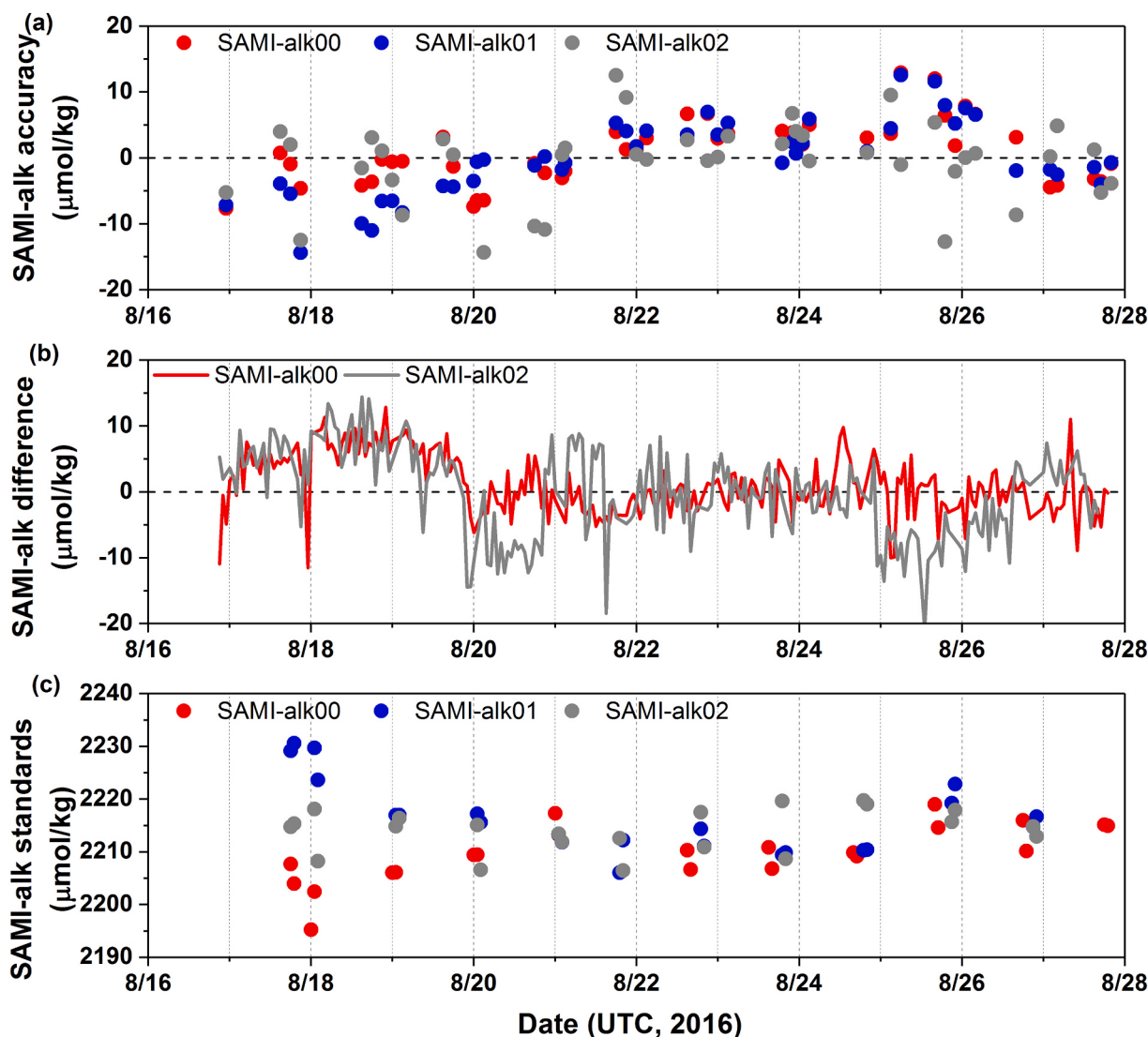


Fig. 3. (a) SAMI-alk accuracy compared to bottle A_T ; (b) Differences of SAMI-alk00 (red line) and SAMI-alk02 (grey line) compared to SAMI-alk01 (SAMI-alk00/alk02 – alk01). Dashed line indicates zero line; (c) Twice daily standard measurements from three SAMI-alks. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the tank, not from the sensor locations. In terms of mean errors, SAMI-pH (p66) and two SeapHOx are more consistent ($+0.003$), but SAMI-pH (p87) has a negative mean error (-0.003), making a significant but constant offset between the two SAMI-pHs (see next).

Sensor-to-sensor pH comparisons were also performed (Table 3). In addition to comparison of intra-category pH sensors, data from SAMI-pH (p66) and SeapHOx (SP032) was used as an example of inter-category comparison. The mean difference between the two SAMI-pHs was 0.0059 ± 0.0037 pH units ($n = 1115$) (Fig. 4b and Table 3). The value of ± 0.0037 is interpreted as the quadratic addition of the noise of SAMI-pH (i.e. $\pm 0.0026 = \pm 0.0037/1.4$), close to the previously reported value of $\sim \pm 0.003$ based on replicate sample measurements (Lai et al., 2018). The automated pH perturbation correction is the major source of noise (Lai et al., 2018), but this correction is important for accuracy of indicator-based pH measurements (Clayton and Byrne, 1993; Li et al., 2020). SAMI-pHs differ slightly in the commercial optical components (e.g. interference filters, LEDs) for construction. Experience has shown that SAMI-pH is accurate within ~ 0.004 by using the same mCP molar absorptivities for every SAMI-pH to calculate pH. Differences among SAMI-pHs (e.g., 0.0059 in this experiment) can be reduced to ~ 0.002 by accurately measuring their individual molar absorptivities (Seidel et al.,

2008). For the comparison of two SeapHOx (Fig. 4c and Table 3), the overall difference was 0.0013 ± 0.0053 pH units ($n = 1115$). Before the temperature testing (August 24 at 22:00), the two SeapHOx showed excellent consistency (0.0011 ± 0.0028 , $n = 841$, Fig. 4c). The sawtooth pattern in Fig. 4c is due to the lagging response of the SeapHOx to the rapidly changing temperature (Fig. 2a). The Durafet electrode used on a SeapHOx is mostly situated in an air-filled sensor housing and has a large internal reference gel volume that slows down thermal equilibration (Martz et al., 2010). This property is instrument-specific leading to the observed transient difference. The sawtooth pattern is not observed in the SAMI-pH comparison data (Fig. 4b) because the indicator equilibrium response is very rapid (Liu et al., 2011). However, there are some short spikes from August 25 to 26 (Fig. 4b) because optics and electronics inside the SAMI housing have slightly different temperature from that of surrounding waters potentially causing optical drift during rapid temperature changes. The comparison between SAMI-pH (p66) and SeapHOx (SP032) (Fig. 4d) resulted in a mean difference of -0.0024 ± 0.0045 pH units ($n = 1115$). Comparisons summarized in Table 3 indicate that there are no statistical differences in pH results from SAMI-pH and SeapHOx. Errors in the SeapHOx caused by the rapid temperature changes were mostly averaged out given the data length.

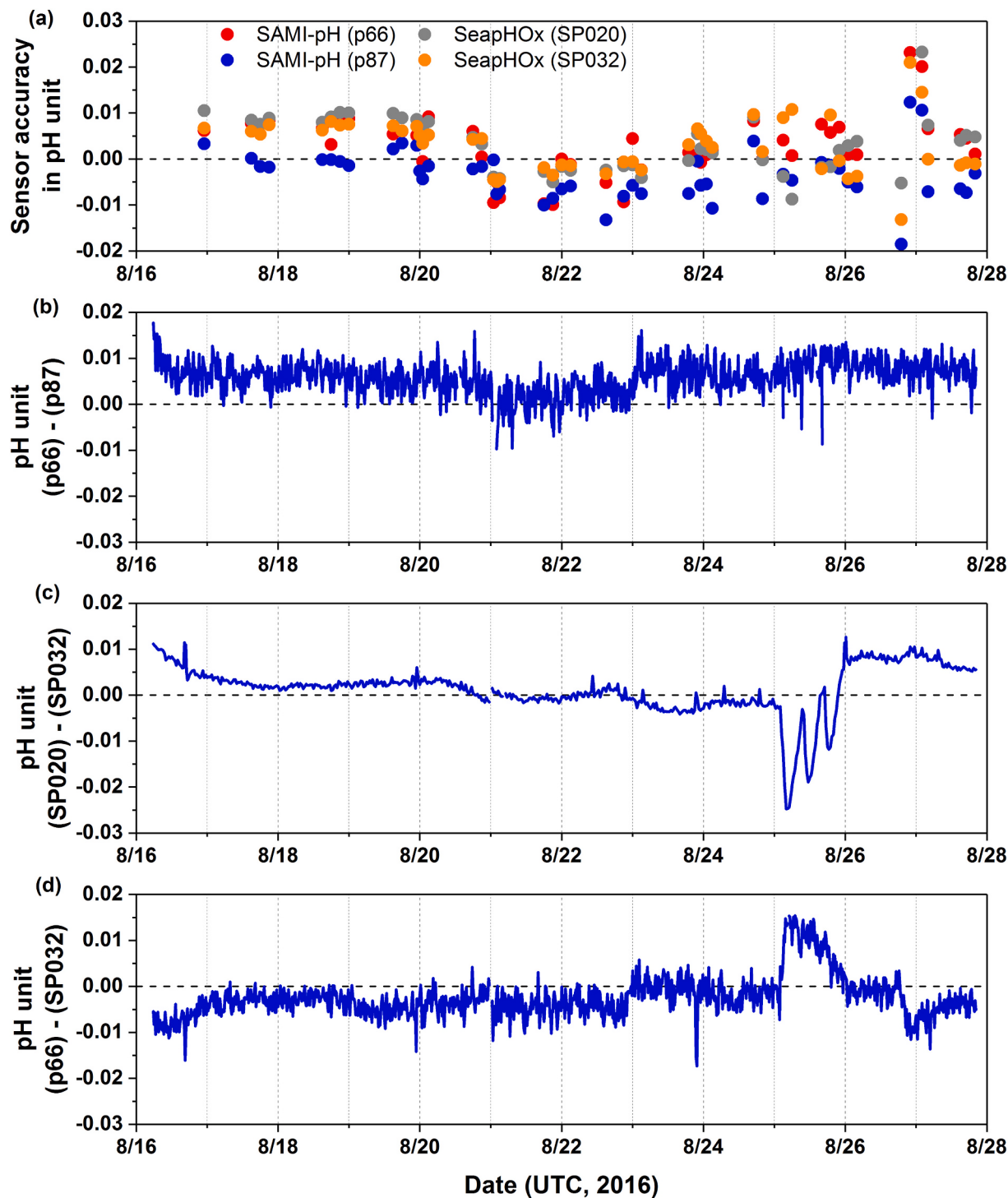


Fig. 4. Inter-comparison of pH sensors. (a) Sensor accuracy compared to discrete pH; (b) Comparison between two SAMI-pH (p66 and p87); (c) Comparison between two SeapHOx (SP020 and SP032); (d) Comparison between SAMI-pH (p66) and SeapHOx (SP032). Dashed line indicates zero line.

Table 2
A summary of pH sensor accuracy compared to discrete pH values ($n = 48$).

pH sensors	Mean error $\pm$ SD
SAMI-pH (p66)	0.0028 ± 0.0068
SAMI-pH (p87)	-0.0034 ± 0.0055
SeapHOx (SP020)	0.0037 ± 0.0074
SeapHOx (SP032)	0.0030 ± 0.0060

Table 3
A summary of pH sensor-to-sensor comparisons ($n = 1115$).

pH sensor pairs	Mean difference $\pm$ SD
SAMI-pH (p66–p87)	0.0059 ± 0.0037
SeapHOx (SP020–SP032)	-0.0013 ± 0.0053
SAMI-pH (p66) – SeapHOx (SP032)	-0.0024 ± 0.0045
SAMI-pH (p66) – SeapHOx (SP020)	-0.0011 ± 0.0041
SAMI-pH (p87) – SeapHOx (SP032)	-0.0083 ± 0.0045
SAMI-pH (p87) – SeapHOx (SP020)	-0.0069 ± 0.0039

4.4. $p\text{CO}_2$ data assessment

SAMI- CO_2 data (shown in Fig. 2d) accuracy was evaluated by comparing with calculated $p\text{CO}_2$ from discrete pH and DIC (Fig. 5a) and directly measured $p\text{CO}_2$ by the Super CO_2 (Fig. 5b). Around the time when compressed air bubbling was initiated (August 22 22:00, Fig. 2), it appears that an adjustment to the Super CO_2 caused a leak in the connection between the equilibrator and LI-COR (based on large deviations from the SAMI- CO_2 data). Therefore, Super CO_2 data were only used prior to the leak. SAMI- CO_2 errors relative to the calculated $p\text{CO}_2$ were $-9.3 \pm 17.7 \mu\text{atm}$ (measured – calculated $p\text{CO}_2$, $n = 40$) (Fig. 5a). The error is dependent on the $p\text{CO}_2$ value ($R^2 = 0.40$, $p < 0.05$). Uncertainty in both the pH and DIC measurements contribute to the $p\text{CO}_2$ uncertainty (Millero, 2007; Orr et al., 2018) in addition to the carbonate system equilibrium constants (Table 4). Five groups of bottle data were chosen to cover the $p\text{CO}_2$, temperature and salinity range in this experiment. Uncertainties assigned to pH (± 0.01 pH unit), DIC ($\pm 2 \mu\text{mol/kg}$), and equilibrium constants were taken from Orr et al. (2018). Table 4 shows that $p\text{CO}_2$ calculation uncertainty increases with higher $p\text{CO}_2$ ($R^2 = 1.00$, $p < 0.05$), suggesting the comparison in Fig. 5a is susceptible to high $p\text{CO}_2$ calculation uncertainty. Using pH and A_T to calculate $p\text{CO}_2$ did not change the comparison statistically as differences using different pairs were $1.6 \pm 3.3 \mu\text{atm}$ ($n = 38$). Additionally, the high $p\text{CO}_2$ levels after addition of HCl on August 21 from SAMI- CO_2 have larger uncertainty because it was only calibrated from ~ 200 to $690 \mu\text{atm}$. It was difficult to predict the increase in $p\text{CO}_2$ from the dry ice addition because an unquantifiable amount of $\text{CO}_2(\text{s})$ sublimation is lost to the atmosphere. Compared to Super CO_2 (Fig. 5b, SAMI- CO_2 – Super CO_2), a concentration-dependent difference was observed separated by the transient spike on August 20 at 22:00: before the addition of HCl, the difference was $-1.6 \pm 2.7 \mu\text{atm}$ ($n = 364$) for $p\text{CO}_2$ between 510 and $530 \mu\text{atm}$; the difference increased to $15.5 \pm 9.3 \mu\text{atm}$ ($n = 168$) between 1058 and $1426 \mu\text{atm}$. The short spikes on August 18 at 19:30 and August 21 at 11:30 (Fig. 5b, red arrows) were caused by a blank measurement by SAMI- CO_2 which pumps deionized water (DI) stored in a reagent bag to the optical cell. This step is typically performed every 255 measurements to improve SAMI- CO_2 long-term stability by

Table 4

An analysis of $p\text{CO}_2$ calculation uncertainty based on the uncertainty from discrete pH and DIC measurements*

Input values				Output values	
pH	DIC	Temperature	Salinity	$p\text{CO}_2$	$p\text{CO}_2$ uncertainty
	($\mu\text{mol/kg}$)	($^{\circ}\text{C}$)		(μatm)	($\pm \mu\text{atm}$)
7.930	2030	24.7	33.8	542	16.6
7.530	2090	24.5	33.8	1453	42.5
7.758	2040	24.2	33.9	825	24.7
7.766	2031	18.7	33.4	788	23.4
7.790	1830	21.1	30.1	691	20.5

* Uncertainties assigned to the input CO_2 system variables and equilibrium constants were taken from Orr et al. (2018). Temperature and salinity were assumed to be perfectly measured (i.e., uncertainty of zero units).

accounting for any changes in light intensity, but it can affect subsequent $p\text{CO}_2$ measurement due to the carryover of the blank solution (Lai et al., 2018).

4.5. Internal consistency

Internal consistency can be evaluated using a number of different strategies. We focus on computation of $p\text{CO}_2$ and DIC because these are the two most commonly desired parameters directly used for air-sea flux calculations and water column mass balances, respectively. First, pH and $p\text{CO}_2$ are similar in terms of CO_2 system calculations. pH combined with A_T (pH- A_T) yields calculated $p\text{CO}_2$, which can be compared with the data from SAMI- CO_2 . This comparison is valuable in view of the popularity of utilizing the pH sensors and salinity-derived A_T to quantify CO_2 gas exchange (e.g. Gray et al., 2018; Williams et al., 2017). A similar comparison can be made for pH by using the $p\text{CO}_2$ - A_T pair. Secondly, DIC time series that have been commonly used to model biological and physical processes can be calculated using different sensor pairs, specifically $p\text{CO}_2$ or pH combined with salinity-derived A_T (e.g. Briggs et al., 2018; Islam et al., 2017; Martz et al., 2009). Previous studies have shown that high noise level results if $p\text{CO}_2$ and pH are used as input parameters (Gray et al., 2011; Raimondi et al., 2019). Our calculations

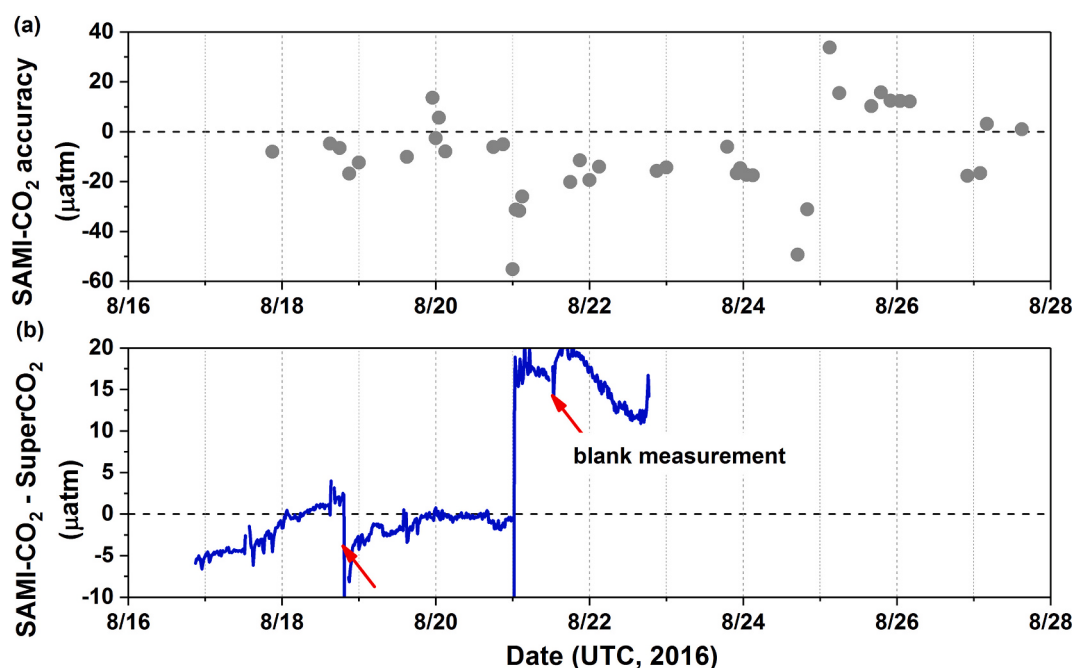


Fig. 5. Assessment of SAMI- CO_2 data calculated from pH and DIC. (a) SAMI- CO_2 accuracy (measured – calculated $p\text{CO}_2$ from pH and DIC). Dashed line indicates zero line; (b) Difference between SAMI- CO_2 and Super CO_2 measurements. Red arrows indicate blank measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reaffirm this point (shown below).

SAMI-alk02 was randomly selected as input A_T among the three SAMI-alks to simplify the analysis. Other SAMI-alk time-series gave similar results and thus, the comparisons are not shown. Results between directly measured values and those calculated from other paired parameters are presented in Table 5. In terms of pCO_2 , a concentration-dependent difference ($p < 0.05$) (calculated – measured pCO_2) is identified for all of the pCO_2 internal consistency tests (Fig. 6) that was also evident in the bottle-based comparisons (see pCO_2 data assessment). At high pCO_2 conditions (1058 and 1426 μatm between acid addition and bubbling compressed air), SAMI- CO_2 data errors are very similar to the Super CO_2 data (Fig. 6). Thus, all calculations from different pH and pCO_2 sensors suggest the errors are mostly caused by thermodynamic constant errors. Larger differences (calculated – measured pCO_2) at high pCO_2 were also previously observed from ship-based studies (McElligott et al., 1998; Patsavas et al., 2015) that use spectrophotometric pH and DIC to calculate pCO_2 . Fig. 6 provides a more direct comparison between measured and calculated pCO_2 because it eliminates the difficulty in handling discrete pCO_2 samples and all measurements and calculations were made at *in situ* temperatures. Fong and Dickson (2019) proposed a series of systematic adjustments to carbonate thermodynamic constants to reduce differences in measured and calculated pH. These adjustments do not significantly affect calculated pCO_2 from A_T and DIC (Fong and Dickson, 2019), thus consistency in terms of pCO_2 is not clear when pH is used as an input parameter. Further more systematic studies are needed to improve our understanding of CO_2 system internal consistency.

Fig. 6 results do not imply errors for studies that use pH sensors to calculate surface-water pCO_2 because the pCO_2 range (Fig. 2d) in this work is above most observed surface values. Sulpis et al. (2020) verified the carbonate thermodynamic constants in Lueker et al. (2000) above 8°C using combined global ocean data products, but this assessment is restricted to surface-water pCO_2 with a maximum of 446 μatm . In terms of calculations for pH from pCO_2 (calculated – measured pH) (Table 5), they are not as good as the Tables 2 and 3 results.

DIC was calculated using pCO_2 or pH (all 4 pH time series) combined with SAMI-alk02. In Fig. 7a, DIC increased by $\sim 15 \mu mol/kg$ due to evaporation and slow CO_2 uptake during the period of static conditions from August 16 at 21:00 to August 19 at 22:00 (~ 2010 to $2025 \mu mol/kg$). DIC increased from ~ 2025 to $2090 \mu mol/kg$ after the addition of carbonate/bicarbonate solution (August 19 at 22:00). Acid addition (August 20 at 22:00) perturbed the tank seawater by changing A_T , pH and pCO_2 , but DIC was only controlled by degassing after the transient

spike. This transient spike could be caused by hourly A_T measurements that did not fully resolve quarter-hour-scale A_T variations, so that coarse linear interpolation in A_T led to a mismatch with pH and pCO_2 . DIC slowly decreased by $\sim 25 \mu mol/kg$ during the next 48 h, while the compressed air (August 22 at 22:00) accelerated this process resulting in a $\sim 55 \mu mol/kg$ decrease in 24 h. The dry ice addition (August 23 at 22:00) then increased DIC from ~ 2010 to $2040 \mu mol/kg$. When the temperature test was performed, a 6-h shoulder structure with DIC $\sim 2075 \mu mol/kg$ was observed matching the period when temperature dropped most rapidly (August 24 at 20:00 to August 25 at 2:00). We do not attribute this to poor mixing in the tank because pH sensors and SAMI- CO_2 were located at different positions (Fig. 1) and their DIC calculations all have the same pattern. It could be because the seawater from the cooling tower piping system had a different DIC. The final step of dilution (August 26 at 22:00) led to a $\sim 185 \mu mol/kg$ decrease of DIC.

Calculated DIC from any of the five pairs closely track the discrete DIC (Fig. 7a). Errors (calculated – discrete DIC) significantly correlate with each other ($p < 0.05$, not shown), suggesting the uncertainties of the DIC samples, SAMI-alk02 data or carbonate thermodynamic constants dominate this comparison. Large errors are often associated with large DIC variations, for example, addition of carbonate solution on August 19 at 22:00, further highlighting the sampling difficulty. Notably, excellent agreement was obtained among the five calculated DIC time series (Table 6 and Fig. 7c) (DIC from pH sensors – DIC from SAMI- CO_2). The differences are within $\pm 5 \mu mol/kg$, a value comparable to the minimum adjustment value of 4 $\mu mol/kg$ in GLODAPv.2020 that considers typical shipboard DIC precision (Olsen et al., 2020). However, the climate goal of $\pm 2 \mu mol/kg$ (Bockmon and Dickson, 2015) has not been fulfilled. This comparison reduces uncertainty consistently applied to DIC calculations from different pH/ pCO_2 sensors and A_T . Lastly, DIC calculated from pH and pCO_2 is noisy due to this pair's high sensitivity to random noise and is thus not shown in Fig. 7. For example, DIC time series calculated from SAMI-pH (p66) and SAMI- CO_2 shows a difference of $-14 \pm 48 \mu mol/kg$ ($n = 1053$) compared with that from SAMI-alk02 and SAMI- CO_2 .

5. Conclusion

This work compares multiple groups of sensors in a well-controlled environment over a time span of 12 days. A total of 10 instruments were deployed in a 5000 L tank (Table 1). The tank chemistry was modified to vary A_T , pH, pCO_2 , temperature, and salinity while keeping various properties constant for each individual test, which allowed us to examine individual instrument response and the ability to calculate CO_2 parameters over a wide range. Except for Super CO_2 's leaking connection, all of the instruments worked well with all possible data acquired. Each instruments' performance demonstrated adequate precision and accuracy for capturing the modified conditions representative of natural variability that could be observed in coastal, open ocean and deep ocean environments. Averaged accuracy for three SAMI-alks is $0.1 \pm 5.5 \mu mol/kg$. pH sensors including SAMI-pH and SeapHOx have an mean error within 0.004 with one standard deviation within ± 0.008 pH units. SAMI- CO_2 agrees well with Super CO_2 within the calibration range ($-1.6 \pm 2.7 \mu atm$). Results in this study have also shown that, like shipboard or laboratory measurement programs, pH or pCO_2 can be combined with A_T to fully characterize the CO_2 system. In high CO_2 waters, calculated pCO_2 may be subject to the uncertainties from CO_2 system thermodynamic constants (McElligott et al., 1998), but DIC time series calculated from pH- A_T and pCO_2 - A_T pairs agree to within $\pm 5 \mu mol/kg$. Increasingly, in situations where A_T sensors are not available, empirical algorithms serve to estimate A_T from correlated variables such as salinity and temperature (Lee et al., 2006; Carter et al., 2016). This strategy has been adopted in many buoy-based studies (e.g. Gray et al., 2011; Briggs et al., 2018; Harris et al., 2013; Islam et al., 2017) and a rapidly growing number of papers based on profiling float pH data (e.g. Bushinsky et al., 2019; Williams et al., 2018). By comparing calculated

Table 5

Results of comparisons between directly measured values and those calculated from other parameters.

Measured	Calculated	Calculated – measured (mean $\pm$ SD)	N
SAMI- CO_2	SAMI-alk02\SAMI-pH (p66)	$11 \pm 25 \mu atm$	1053
	SAMI-alk02\SAMI-pH (p87)	$20 \pm 23 \mu atm$	
	SAMI-alk02\SeapHOx (SP020)	$6 \pm 20 \mu atm$	
	SAMI-alk02\SeapHOx (SP032)	$7 \pm 23 \mu atm$	
	SAMI-alk02\SAMI-pH (p66)	$18 \pm 36 \mu atm$	
Super CO_2	SAMI-alk02\SAMI-pH (p87)	$25 \pm 34 \mu atm$	565
	SAMI-alk02\SeapHOx (SP020)	$11 \pm 32 \mu atm$	
	SAMI-alk02\SeapHOx (SP032)	$13 \pm 30 \mu atm$	
	SAMI-pH (p66)	-0.0031 ± 0.0099	
SAMI-pH (p87)		-0.0086 ± 0.0083	
SeapHOx (SP020)	SAMI-alk02\SAMI- CO_2	-0.0008 ± 0.0085	1053
SeapHOx (SP032)		-0.0018 ± 0.0088	

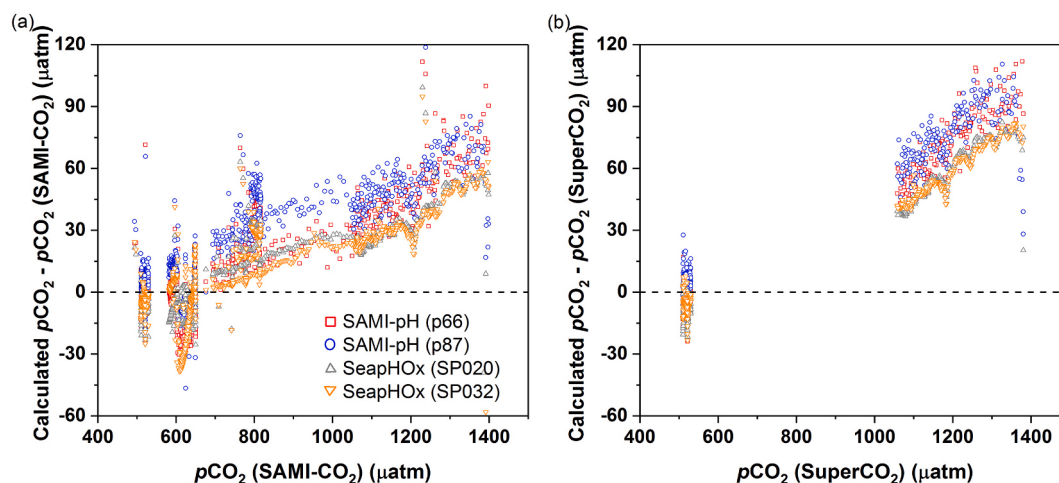


Fig. 6. $p\text{CO}_2$ difference (calculated – measured values) as a function of measured $p\text{CO}_2$ from (a) SAMI- CO_2 and (b) Super CO_2 . Calculated $p\text{CO}_2$ is from SAMI-alk02 combined with four different pH sensors. Dashed line indicates the zero line.

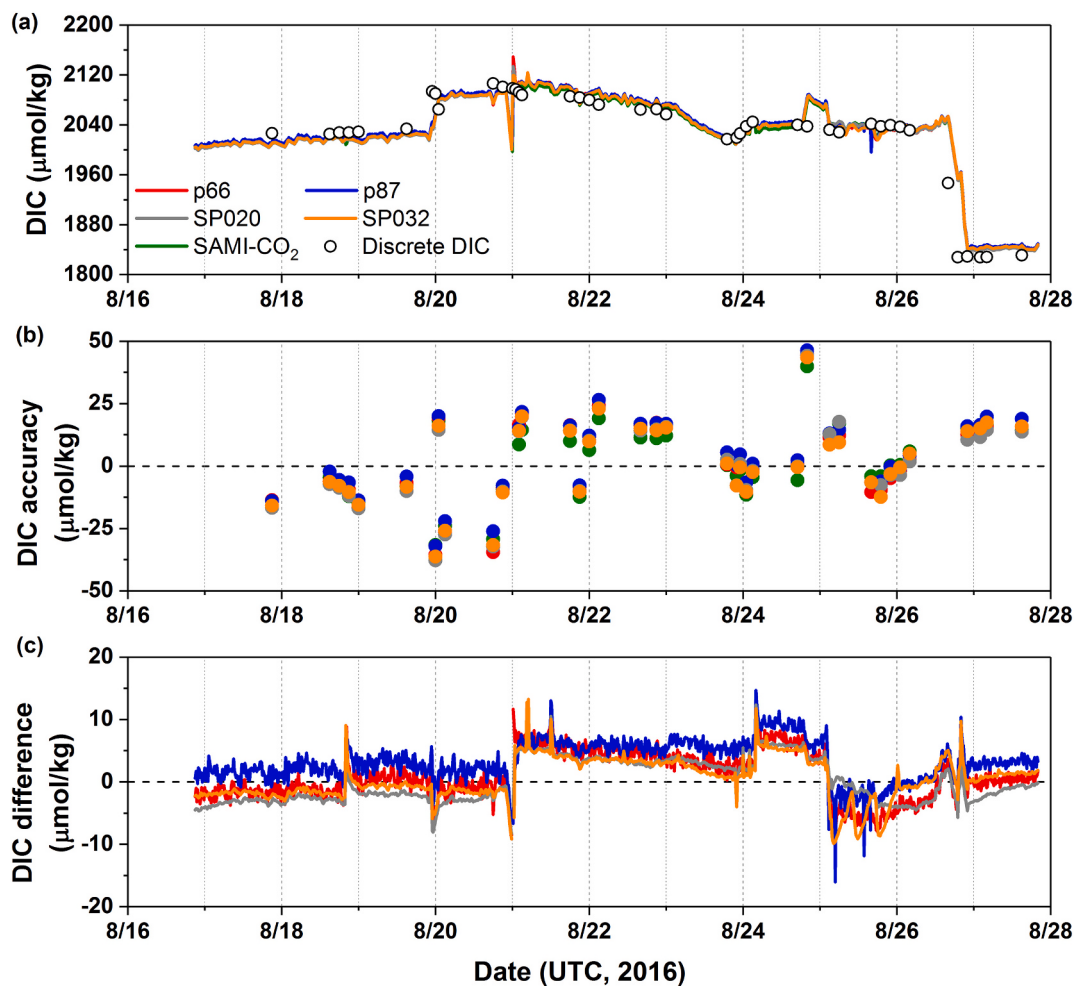


Fig. 7. DIC calculations using different combinations of sensor data. (a) Calculated DIC from SAMI-alk02 combined with SAMI- CO_2 or one of the pH sensors (p66, p87, SP020, and SP032). Labels are abbreviated to the specific SAMI- CO_2 or pH sensors used for calculations. Discrete DIC are shown as black circles; (b) DIC errors (calculated DIC – discrete DIC); (c) Differences among five DIC time series. SAMI- CO_2 as input variable was used as a reference (DIC from pH sensors – DIC from SAMI- CO_2). Dashed lines indicate zero lines.

DIC from different pairs, co-deployment of pH and $p\text{CO}_2$ sensors with estimated A_T can be used for *in situ* data quality control and serve as a sensitive indicator of drift, e.g., due to sensor biofouling (Gray et al.,

2011). Autonomous sensors that are capable of measuring two parameters are making progress (Wang et al., 2015; Briggs et al., 2017; Briggs et al., 2020) and give rise to new opportunities for future testing and

Table 6

Results of DIC calculations. The DIC calculated from SAMI-CO₂ and SAMI-alk02 was used as a reference ($n = 1053$). Discrete DIC was also used to determine the accuracy of DIC calculations ($n = 38$).

Instruments paired with SAMI-alk02	Compared to DIC (SAMI-CO ₂ /SAMI-alk02)	Compared to discrete DIC (μmol/kg)
	mean ± SD (μmol/kg)	
SAMI-CO ₂	-	1.2 ± 14.7
SAMI-pH (p66)	1.0 ± 3.8	2.0 ± 16.6
SAMI-pH (p87)	3.3 ± 3.5	3.3 ± 17.6
SeapHOx (SP020)	0.1 ± 4.2	1.0 ± 16.4
SeapHOx (SP032)	0.5 ± 4.0	1.2 ± 16.2

applications.

This 12-day study cannot detect problems in long-term drift and reliability, which require experiments over longer periods. Challenges such as biofouling and particles are not present in the tank, but commonly affect sensor performance (Manov et al., 2004). There are also other sensor-related environmental conditions that are not controlled, such as pressure effects in deep-sea oceans (Johnson et al., 2016) and large salinity swings caused by tidal cycles (Gonski et al., 2018). Therefore, it is paramount that rigorous data quality control be routinely implemented in sensor deployments.

Declaration of Competing Interest

Michael D. DeGrandpre is a co-owner of Sunburst Sensors, LLC, the company that manufactures the SAMI sensor technologies.

Acknowledgement

We thank Wiley Wolfe from Scripps Institution of Oceanography for processing SuperCO₂ data, Chun-Ze Lai from the University of Montana for preparing SAMI-alks. Cory M Beatty from the University of Montana helped with SAMI-pH and SAMI-CO₂ preparation, logistics, and deployment. This research was supported by the U.S. National Science Foundation OCE-1459255. These data are available via the Biological and Chemical Oceanography Data Management Office (BCO-DMO).

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