

ABSTRACT OF TECHNICAL REPORT BY

Jesse M. Vance for the degree of Masters of Science in Oceanography on June 14, 2012.

Title: Proof-of-Concept: Automated high-frequency measurements of PCO_2 and TCO_2 and real-time monitoring of the saturation state of calcium carbonate.

The rapid increase in atmospheric carbon dioxide (CO_2) over the last 250 years has led to the absorption of approximately 550 billion tons of anthropogenic CO_2 by the global ocean. This oceanic uptake of CO_2 has resulted in decreasing pH and alterations to carbonate chemistry, threatening many ecologically and economically important marine species. The majority of biological production takes place on highly dynamic coastal margins, which require instrumentation capable of high-frequency measurements. In practice, measurements of sufficient resolution often do not include all required analytical parameters necessary to constrain the carbonate chemistry in order to investigate biogeochemical processes relevant to ocean acidification.

This report provides a proof-of-concept for the development of an instrument designed to make autonomous measurements of the partial pressure of CO_2 (PCO_2) and total CO_2 (TCO_2) in a continuous sample stream at high frequency, based on combination of two existing measurement techniques. The objective is to provide measurements sufficient to constrain the carbonate chemistry in ocean waters while capturing the variability seen over short timescales in estuaries and on coastal margins. By constraining the carbonate chemistry and performing real time calculations of the saturation state of calcium carbonate and other carbonate parameters, this instrument can be utilized as a monitoring tool for fisheries in need of high resolution time series carbonate data.

In our combined system, PCO_2 is determined by measuring the infrared absorbance due to CO_2 in the re-circulated gaseous headspace of a shower-type equilibrator. For TCO_2 analysis, a low-flowing seawater sample stream is acidified and passed through a microporous membrane contactor. The evolved CO_2 diffuses

into a high-flowing CO₂-free strip-gas stream and is measured by infrared absorbance in the same manner as the PCO₂ method.

The results of laboratory testing indicated the instrument is able to resolve TCO₂ changes with 0.5% precision. The system responds to changes in TCO₂ with a time constant of 12 seconds. TCO₂ analysis of gravimetrically prepared liquid carbonate standards and discrete field samples that were cross-analyzed at the Hales lab at Oregon State University indicated the internal accuracy of the system is better than 1%. PCO₂ measurements made with the combined PCO₂/TCO₂ system were within 3.5% of measurements made on synchronously-collected discrete samples preserved with HgCl₂ and subsequently analyzed in the Hales lab. However, absolute accuracy has yet to be validated for both PCO₂ and TCO₂ measurements.

Field observations carried out at Whiskey Creek Shellfish Hatchery at Netarts Bay on the Oregon coast illustrate the instrument's ability to capture the high variability seen in the bay. The maximum rates of change seen in carbonate conditions were 123 μM hr⁻¹ for TCO₂ and 103 μatm hr⁻¹ for PCO₂, corresponding to environmental changes of 2.4°C hr⁻¹ in temperature, and 2.6 psu hr⁻¹ in salinity. Our interpolation method developed to model alkalinity between synchronized TCO₂ and PCO₂ measurements predicts the saturation of calcium carbonate minerals with an internal precision of 1.6%. The error of the resultant high-resolution time series of calcium carbonate saturation is estimated to be less than 3.6%. I conclude that this instrument is capable of producing quality time series of carbonate data at sufficient resolution to be a powerful tool for coastal biogeochemical research and deepening our understanding of the impacts of ocean acidification.

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**Proof-of-Concept: Automated high-frequency measurements of PCO_2 and TCO_2
and real-time monitoring of the saturation state of calcium carbonate**

By

Jesse M. Vance

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1. Introduction

1.1 Topic and Relevance

Ocean acidification, referred to as “the other CO₂ problem,” is the result of oceanic uptake of anthropogenic carbon dioxide emissions [1]. The ocean is a substantial carbon reservoir, containing approximately 38,000Gt, and plays a dominant role in regulating atmospheric CO₂ via gas exchange [2]. During the last 250 years (the Anthropocene) the amount of carbon dioxide in the atmosphere has increased from approximately 280 parts per million by volume (ppmv) to 394 ppmv due primarily to energy production and land-use practices, dramatically altering Earth’s carbon reservoirs. [1]. Fossil fuels are the product of prolonged photosynthesis and burial of organic matter over geologic timescales. By extracting and combusting this carbon over short time scales, we have effectively added this as “new” inorganic carbon to the atmosphere.

The carbon cycle is critical to Earth’s long-term climatic stability [3]. Antarctic ice cores have shown that atmospheric CO₂ has varied between 180-300 ppmv over glacial/inter-glacial cycles [4]. However, at no point in the last 800,000 years has atmospheric CO₂ been greater than that until recently. Furthermore, the concentration of atmospheric CO₂ is rising more than 100 times faster than at any point in the last 650,000 years [2].

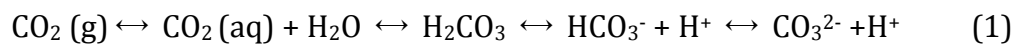
Large-scale studies have shown that the ocean has absorbed 550 billion tons of anthropogenic CO₂ [5]. This absorption of CO₂ results in the lowering of seawater pH, which has been well documented by time series data [2]. Ocean stations ALOHA and HOT have shown a rise in surface ocean PCO₂ and concomitant decrease in pH over the past 20 years consistent with rising atmospheric CO₂ [1]. In recent years the effects of ocean acidification on marine biota have increased concern.

Ocean acidification may have profound impacts on a variety of ecosystems. Elevated CO₂ and the low mineral stability associated with it have already been shown to severely impact early development and larval performance of *Crassostrea gigas*, an oyster species that is essential to the US West Coast shellfish industry [6, 7]. Coastal margins, particularly estuaries, are highly dynamic and require high-frequency measurements in order develop our understanding of the physical and

biological processes that drive variability. Two analytical parameters must be measured to constrain the carbonate chemistry.

1.2 Carbonate Chemistry

Atmospheric carbon dioxide is equilibrated with the surface ocean by air-sea gas exchange over the timescale of a year [8]. CO₂ is unique from other major atmospheric gases in that it reacts with the water molecules [9]. When CO₂ is dissolved in seawater it reacts to form carbonic acid, which dissociates into bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions, releasing hydrogen ions (H⁺). These reactions are summarized in Equation 1.



Total CO₂ (TCO₂) is defined as the sum of the concentrations of these carbonate species.

$$\text{TCO}_2 = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (2)$$

where CO₂* is the combined aqueous CO₂ and H₂CO₃ which are virtually indistinguishable analytically. The production of hydrogen ions lowers pH, which is defined as the negative log of the activity or concentration, depending on scale, of hydrogen ions.

$$\text{pH} = -\log\{\text{H}^+\} \quad (3)$$

At lower pH the equilibrium shifts to reduce the proportion of carbonate ion. Carbonate availability is critical to calcifying organism, which form skeletal structures of calcium carbonate written as



The saturation state, Ω , describes the thermodynamic favorability for calcium carbonate precipitation.

$$\Omega = [\text{Ca}^{2+}][\text{CO}_3^{2-}]/K_{\text{sp}} \quad (5)$$

where K_{sp} is a the temperature, salinity and pressure-dependent solubility product for calcium carbonate. When omega is greater than one, precipitation is favored; whereas dissolution is favored when omega is below one. As CO₂ is dissolved into seawater it favors calcium carbonate dissolution via the reaction



1.3 Analytical Methods

The concentrations of the inorganic carbon species and the saturation state of calcium carbonate cannot be measured directly but rather can be calculated if any two of the analytical parameters P_{CO_2} , TCO_2 , Total Alkalinity or pH are measured.

Total alkalinity (TA) and pH offer the most economic approaches to measuring carbonate chemistry; however, these two parameters are not the best choices for accurate constraint of the carbonate system. TA is generally defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors. It can be described as the acid-neutralizing capacity. In practice, this is not well defined. It can be written as a charge balance

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (7)$$

The contributions of bicarbonate, carbonate, borate and hydroxide ion concentrations account for 99% of TA. pH, as defined above, is difficult to accurately measure in seawater and is expressed on four different scales. The free hydrogen scale takes into account only the hydrogen ion. The total hydrogen scale includes sulfate. The seawater scale includes both sulfate and hydrogen fluoride. The NBS scale is calibrated to buffer solutions of accepted standard values.

P_{CO_2} is the partial pressure of CO_2 in a gaseous headspace that is in equilibrium with the water. This is related to the dissolved aqueous CO_2 by Henry's Law as shown in Equation 8.

$$P_{CO_2} = [CO_2^*]/K_H \quad (8)$$

K_H is the Henry's law constant for CO_2 and is dependent on temperature, salinity and pressure. This parameter is analytically easy to measure and the equations that govern it are well defined.

TCO_2 is clearly defined, as shown above. This parameter can be directly measured by coulometry, gas chromatography or infrared detection. In each method the seawater is acidified and the evolved CO_2 gas is measured.

TCO_2 and P_{CO_2} are the parameters of choice in constraining the carbonate system because of their well-established definitions and precise analytical methods. Both parameters have been measured at high frequency with a non-dispersive

infrared (NDIR) detector. PCO_2 measurements have been made using various shower-type equilibrators [10-12]. Bandstra and Hales developed a method for high-frequency measurement of TCO_2 using a commercially available microporous membrane contactor and NDIR detector [13].

1.4 Project Objectives

I have built an automated system to measure the PCO_2 and TCO_2 in a continuous sample stream at high frequency based on previously developed methods. This instrument has the capability of constraining the carbonate chemistry via real time calculations of saturation state of calcium carbonate and other carbonate parameters. The sampling rate is 1Hz, providing the ability to resolve the high variability over short timescales seen in estuaries and on coastal margins. In addition to measuring a continuously flowing sample stream, the system has the capability of measuring discrete samples. This instrument also serves as a tool for real-time monitoring of seawater quality that can be used for economically relevant fisheries.

Here I provide a proof-of-concept for the nearly simultaneous measurements of PCO_2 and TCO_2 using an automated system to generate a high-resolution time series of carbonate chemistry data. We describe the analytical methods, instrument design, software programming and numerical methods for data analysis. We present operational lab test results and field data collected in Netarts Bay, Oregon in 2012.

2. Methods

2.1 Principle of Methods

2.1.1 PCO_2 Analysis

Continuous measurement of PCO_2 of seawater relies on the rapid equilibration between aqueous dissolved CO_2 in seawater and a gaseous headspace. This is typically accomplished using a flow-through apparatus in which the flow of water and air are tightly controlled through an equilibration chamber. The residence time of the gas in the headspace of the chamber should be greater than that of the water to ensure equilibration. We have constructed a “shower-type” flow-through equilibrator similar to previous methods [11], adapting the

membrane-equilibrator approach of Hales et al. [14]. The air in the headspace is recirculated through the water in the equilibrator chamber and the CO₂ concentration in the equilibrated air is detected by NDIR absorbance.

2.1.2 TCO₂ Analysis

For continuous TCO₂ measurements we follow the method developed by Bandstra et al. in the Hales lab at Oregon State University [13]. In this approach a low flow-rate stream of seawater is acidified, shifting the equilibrium from carbonate and bicarbonate species to dissolved CO₂. The CO₂ gas diffuses through a microporous membrane contactor and is swept away by a high-flowing stream of CO₂-free carrier gas and is detected by NDIR [13]. The mass balance across the membrane contactor is

$$F_L \text{TCO}_{2,\text{in}} = F_L \text{TCO}_{2,\text{out}} + \gamma F_G X_{\text{CO}_2,\text{out}} \quad (9)$$

where F_L and F_G are the liquid and gas flows respectively and γ is a unit-conversion factor [13]. The stripping efficiency, E is defined by the removal of TCO₂ from the seawater in the stripper.

$$E = (F_L \text{TCO}_{2,\text{in}} - F_L \text{TCO}_{2,\text{out}}) / F_L \text{TCO}_{2,\text{in}} \quad (10)$$

Taking the mass balance and the stripping efficiency it can be shown that the TCO₂ is related to the gas and liquid flows, stripping efficiency and molar fraction of CO₂ as shown.

$$\text{TCO}_{2,\text{in}} = (F_G / F_L) (\gamma X_{\text{CO}_2,\text{out}} / E) \quad (11)$$

This indicates that if the gas and liquid flow rates are tightly controlled and the stripping efficiency remains constant then the TCO₂ of the analyzed seawater is directly proportional to the XCO₂ detected by NDIR.

2.2 Instrument Design

2.2.1 System Description

We have designed an automated carbonate chemistry analyzer to monitor the saturation of calcium carbonate in real time at high resolution in seawater by measuring PCO₂ and TCO₂ to constrain the carbonate chemistry. Computer-operated valves and pumps control the operational modes and calibration methods. The

system has four modes of operation: PCO₂ only, TCO₂ only, combined PCO₂/TCO₂, and a discrete sampling mode. Figure 1 shows the configuration of air and liquid flow through the system during PCO₂ and TCO₂ operations.

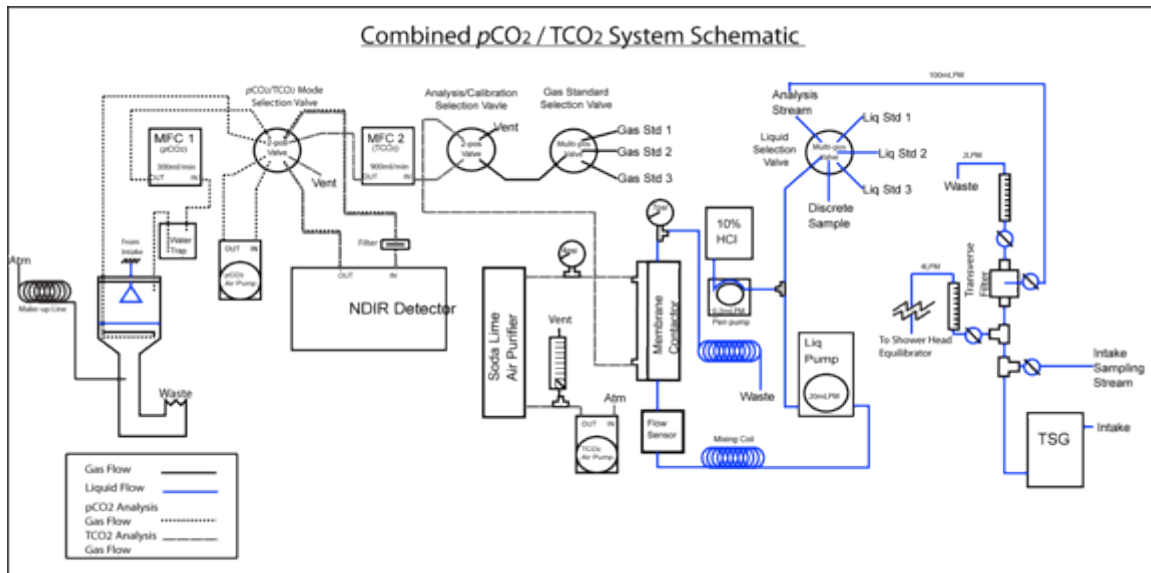


Figure 1. Schematic of air and liquid flows in combined PCO₂/TCO₂ system. Dashed lines show the gas flows for PCO₂ and TCO₂ analysis.

The electronics and non-wetted components of the system are housed in an enclosure constructed of acrylonitrile butadiene styrene (ABS) plastic (available at www.digikey.com, #377-1793-ND). Electronic components were mounted on an aluminum shelf inside the enclosure. The layout is shown in Appendix H. Watertight connectors and water-resistant switches were used for environmental robustness.

During PCO₂ operation air is re-circulated through the equilibration chamber by a Hargraves BTC diaphragm pump (available at www.hargravesfluidics.com, #H022C-11). The gas flow rate is maintained at 300ml/min by an Alicat MC model mass flow controller (available at www.alicatscientific.com, #MC-1SLPM-D/GAS:Air,5V,RIN,HC). During PCO₂ mode an 8-port low-pressure VICI Cheminert 2-position valve (available at www.vici.com, #C22-6188EH) places the NDIR detector into the recirculation loop so that the CO₂ content of the gaseous headspace is continuously measured. We have elected to use a Li-Cor model 840 (available at www.licor.com, #LI-840A). It is an absolute rather than differential detector with a

single optical bench and does not require a continuous stream of CO₂-free gas to a reference cell. Immediately upstream of the LI-840 is a 1- μ m polytetrafluoroethylene (PTFE) filter to catch aerosols and water droplets.

The shower-type equilibrator was constructed out of polyvinyl chloride (PVC) plastic, shown in Appendix AC. The chamber volume is 1.2L with a raised drain to maintain a standing water volume where the headspace is 0.85L. The liquid flow through the chamber is set to 4 LPM with a rotameter and gate valve. The residence time of the water in the chamber is approximately 13 seconds. Gas exchange is maximized for rapid equilibration. Incoming water is sprayed through a fire sprinkler at the top of the chamber. Gas in the re-circulation loop returns through perforated tubing submerged in the water inside the chamber. The chamber is fitted with a platinum resistive temperature detector (RTD) probe (available at www.minco.com, #S604PD75Y36T, #TT291PD1EG) and an Allsensors differential pressure sensor (available at www.allsensors.com, #1PSI-D-4V) for temperature and pressure corrections to the PCO₂ measurements.

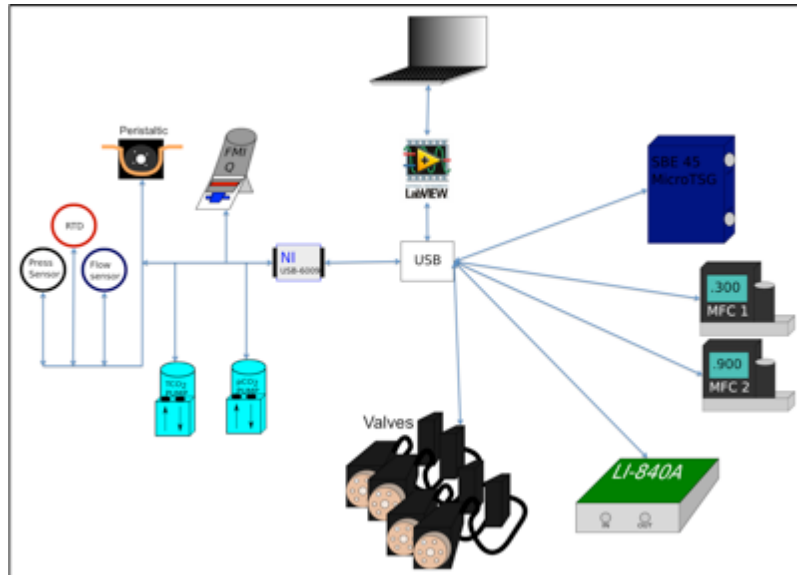
During TCO₂ operation the liquid sample to be analyzed is selected for by a 6-port VICI Cheminert multi-position valve (available at www.vici.com, #EMHMA-CE,). The analysis stream is driven by an FMI QV model metering pump fitted with an RH pump head and ceramic piston (available at www.fmipump.com, #QVRH00). An FMI V300 stroke rate controller (available at www.fmipump.com, #V300), set by an analog voltage signal, drives the pump motor to maintain a stable flow rate of 20ml/min. The flow is monitored by a MacMillan model 101 flowmeter (available at www.mcmflow.com, #Model101-3-D-K-A4-Y). The sample stream is acidified by 10% hydrochloric acid, which is injected at a rate of 0.1ml/min by a Watson-Marlow model 400F/B1 peristaltic pump. Downstream of the pump is a mixing coil constructed out of 1 m of natural peek tubing that has an outer diameter of 1/16" and an inner diameter of 0.04" (available at www.vici.com, #TPK140-10F). The analysis stream flows through the lumen side of a Liqui-Cel MiniModule membrane contactor (available at www.liqui-cel.com, #MiniModule1x5.5). Downstream of the membrane contactor the effluent is restricted by an additional 1m coil of peek

tubing to maintain approximately 7psi of backpressure.

During TCO₂ operation the 8-port, 2-position valve selects the TCO₂ carrier gas stream for analysis by the Li-840. The carrier gas stream is atmospheric air that has been passed through a purifying column of soda lime that removes CO₂ from the gas (available at www.drierite.com, #27068). A second Hargraves BTC diaphragm pump drives TCO₂ gas flow. Gas flows on the shell side of the membrane contactor countercurrent to the liquid flow. Shell side pressure is maintained at approximately 4psi with a relief valve, set to be lower than the lumen-side liquid pressure to prevent bulk carrier gas transport across the membrane. This pressure is sufficient to activate a second Alicat MC model mass flow controller that maintains a stable gas flow at 900ml/min. The carrier gas is vented downstream of the LI-840. In the field, a Sea-Bird Electronics 45 MicroTSG (available at www.seabird.com, #45) is used to measure the temperature and salinity of the seawater sample stream.

The NDIR detector, mass flow controllers, thermosalinograph, and valve actuators are interfaced with RS-232 for serial communications. Each of these peripherals was wired to an FTDI Chip RS232 to USB converter (available at www.ftdichip.com, # USB-RS232-WE-1800-BT_5.0). The liquid flow sensor, pressure sensor and rtd probe produce voltage signals and are all interfaced with a National Instruments USB-6009 multichannel data acquisition (DAQ) card (available at www.ni.com, #USB-6009). The serial devices and DAQ card are connected to a 7-port Belkin USB hub (available at www.belkin.com, #F5U701-BLK), which is used to interface to the controlling computer and software.

Figure 2. Illustration of control and data interfaces. The valves, MFCs, TSG and LI-840A are interfaced with serial to USB converters. A digital – analog card is used to control the operation of pumps and receive voltage signals from sensor. All devices are controlled by a laptop computer using a program written using LabView software.



2.2.2 Software

The instrument is controlled and operational data is collected using a program developed with LabView software (available at www.ni.com, #776678-35). Serial devices are managed by subprograms. In brief, the program controls the operations by switching valves, powering pumps and setting flow rates. Measured and operational data are collected and displayed graphically in real time as well as written to a text file. The general operation scheme is shown in Figure 3 .All peripherals are interfaced with the computer by USB connection. The USB ports and serial connections are automatically assigned identification by the computer. The connections for each component of the instrument must be specified and are used to identify the devices in the program.

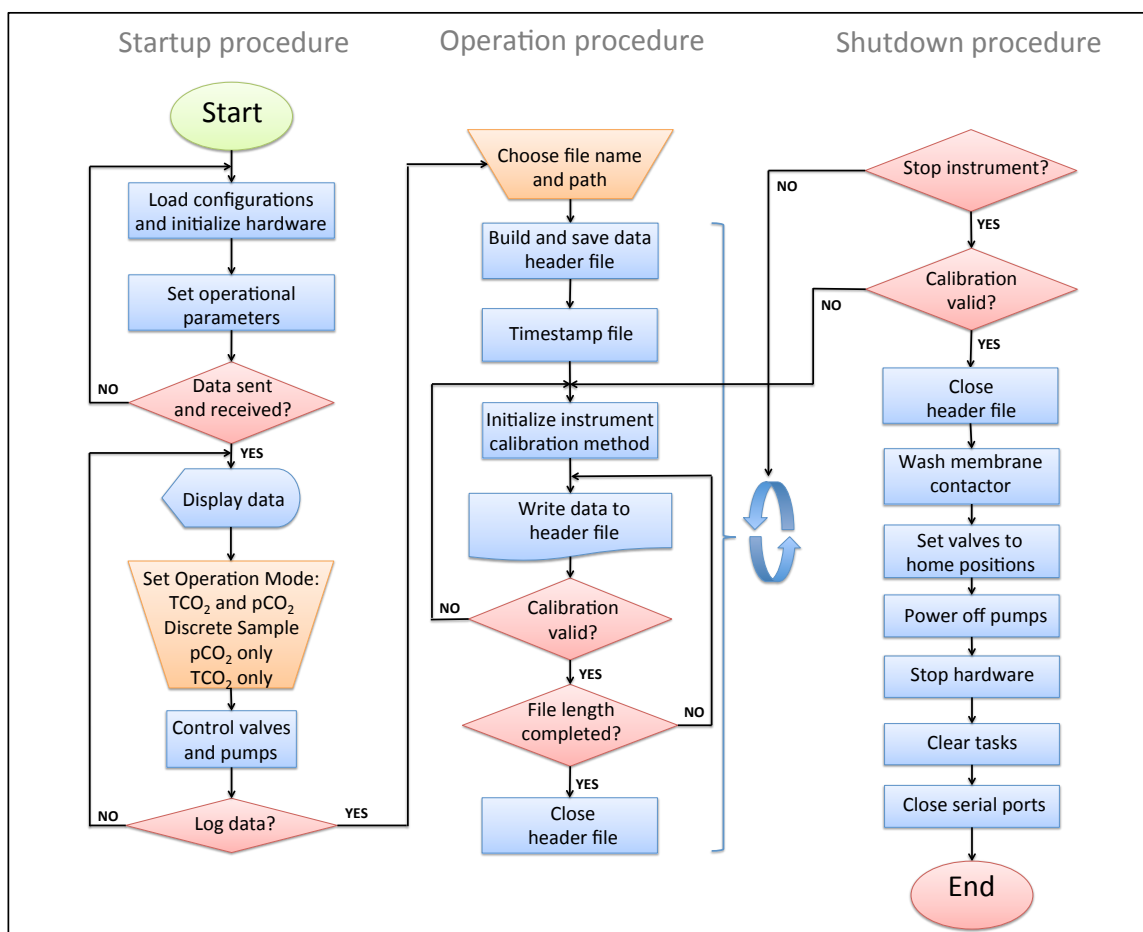


Figure 3. Flowchart of general automated operation scheme, showing system startup, analysis and shutdown procedures. Red denotes a stop or wait function; blue denotes system processes; orange denotes user input.

Upon startup the program loads the hardware configurations and initializes serial communications. If no errors are reported the system idles with valves in their home positions and data are displayed graphically. The bottom left portion of the interface screen contains user-controlled settings as shown in the screenshot in Appendix H. The user inputs the number of the gas and liquid standards, their values and the durations for which they are run. The time between system calibration procedures is set by the user and a delay before the first standard sequence after data logging has been initiated can be specified. The gas flow rates are programmable while the liquid flow is set by the voltage signal sent to the stroke rate controller. PCO_2 may be averaged across a user specified interval; the default is 10 seconds. The rate at which data is sampled is specified and is typically set to 1

second. The user sets the file duration for data output, for which the default is 1 hour.

The user may set the operational mode at any time. When operating in combined PCO₂/TCO₂ mode, the durations of the PCO₂ and TCO₂ intervals are set by the user. Once all parameters have been set, the user must press a button on the screen to begin logging data. It is standard protocol that a calibration procedure is carried out at the beginning and end of all data acquisition to maintain data quality. After a calibration procedure the linearity of the response is displayed graphically.

There are separate subprograms for calibration of the detector response and TCO₂ measurements. The detector is calibrated against three gas standards. When the gas calibration is initiated the valves are programmed to step through the tanks based on the number of standards inputted. After 15 seconds the gas signal is stable and is then averaged across the remainder of the standard duration and outputted to an array. This is repeated for each gas standard and a linear regression is performed between the output array and an array containing standard values. The same process is carried out for liquid TCO₂ standards, however in this case the signal is not averaged until after 85 seconds. The slope and intercept of the linear regression for the gas calibration is applied to the XCO₂ for the liquid analysis. During standard operations these slopes and intercepts are applied to calibrate PCO₂ and TCO₂ data in real time. The time elapsed between calibrations is specified and is set to 8 hours under standard operation. Additionally, calibration procedures can be run at any time by pressing the "Run Standards" button on the screen.

During combined PCO₂/TCO₂ mode the program loops through a sequence structure that controls operations. The sequence starts by turning on the TCO₂ air, liquid sample, and acid-reagent pumps, and turning off the PCO₂ air pump. Next the valves are set for TCO₂ operation and the system waits for the TCO₂ interval duration. Once complete, the TCO₂ air and peristaltic pumps are turned off and the PCO₂ air pump is turned on. Next the valves are set for PCO₂ operation. For the first 30 seconds of the PCO₂ interval the liquid metering pump is set to 15ml/min and the liquid valves select a reservoir containing a 1% bleach solution and the wetted components are washed to limit biological fouling. TCO₂ pumps are then powered

off for the remainder of the PCO_2 interval. The liquid metering pump is turned on and the membrane contactor is flushed with the sample stream for 60 seconds prior to TCO_2 analysis. This sequence is repeated until the calibration is no longer valid and the calibration procedure is initiated by either the set interval or manual action.

Calibrated PCO_2 and TCO_2 values are required to calculate the aragonite saturation in real time. When in TCO_2 mode the response value is averaged across the TCO_2 interval, after waiting 120 seconds for the signal to fully stabilize. The gas and liquid calibration slopes and intercepts are applied to the mean value and it is displayed as the mean TCO_2 on the screen. The PCO_2 is calculated by applying pressure of the headspace in the equilibration chamber to the gas calibrated XCO_2 values. The PCO_2 is averaged at the default 10-second interval. Thermodynamic equilibrium constants for the carbonate system are calculated from the temperature and salinity, measured by the SBE45 MicroTSG, at the set sampling interval. The concentration of calcium is calculated from the salinity according to the relationship

$$[\text{Ca}^{2+}] = (S/1.80655) \times (0.02127/40.078) \quad (12)$$

The mean PCO_2 and TCO_2 values and thermodynamic constants for the conditions are then used to calculate the concentrations of dissolved aqueous CO_2 , bicarbonate and carbonate ions. Finally the saturation state is calculated from the concentrations of carbonate and calcium ions and the aragonite solubility at the environmental temperature and salinity. This process is illustrated in Figure 4.

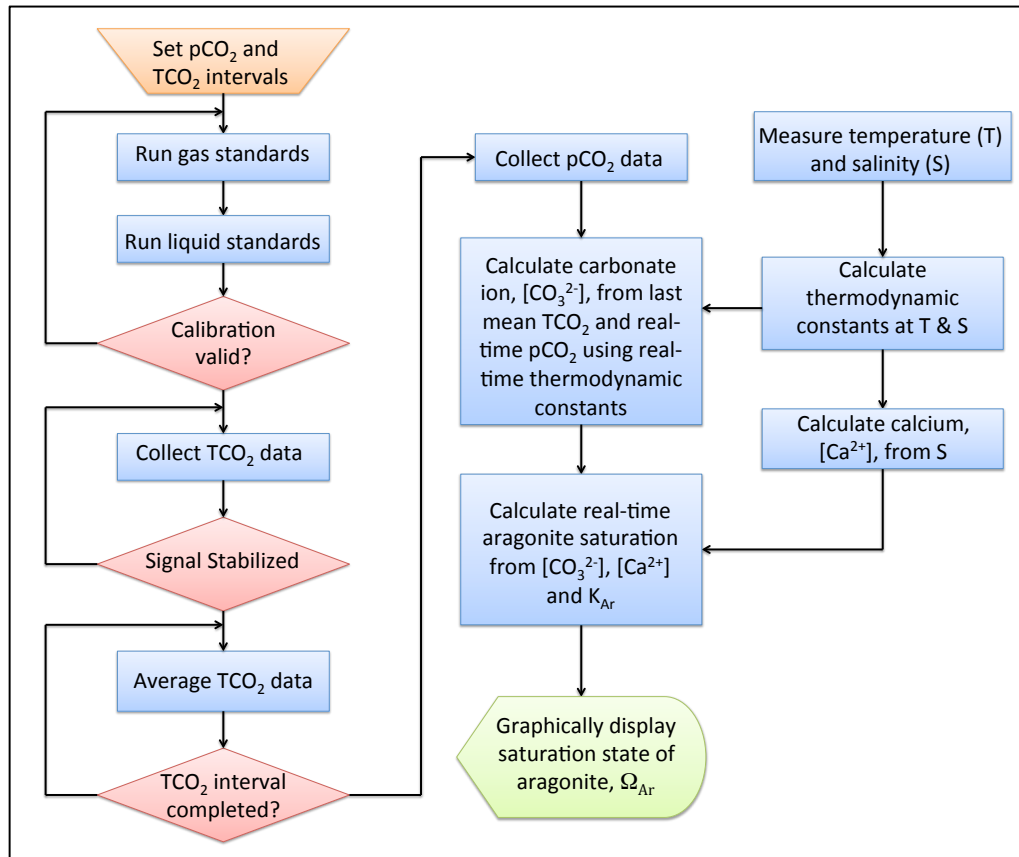


Figure 4. Flowchart illustrating system processes and calculations performed to calculate the saturation state of aragonite in real time while in combined $p\text{CO}_2/\text{TCO}_2$ operational mode.

During $p\text{CO}_2$ -only and TCO_2 -only operational modes the pump and valve controls are set in a continuous loop between calibrations. The thermodynamic equilibrium constants and calcium concentration are calculated continuously, regardless of operational mode; however, during stand-alone modes, there are no calculations of carbonate ion concentrations or saturation state.

We built in functionality to analyze discrete samples. The user presses a button on the screen to run a discrete sample. Once pressed the mode is set to discrete sample mode and pump and valve operations are set to manual control. In discrete sample mode a new header file is created and the name is appended with a “discrete_sample” identifier that raw and calculated data are written to.

2.3 Calibration Procedures

2.3.1 Reagents

Gas standards were gravimetrically prepared by Scott-Marin (available at www.scottmarrin.com, #02-050A-590B). Reference gas mixtures contain target concentrations of CO₂ in Ultra-pure Air™. Three gas standards were used to calibrate the NDIR detector with values 189ppmv, 792ppmv, and 1396ppmv.

Liquid TCO₂ standards were gravimetrically prepared in the laboratory from crystalline sodium bicarbonate (available at www.fishersci.com, #S233500), anhydrous disodium carbonate (available at www.fishersci.com, #424285000) and carbonate-free artificial seawater. Artificial seawater was prepared in 10L from 10g calcium chloride (available at www.vwr.com, EM1.02382.0500), 100g magnesium sulfate (available at www.vwr.com, JT2500-7), 315g sodium chloride (available at www.vwr.com, #3624-05) and filtered, deionized water. Liquid standards were prepared in a 2L volumetric flask and stored in gas-impermeable bags that had been fitted with 1/8 OD outlets and gated valves. Three liquid standards were used to calibrate the TCO₂ response with values 1.mM, 1.7mM and 2.4mM.

10% (v/v) hydrochloric (HCl) acid used to acidify the sample was prepared by diluting 37.%(v/v) HCl (available at www.vwr.com, #9530-33) stock in deionized water.

2.3.2 Methods

Calibration procedures are automated and controlled by subprogram within the instruments operation program. The LI-840A detector is calibrated using three gas standards. During the gas calibration subprogram a 10-port stainless steel VICI Valco multi-position valve (available at www.vici.com, #EMTMA-CE, #EMTCA-CE) selects the reference gas cylinder. The 4-port and 8-port 2-position valves are set such that the outlet of the standard valve is routed to the (TCO₂) mass flow controller, which maintains a flow of 0.900 LPM to the detector. Each standard is run for programmable duration, for which the default is 60 seconds.

TCO₂ analysis is calibrated using three liquid carbonate standards. During the liquid calibration subprogram the 6-port Cheminert VICI multi-position valve selects the carbonate standard to be introduced into the analysis stream. The 2-

position valves and pumps are set as they are in TCO₂ mode and the liquid standards are analyzed in the same manner as a sample. Each standard is run for programmable duration typically set to 120 seconds.

Real time calibration curves are generated for each subroutine. There is a hold time while the signal stabilizes. This is set to 25 seconds for gas calibration and 85 seconds for liquid calibration. After the stabilization the signal at the detector is averaged until 5 seconds prior to the end of the standard duration so as to not include artifacts related to valve switching. The mean standard values are added to a data array and a linear regression is calculated between the standard data and the known standard values inputted by the user. The regression data are shown graphically after the calibrations are run.

2.4 *Sampling Method*

2.4.1 *Lab Tests*

Several trials were conducted during instrument development. Standard calibration procedures for gas and liquid analysis were carried out as described above. These laboratory calibration procedures were used to investigate the precision and reproducibility of the system as well as its response time.

The response of the system can be modeled with a first-order exponential as described by Bandstra (2006).

$$C(t) = C_o + (C_f - C_o)(1 - e^{-t/\tau}) \quad (13)$$

Here C_o is the initial value and C_f is the final value across a stepped increase in TCO₂. The step function is accomplished by using the valves to switch between to liquid reference standards. The time-constant, τ , in this equation is solved for by fitting a curve to the data and is a characteristic of the instrument. This indicates the response time of the system. The time elapsed from valve switching to a new stable signals depends on the magnitude of the difference in values and user-defined signal stability.

To test internal consistency of TCO₂ measurements, liquid carbonate samples were prepared in the same manner as the standards but in 500ml volume and stored in 300ml tinted glass bottles. These samples of known concentration were

introduced in the discrete sample operational mode. Some of these samples were split and also run on the TCO₂ analyzer in the Hales lab at Oregon State University. Additionally calibration standards were introduced as samples.

2.4.2 Field Tests

In the field, calibration procedures were used to assess the TCO₂ response reproducibility over time. The mass flow controllers and the liquid flow meter monitor the air and liquid flow stability respectively. Samples of the source water were taken and introduced in discrete sample operational mode to verify that the system response is the same under different modes of sample introduction. Discrete samples of source water were taken and run in the Hales lab for PCO₂ and TCO₂ analysis to validate field measurements.

2.5 Field Deployment

2.5.1 Setting

Netarts Bay is a small, shallow, lagoon-type estuary located on the northern central coast of Oregon (Figure 5). Its geomorphology is that of a bar-built estuary [15]. The estuary comprises 10.88 km² with a watershed of approximately 49 km² [16]. With little freshwater input it is dominated by conditions in the adjacent coastal ocean. Whiskey Creek Shellfish Hatchery is located on the eastern edge of the bay approximately halfway between northern and southern shorelines. The hatchery pumps in seawater for its oyster seed production from a channel along the eastern edge of the bay. The intake pipe sits 0.5 m above the seafloor at an average depth of 2 m. The bay experiences high variability in salinity seasonally with average conditions being 31 psu.

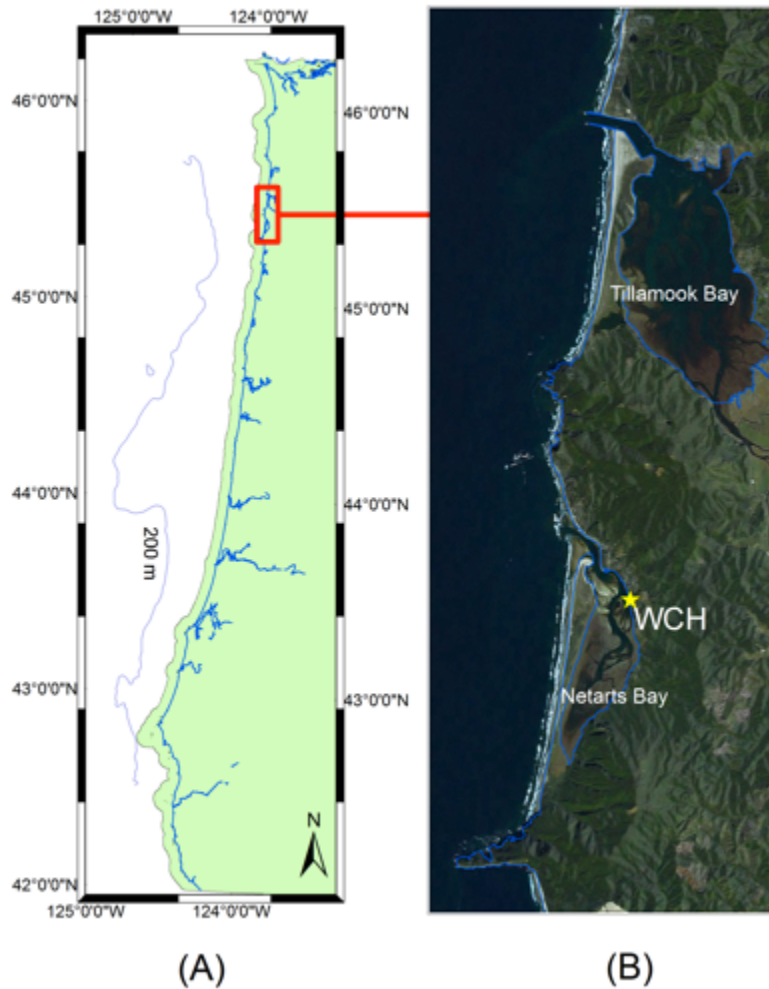


Figure 5. Geographic location of field site. (A) Map of the Oregon coast with box indicating location of (B) Netarts Bay with the approximate location of WCH labeled.

We plumbed into the main intake line with $\frac{1}{2}$ in OD nylon tubing. The intake water is run through the Seabird 45 MicroTSG. The intake flow is split sending seawater to the shower-type equilibration chamber and to a 300 μ m cartridge filter. The flow through the filter is maintained at 2 LPM with a gate valve. The filter housing is fitted with $\frac{1}{8}$ in OD tubing to draw filtered seawater for TCO₂ analysis. The gate valve down stream of the filter maintains backpressure to supply \sim 200ml/min to the liquid selection valve. The intake flow is constant and maintained by the hatchery for continuous flow-through analysis.

2.5.2 Automated Operation

The system is designed to autonomously measure PCO_2 and TCO_2 at set intervals in a continuous flow-through setting. Once the gate valves in intake sample lines are set, flows are held constant. The interface program controls instrument operations. Upon startup, the user defines the values for gas and liquid standard and their durations. The user then chooses the operational mode and the interval at which the system is calibrated. In the combined $\text{PCO}_2/\text{TCO}_2$ mode, the user sets the intervals for PCO_2 and TCO_2 operations. Typically TCO_2 is measured for 5 minutes twice per hour and PCO_2 is measured the remainder of the time. In the combined mode, the aragonite saturation is calculated in real time using the current calibrated PCO_2 and most-recent calibrated TCO_2 data and thermodynamic constants calculated from the temperature and salinity measured by the TSG.

2.6 Maintenance

2.6.1 Reagent Usage

In the field, under standard $\text{PCO}_2/\text{TCO}_2$ operation and calibration procedures, 160ml of liquid carbonate standards are consumed each day. Liquid standards are made in 2L volumes with some losses due to preparatory rinses of bags during transport and filling. Therefore under typical operations, liquid standards last for 10 days.

2.6.2 Cleaning Procedures

Main $\frac{1}{2}$ in OD lines for intake flow, rotameters, the equilibration chamber and TCO_2 filter cartridge accumulate biological growth and must be cleaned every 3-6 weeks, depending on season and environmental conditions. The cleaning procedure for primary lines starts by washing with 1% (v/v) bleach, followed by flushing with fresh water and then washing with 1% (v/v) HCl, followed by additional flushing with fresh water. The bleach solution is prepared using Clorox bleach diluted with tap water in a 5gal bucket. The HCl solution is prepared by diluting commercial grade muriatic acid with tap water in a 5gal bucket. Cleaning solutions and freshwater are driven by a submerged pump capable of pumping at 4LPM.

To reduce fouling of the membrane contactor and maintain stability of TCO₂ response, a wash procedure was written into the system operation program. After TCO₂ analysis, a 1% (v/v) bleach solution is pumped through the liquid sample stream at a rate of 15ml/min for 30 seconds. After prolonged use or excessive biologic soil accumulation, the membrane contactor is cleaned according to the manufacturer's specifications. This includes a 10min flush with distilled water followed by a 45min wash with 2%(w/v) NaOH; then a 45min wash with 3%(v/v) HCl and finally a 15min flush with distilled water. This procedure is performed every 8 weeks or as needed.

2.7 *Data Analysis*

2.7.1 *Data Processing*

The instrument is designed to make continuous measurements and log data at 1Hz. The high frequency of measurements results in large data sets. A series of programs were written in Fortran to process these data. The primary function of this instrument is to constrain the carbonate chemistry and collect time series data for the saturation of calcium carbonate minerals. To accomplish this the raw data must be consolidated, calibrated, temperature and salinity-corrected and the carbonate parameters calculated.

First a setup file is created listing the raw data files that are to be consolidated. This setup file contains the parameters used to convert analog voltages from the sensors to temperature, pressure and flow rate values. The program consolidates the data into a single text file with appropriate header with calculated values from sensor voltages.

Following consolidation the data is organized into PCO₂, TCO₂, gas standard and liquid standard modes by extracting data according to valve positions. When valves are switched, the system has a characteristic response time. PCO₂ mode data are extracted from 45 seconds after valves switching to 2 seconds prior to valve switching. These data are smoothed by taking the mean across 10-second intervals. TCO₂ mode data are extracted from 120 seconds after valve switching to 2 seconds prior to valve switching. TCO₂ mode data is averaged across the entire interval and

thus each TCO_2 interval is treated as a single point with the standard deviation calculated. Gas and liquid standard data is extracted between valve switches and are processed in their own respective programs. There are four output files from the program, one for each mode.

Gas and liquid standards data are processed in separate programs, both following the same method to generate calibration curves. Data is extracted and the mean calculated from 35 seconds prior to valve switching to 5 seconds prior to valves switching. This ensures that the average standard value is taken after the signal has stabilized and that no artifacts associated with valve switching are included. Separate setup files are used for both gas and liquid calibration programs that contain information regarding the number of standards and their values. These setup files tell the program how many times to repeat the procedure above. The average measured standard values are fed into a data array and the known concentrations for each standard are fed into a separate array. Once the final standard in a sequence is completed, a linear regression is performed between the two data arrays. The timestamp for each regression analysis is taken as the average of all standard data within the calibration sequence. This process is repeated for each calibration procedure in the time series. There are two output files from each program. The first output file contains the average measured values for each standard and the number of data point taken for each. The second output file contains the sequence times, slopes, intercepts and Chi-squared values.

There are separate programs for calibrating PCO_2 and TCO_2 data. In each case the program steps through the XCO_2 data and synchronizes it with the calibration values. The slopes and intercepts are interpolated between standard sequence times by simply taking the difference between initial and final values divided by the number of points between and adding this incrementally to the initial value. The interpolated slopes and intercepts are then applied to the data. For TCO_2 data the upper and lower bounds are calculated at plus or minus one standard deviation.

2.7.2 Generating Carbonate Time Series

A subroutine was written to calculate the thermodynamic equilibrium constants at a given temperature, salinity and pressure using the equations that are

accepted under standard operating procedures within the *Guide to Best Practices for Ocean CO₂ Measurements* [17]. Calibrated PCO₂ and TCO₂ measurements are used to constrain the carbonate chemistry and calculate the other parameters such as aragonite and calcite saturation states. However, these measurements cannot be made at the same time with this system. Therefore to construct a continuous time series for all carbonate parameters, TCO₂ data must be interpolated across the PCO₂ mode intervals. To capture natural variability in the seawater, carbonate data is modeled using the alkalinity-salinity relationship through the PCO₂ interval. An overview of this process is shown in Figure 6.

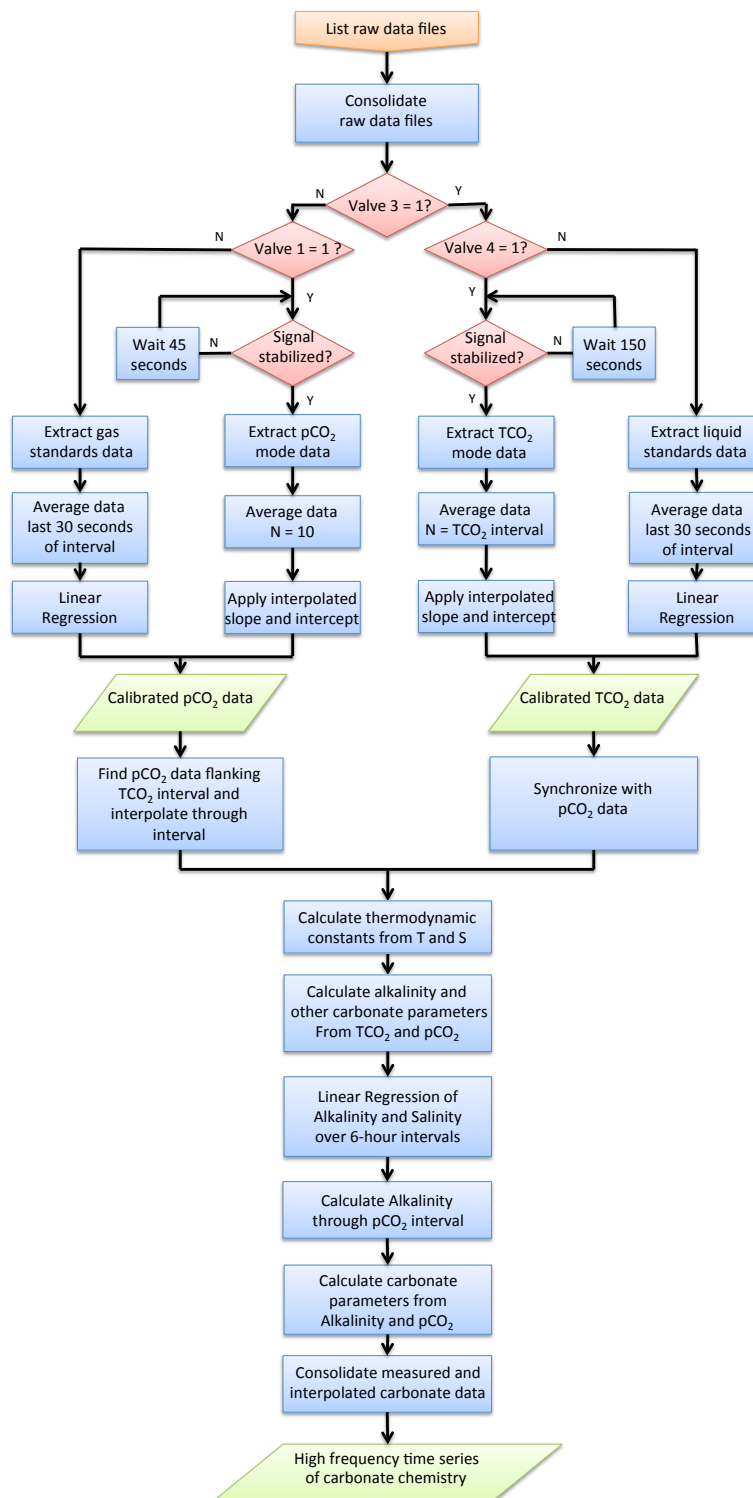


Figure 6. Flowchart illustrating the process of constructing time series data for carbonate chemistry from data collected during combined PCO₂ and TCO₂ mode operation.

The calibrated PCO_2 and TCO_2 measurements are used in a program written to establish the alkalinity-salinity relationship and its variability through time. For each TCO_2 value the program finds the flanking PCO_2 values. The PCO_2 is then interpolated across the TCO_2 interval and mean PCO_2 value is synchronized with the TCO_2 value. An output file contains synchronized PCO_2 , TCO_2 , salinity, depth (pressure) and the analysis (equilibrator) and source (TSG) temperatures. From these data the remaining carbonate parameters are calculated and written to an output file. TCO_2 is corrected for density and converted from units of micromoles/L to micromoles/kg seawater, as are the concentrations of ions. pH is given on the seawater scale and alkalinity is given in units of microequivalents/kg.

The program then steps through the time series of carbonate data and looks for alkalinity and salinity data within a 6-hour window. The midpoint of the time window is stepped forward in 30-minute increments. If the window has at least three points, a linear regression is performed between the alkalinity and salinity data arrays. Linear regressions are performed recursively throughout the data set. The output file contains the sequence numbers, times, slopes, intercepts and chi squared values.

The alkalinity-salinity fit data is then synchronized with the PCO_2 data using the midpoint of each time window. Alkalinity is calculated from salinity using the time-appropriate linear regression throughout the PCO_2 interval. The carbonate parameters are then calculated from alkalinity and PCO_2 data, following the procedures suggested by Zeebe and Sarmiento and Gruber [9, 18].

3. Results & Discussion

3.1 Response Time

The TCO_2 response of the system is dictated by the gas and liquid flow rates and the stripping efficiency of the membrane contactor. Bandstra found that the stripping efficiency of the membrane contactor used in our methods is close to 100% [13]. Under stable conditions, the system has a characteristic response time that can be found by modeling the data according to Equation 13 listed above. The

response can be measured by introducing a step function change in inlet conditions, accomplished by switching between two liquid TCO₂ standards. Using this model, the response time constant was calculated to be approximately 12 seconds. With τ established, the response time can be determined for a known change in TCO₂. Figure 7 shows that it takes approximately 60 seconds to adequately respond to a nearly 400ppmv change in XCO₂. This corresponds to 5 time constants and 99.5% of the system step change. The typical change in XCO₂ at the detector between PCO₂ and TCO₂ measurements is 600ppmv. Therefore it takes approximately 75 seconds to get to within 0.1% of the signal for the switch to TCO₂. This model can be used to determine the minimum time to wait before accepting measurement data. As previously noted the stabilization time for TCO₂ measurements is typically set to 120 seconds to minimize error in the calculations of real-time and processed data.

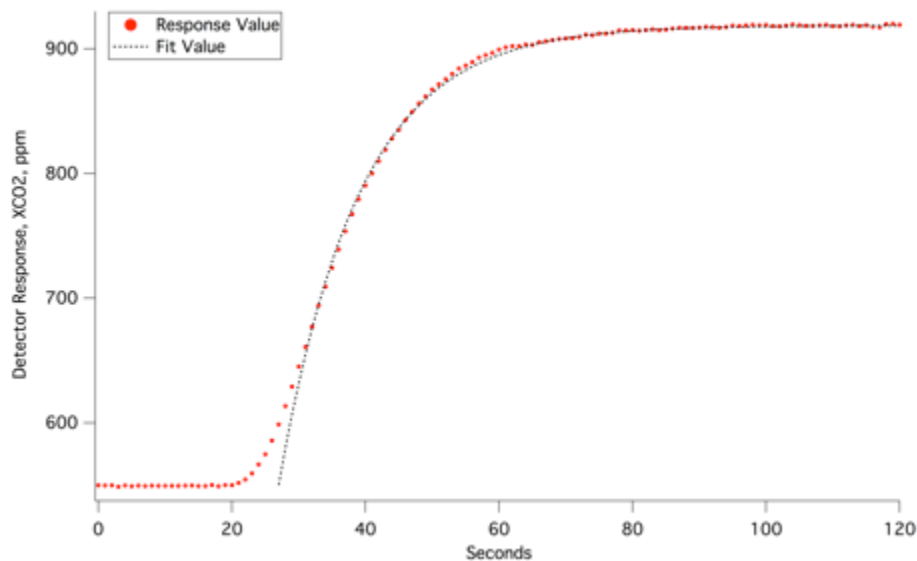


Figure 7. System response to changes in TCO₂. Input was controlled by valve switching between liquids of known carbonate concentrations. The data is modeled using Equation 13 to determine the systems e-folding time of 12 seconds.

3.2 System Stability and Precision

The system is capable of sufficiently high precision. Figures 8 and 9 show linear fits used to calibrate the detector and TCO₂ measurements respectively. The root mean square error (RMSE) of the linear regression in Figure 8 for the calibration of the detector was 0.461% with an R² value of 0.99998. Figure 9 shows

a linear fit used to calibrate TCO₂ measurements with calibrated detector response values. The RMSE of the linear regression in this plot is 0.015% with an R² value of 1.00000. Two of the three prepared standards used to produce this curve were injected between two calibration sequences. The TCO₂ values calculated with this linear regression agreed with the preparation solutions to within 0.5%.

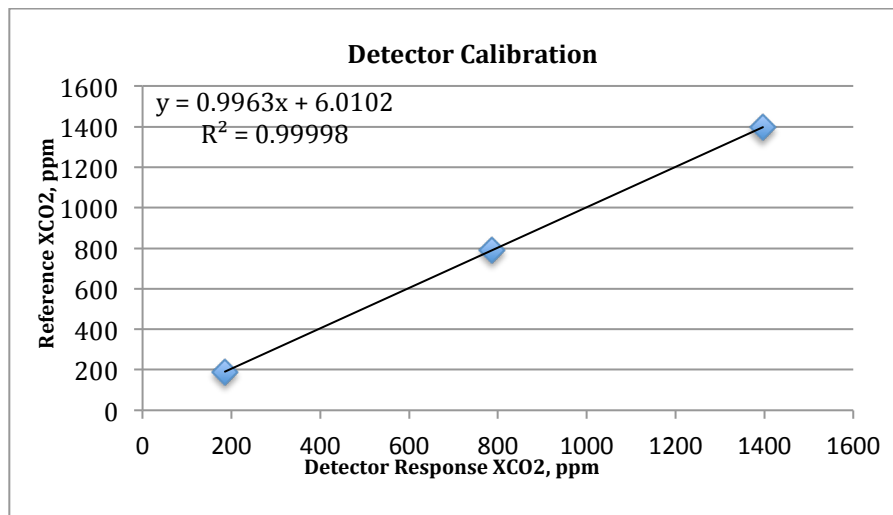


Figure 8. Gas calibration curve for response of the NDIR detector. This graph shows the detector response in mole fraction of CO₂ in ppm versus the mole fraction of CO₂ in the reference gas standard.

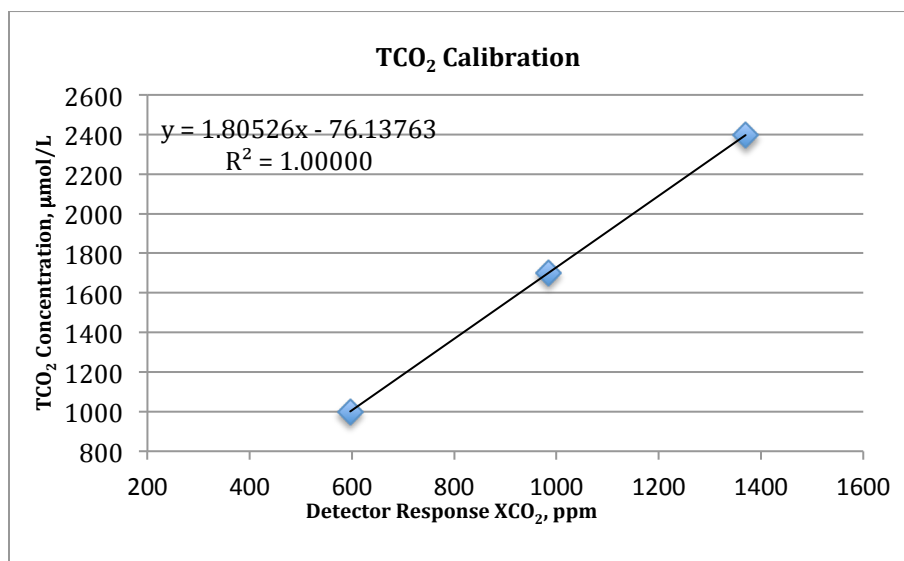


Figure 9. TCO₂ calibration curve for response of the system. This graph shows the detector response in mole fraction of CO₂ in ppm versus the prepared TCO₂ concentration in the reference liquid standard.

Figure 10 shows the results of a stability test in which a homogeneous seawater sample was run as a discrete sample for 20 minutes. During this interval the mean deviation of the detector response was 0.45%. The seawater TCO_2 was determined to be $1905.6 \mu\text{M}$ by this system. This seawater was also analyzed at the Hales lab at Oregon State University and was within 0.3% of this measured value.

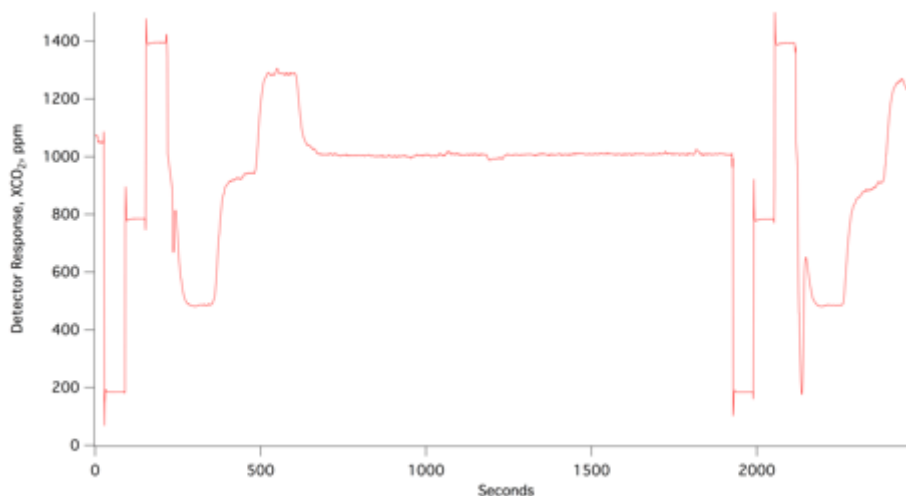


Figure 10. Test of system stability during TCO_2 mode. Detector response is proportional to TCO_2 of sample. A homogeneous seawater sample that had a TCO_2 concentration of $1911.78 \mu\text{M}$ was injected continuously for 20min. The mean deviation of response was 0.45% throughout the interval.

Long-term stability and reproducibility of the system is exhibited in Figures 11 and 12. Figure 11 shows the uncalibrated detector response for gas standards during automated calibration procedures while under normal continuous combined $\text{PCO}_2/\text{TCO}_2$ operations. The signal was reproducible to within 0.18% over 4 days. The mean slope was 1.0155, with a relative standard deviation of 0.186%. The mean R^2 value was 0.99997 for the fits of these data. With no drift in the detector response, the stability of liquid TCO_2 measurements was assessed over this same time period by analyzing the uncalibrated response for a set of liquid standards.

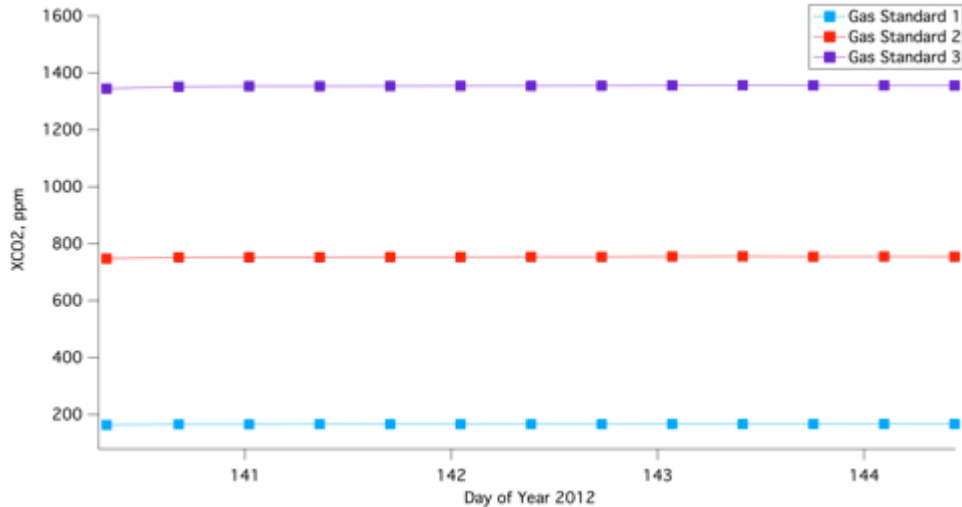


Figure 11. Mean gas standard values during calibration procedures spanning 4 days. Values are within 0.18% agreement of each other. The calibration curves had a mean slope of 1.0155 with a mean deviation of 0.186% over this time.

Figure 12 shows the uncalibrated liquid TCO_2 standard responses during the same calibration procedures as the gas values shown in Figure 11. The TCO_2 response signal was reproducible to within 0.51% over the 4 days, indicating an acceptable level of precision. The mean slope of the TCO_2 calibration curves was 1.8678, with a mean deviation of 0.453%. The mean R^2 value for these calibrations was 0.99995.

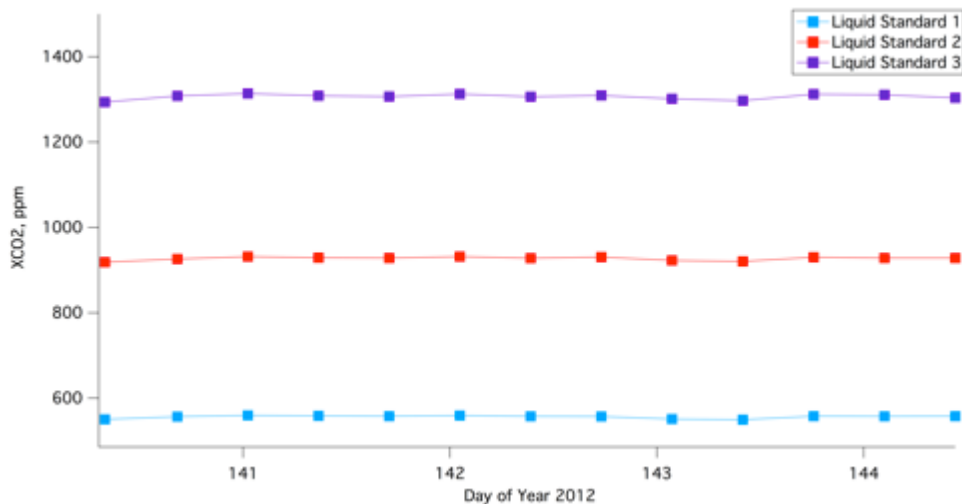


Figure 12. Mean liquid standard values during calibration procedures spanning 4 days. Values are within 0.51% agreement of each other. The calibration curves had a mean slope of 1.8678 with a mean deviation of 0.453% over this time.

The reference materials used to assess precision were consistent throughout the test. However these replicates were injected by automation in one location under essentially the same conditions. More rigorous testing of reproducibility and precision of the system is desirable.

3.3 *Validation*

Absolute accuracy was not evaluated for PCO_2 and TCO_2 measurements. Measurements of PCO_2 and TCO_2 were verified by comparison to an established chemical oceanographic research laboratory. Internal consistency of TCO_2 measurements was validated by analyzing samples of gravimetrically prepared carbonate reference liquids that were prepared similarly to TCO_2 calibration standards.

Discrete samples were collected in the field from the same water source at WCH in 300ml tinted glass bottles, poisoned with 300 μl of saturated mercuric chloride solution and sealed with metal caps. Discrete samples were analyzed at the Hales lab within the College of Earth, Ocean and Atmospheric Sciences at Oregon State University (OSU). Figure 13 shows a time series of continuous PCO_2 measurements made using the combined system. Discrete sample were analyzed at OSU and synchronized with the instrument data. The samples were within 3.47% of the PCO_2 measurements made with the combined system. Table 1 shows discrete sample data with the percent difference calculated for each. This is an expected level of disagreement considering the sources of error during sample collection, transport, time elapsed after collection and OSU laboratory methods.

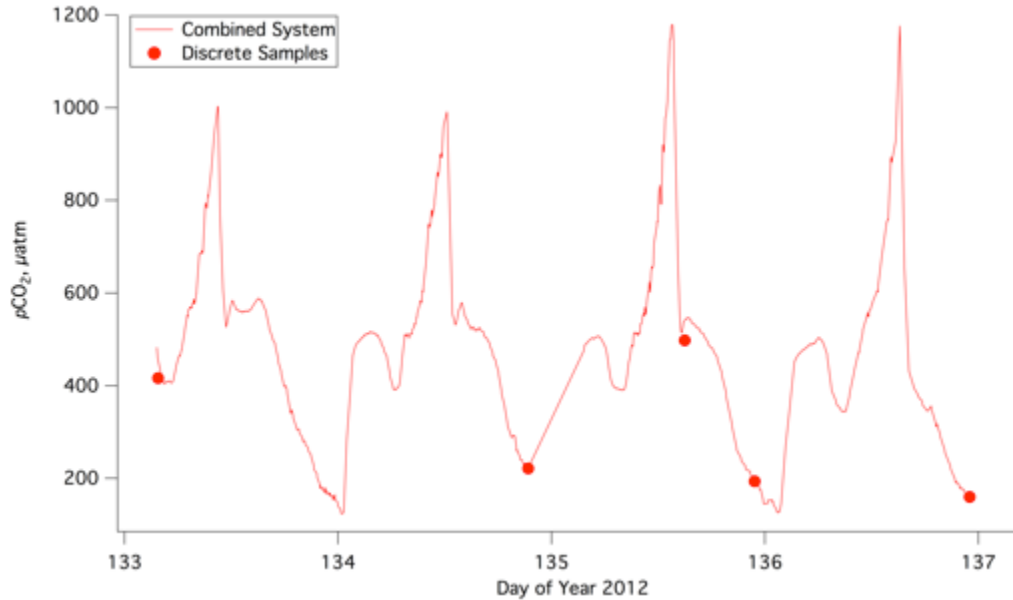


Figure 13. Time series of continuous $p\text{CO}_2$ measurements taken in the field at WCH. Discrete sample data were synchronized to assess accuracy of measurements. Samples were within 3% of measured values.

Analysis	Collected	$p\text{CO}_2$	T	S	% Difference
WCH System	5/12/12	454.937	11.40	32.34	6.71
OSU Lab	20:46	425.400			
WCH System	5/14/12	230.397	13.61	31.78	1.39
OSU Lab	14:23	233.630			
WCH System	5/15/12	540.687	10.90	32.17	6.65
OSU Lab	7:58	505.870			
WCH System	5/15/12	196.735	14.20	31.01	1.21
OSU Lab	15:50	194.360			
WCH System	5/16/12	167.647	14.61	31.59	1.11
OSU Lab	16:00	169.520			
WCH System	5/31/12	231.618	14.91	27.72	5.64
OSU Lab	0:00	218.911			
WCH System	5/31/12	400.543	14.20	27.92	4.23
OSU Lab	3:18	383.952			
WCH System	5/31/12	529.083	14.10	27.92	0.81
OSU Lab	5:44	524.824			
Average % Difference					3.47

Table 1. Extracted time series data from field measurements and discrete sample values. $p\text{CO}_2$ measurements were within 3.47% agreement.

To validate TCO₂ measurements and assess accuracy, internal standards were made in the lab using the standard protocols for liquid carbonate references solutions. Internal standards were made in 0.5L volumes and were injected into the system in discrete sample mode. Additionally, liquid TCO₂ calibration standards were injected and the TCO₂ measured according the calibration curves that they generated. Figure 14 shows the TCO₂ measurements of 31 samples of known carbonate concentrations with in the calibration range of 1.0mM to 2.4mM. The mean percent error was 0.884%. The mean RSME for the calibration curves that were used for these measurements was 0.314%.

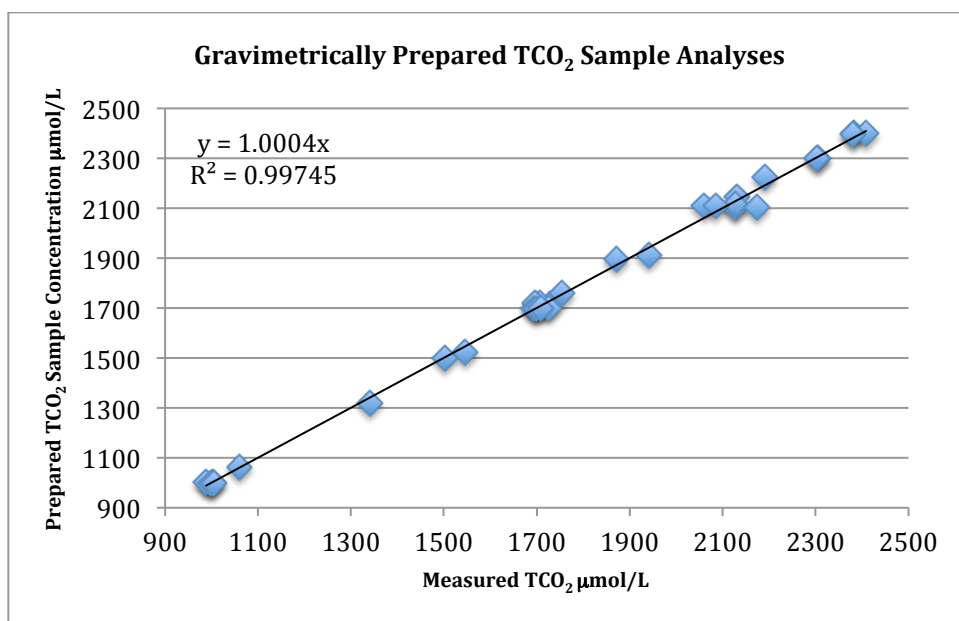


Figure 14. TCO₂ analyses of 31 liquid samples with known carbonated concentrations. Samples were prepared gravimetrically in either 2L or 0.5L volume. The mean percent error for the combined system was 0.884%.

These test represent a verification of the preparation of gravimetric liquid standards. Standards were prepared using research grade reagents and calibrated glassware and measuring equipment. These tests serve as an unverified test of internal accuracy as the carbon content of these reagents were not independently verified during the time of these tests. Therefore these tests cannot be used to rigorously assess accuracy. Certified reference materials are still needed to assess the absolute accuracy of the instrument.

In the absence of such reference materials, discrete samples were collected in the field during TCO₂ analysis and run in the OSU lab for comparison. Table 2 shows the sample collection times with the calibrated TCO₂ measured on both systems and the percent difference. The samples collected ranged in TCO₂ from approximately 1793 to 1986 μM. Analyses between the two systems were within 0.963% agreement.

Samples Collected	WCH TCO₂ μM	OSU TCO₂ μM	% Difference
5/23/12 22:38	1852.224	1843.308	0.482
5/31/12 0:00	1792.330	1794.402	0.116
5/31/12 2:17	1869.061	1903.792	1.841
5/31/12 3:18	1943.081	1945.252	0.112
5/31/12 5:44	1963.634	2008.649	2.266
Average % Difference			0.963

Table 2. Discrete samples collected at the field site used to validate TCO₂ measurements. The mean percent difference between measurements made with the combined system and at OSU was 0.963%.

Comparing the measurements between the systems, there is increased error with increasing concentration. Figure 15 shows the linear relationship between measurements. The slope is very close to 1 indicating reasonable agreement. However, there is increased deviation at higher concentrations of TCO₂. This is further borne out in Figure 16, which shows the linear relationship between percent differences and TCO₂ illustrating a bias of greater error with increasing TCO₂. This can be explained by a lack of precision in liquid standard preparation at the OSU lab during these analyses, which resulted in an inaccurate slope value during calibration. The mean standard error of the calibration curves for the OSU system was approximately 3% with a larger deviation at high concentration, while the standard error of the calibration curves for the WCH system during these analyses was 0.5%. That said, the operations of OSU system have been rigorously validated and this test provides some indication that the combined system at WCH is capable of reasonably high accuracy.

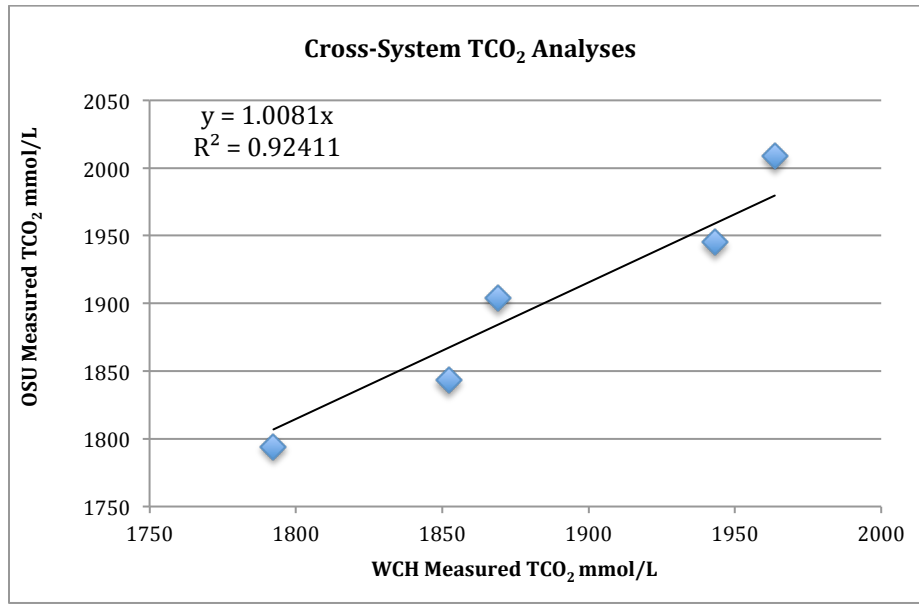


Figure 15. Comparison between TCO₂ measurements made by the OSU lab system and the combined system at WCH of 5 discrete field samples. Deviation is increasing with TCO₂ concentration.

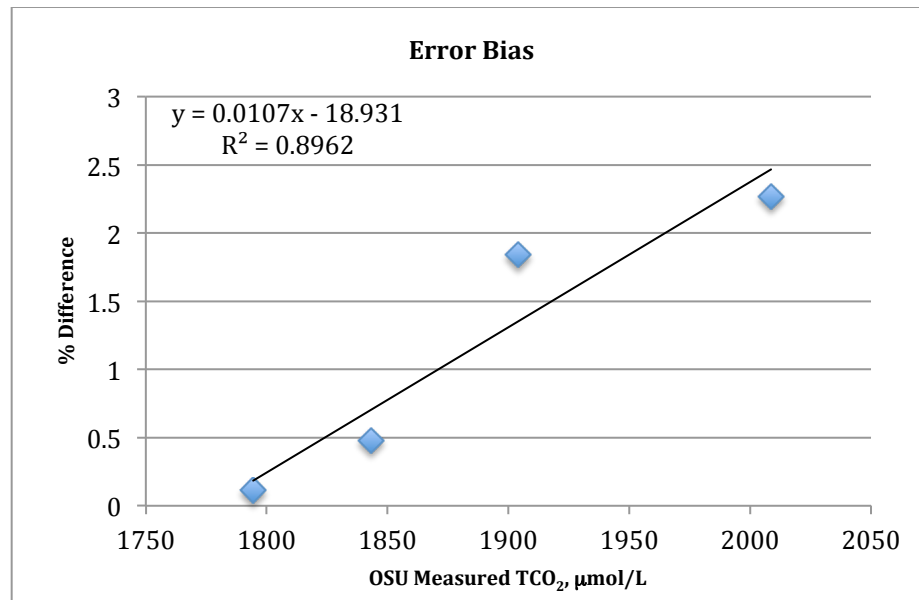


Figure 16. Linear model shows increasing percent error with TCO₂ concentration that is the result of inaccurate slope in the calibration curve for the OSU system.

3.4 Discrete Sample Mode

The combined system is designed be able to analyze discrete samples for both PCO₂ and TCO₂ measurement in addition to normal flow-through operations. Additionally, discrete sampling mode was used extensively to introduce internal samples during TCO₂ measurement validation tests. To validate the equilibrator apparatus and PCO₂ and TCO₂ measurements during sampling, the discrete sampling and flow-through methods were compared.

3.4.1 PCO₂ Mode

To assess the PCO₂ measurements of discrete samples the intake was sampled and compared to flow-through operation. First, the system was set to PCO₂ mode under normal flow-through operations and allowed to equilibrate. After stable PCO₂ measurements were made the intake water was sampled into a 300ml tinted glass bottle and the discrete sampling mode was engage using the software controls. Equilibration using the shower-type and discrete sampling apparatus was then compared. The detector response was calibrated using the slope and intercept values in Table 3 and the PCO₂ at the analysis temperature was calculated from the equilibrator headspace pressure and the detected XCO₂. Temperature corrections were made according to Equation 19 for both equilibrators.

$$pCO_{2Source\ T} = pCO_{2Analysis\ T} \times EXP(0.0423*(Source\ T - Analysis\ T)) \quad (19)$$

The calibrated, temperature-corrected PCO₂ measurements were within 0.453% agreement.

Analysis	XCO ₂	Equilibrator Pressure	Equilibrator Temp	Source Temp	Salinity	pCO ₂ at Equilibrator Temp	pCO ₂ at Source Temp
Flow-throug	234.777	0.995	15.112	14.911	27.629	234.837	232.845
Discrete Samr	242.868	0.996	15.800	14.890	27.625	242.975	233.805
Gas Slope	0.9925562	Gas Intercept	2.916134802			% Difference	0.453

Table 3. Test of PCO₂ measurements using the discrete sampling mode. The time of analyses is given with the XCO₂ value, which was calibrated according to the parameters shown. Equilibrator and source temperatures are given and were used to make temperature correction to compare PCO₂ measurements at the source temperature using two different equilibrators on the same system.

3.4.2 TCO₂ Mode

Assessment of TCO₂ measurements in discrete sampling mode was carried out similarly to the PCO₂ validation. Intake water was sampled in 300ml tinted glass bottles and injected into the system for analysis. Calibrated TCO₂ measurements for both delivery methods were compared and found to be within 0.318% agreement. Table 4 shows the TCO₂ analysis data for each source and delivery. The mean XCO₂ response is calibrated according to the mean TCO₂ slopes and intercepts shown. The calibrated TCO₂ measurements were compared and the percent difference taken.

Source	Delivery	Run Date	TCO ₂ XCO ₂	Ave Flow Rate	Ave MFC mass flow	Average TCO ₂ slope	Average TCO ₂ intercept	Average TCO ₂ μM	% Difference
Intake	flow-thru	23-May	806.380	19.854	0.901	2.076	159.091	1833.218	0.025
Sample	in bottle	23-May	807.447	19.977	0.899	2.074	159.392	1833.675	
Intake	flow-thru	7-Apr	1022.524	20.751	0.900	1.813	-24.558	1829.387	0.399
Sample	in bottle	7-Apr	1017.281	20.811	0.900	1.816	-25.395	1822.095	
Intake	flow-thru	16-Mar	1059.791	20.144	0.900	1.887	-78.597	1920.926	0.546
Sample	in bottle	16-Mar	1055.764	20.071	0.900	1.888	-82.463	1910.476	
Intake	flow-thru	14-Mar	892.705	20.058	0.900	1.683	100.065	1602.374	0.366
Sample	in bottle	14-Mar	895.091	20.181	0.901	1.686	99.111	1608.248	
Intake	flow-thru	8-Mar	1091.463	20.598	0.900	1.786	-22.187	1927.259	0.251
Sample	in bottle	8-Mar	1095.753	20.601	0.900	1.789	-27.854	1932.110	
Average % Difference									0.317

Table 4. Test of TCO₂ measurements using the discrete sampling mode. The source, delivery and run date identify each analysis. The mean TCO₂ slopes and intercepts are applied to the XCO₂ values and the calibrated TCO₂ measurements are compared. The average percent difference between flow-through and discrete sampling methods is 0.317%.

3.5 Field Data

3.5.1 Real Time Data

The objectives for this instrument include real-time calculations of the carbonate parameters, including the saturation state of calcium carbonate minerals, from the nearly simultaneous measurements of PCO₂ and TCO₂ in the seawater. Real time measurements are dependent on accurate calibration of the detector and TCO₂ measurements. Figure 17 shows the raw data during a calibration procedure and the mean standard values used for the linear regression.

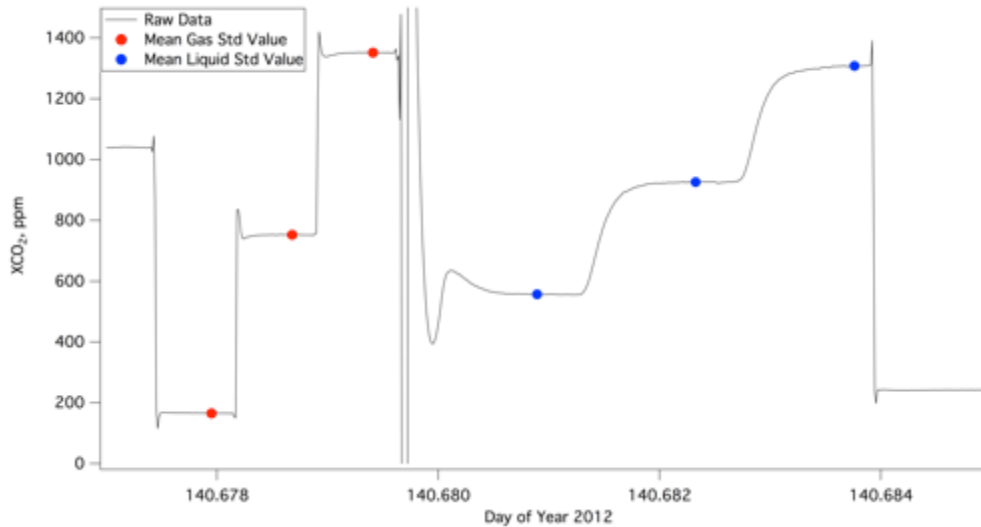


Figure 17. Raw data during calibration procedure with mean gas and liquid standard values used for the linear regression.

Figure 18 shows raw data under typical combined $p\text{CO}_2/\text{TCO}_2$ operations. Automated calibration procedures are performed every 8 hours under standard operation. The default $p\text{CO}_2$ and TCO_2 intervals are 1500 and 300 seconds respectively. Therefore there is a 5-minute interval of continuous TCO_2 measurement every 30 minutes.

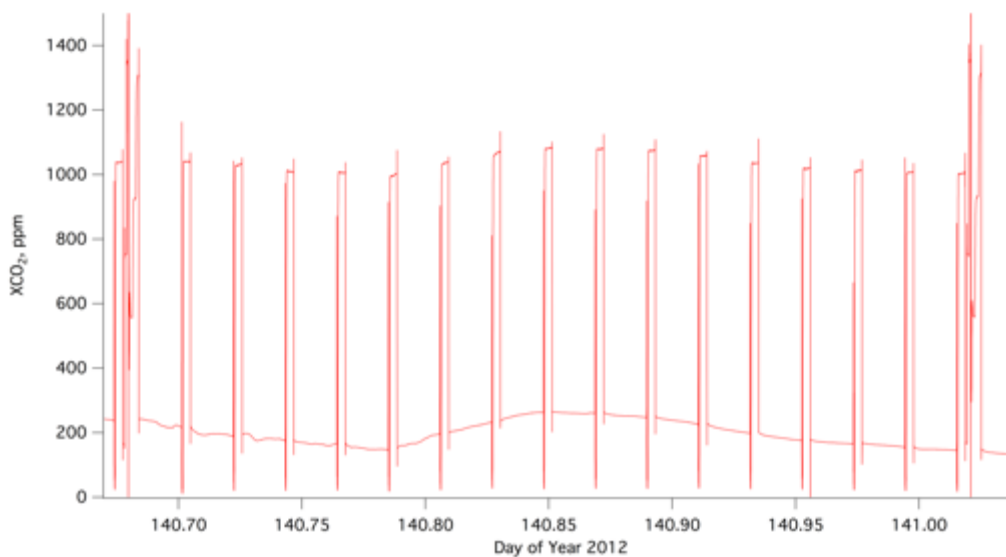


Figure 18. Raw data during standard $p\text{CO}_2/\text{TCO}_2$ operation. TCO_2 measurements are taken for 5-minute intervals every 30 minutes with $p\text{CO}_2$ measurements made in the interim. Calibration procedures are performed every 8 hours.

The saturation of aragonite is calculated in real time according to methods discussed in section 2.2.2. Figure 19 shows an example of such data. The red markers represent real time data. The black line in the graph is the saturation calculated in the post-processing methods. The offset in this case was due to inaccuracies in the real-time calibration and inconsistencies in the averaging of TCO_2 values. Averaging of TCO_2 data likely began before the signal stabilized, resulting an inaccurate slope value (within 0.383%) and large differences in the intercepts (mean difference of 93.759%, see Appendix E). This leads to higher TCO_2 values and an overestimate of saturation state.

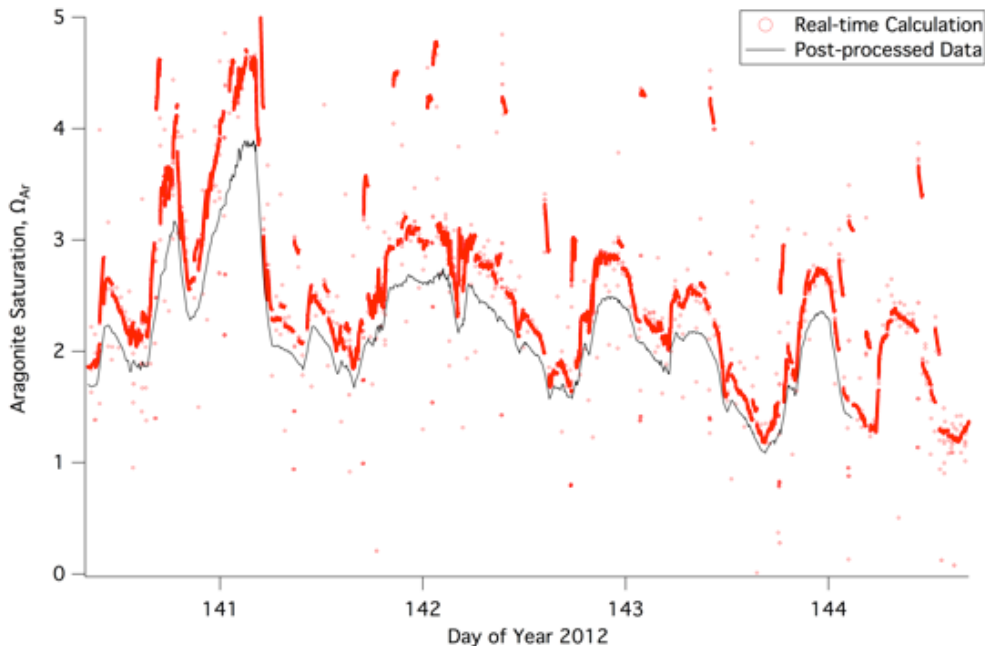


Figure 19. Real-time aragonite saturation calculated from last mean calibrated TCO_2 value and real-time $p\text{CO}_2$. Thermodynamic equilibrium constants are calculated from temperature and salinity.

3.5.2 Processed Data

A series of quality control measures, calculations and organization of the raw data goes into consolidating accurate time series data from field data. The methods developed for the data sets produced by this instrument are discussed in section 2.7.2. After consolidation of the raw data files and corrections are made to analog data, the gas and liquid standards, PCO_2 and TCO_2 data are each extracted. Figure 20

shows an example of extracted PCO_2 mode data overlaid the raw data. The extracted PCO_2 mode data is averaged across 10-second windows. Figure 21 shows an example of extracted TCO_2 mode data. TCO_2 mode data is averaged across the entire stabilized signal and the interval is treated as a single point. The standard deviation of the TCO_2 signal across the interval is calculated and is used as a quality control measure for TCO_2 data processing. TCO_2 measurements with a standard deviation (of XCO_2) greater than 3 do not get calibrated and are left out of the final time series. The standard deviation is also calculated for the PCO_2 interval and values greater than 10 ppmv do not get further processed.

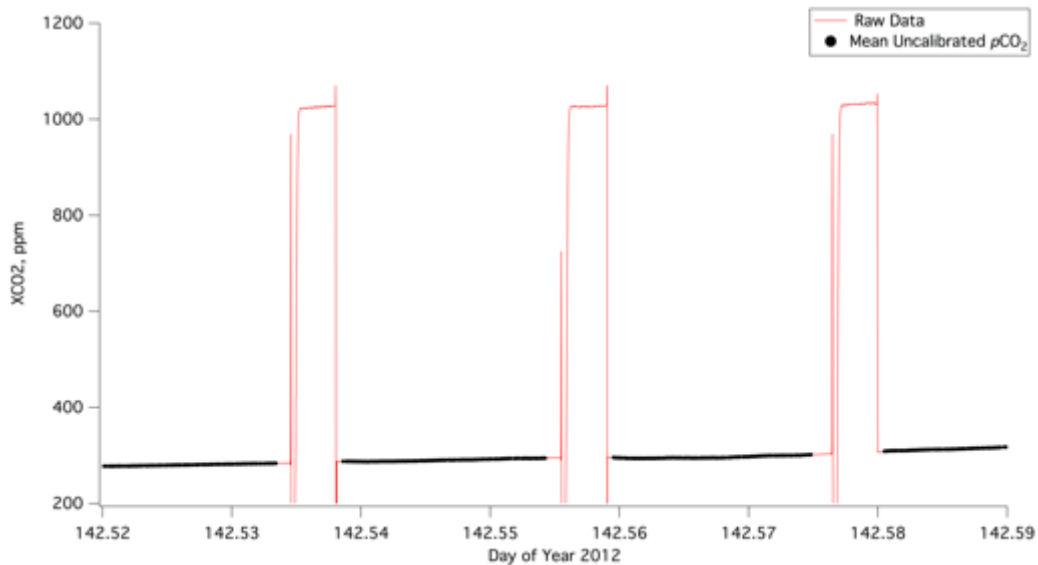


Figure 20. PCO_2 mode data extracted from and then overlaid raw data. PCO_2 data is averaged at 10-second windows.

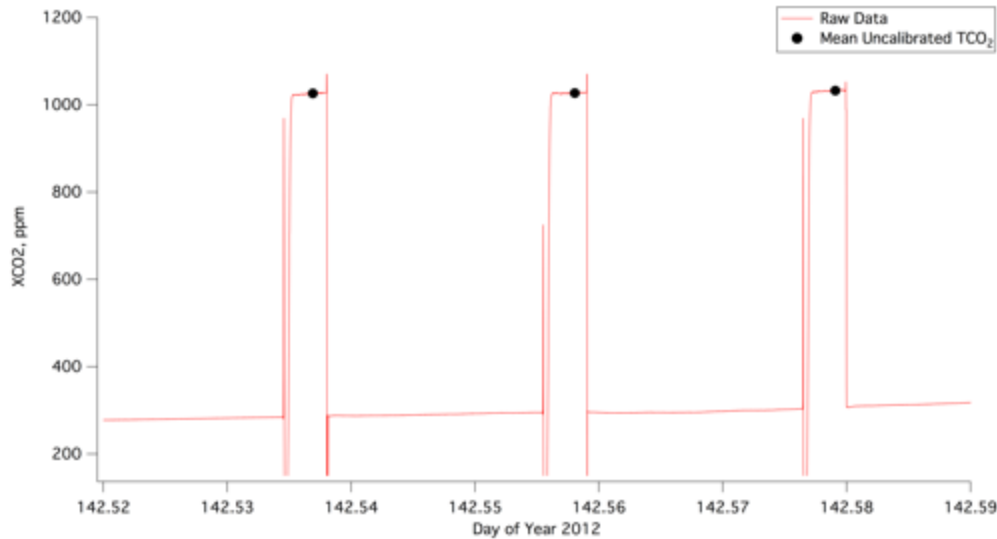


Figure 21. TCO₂ mode data extracted from and then overlaid raw data. TCO₂ mode data is averaged across the entire stabilized signal and the interval is treated as one point.

PCO₂ and TCO₂ mode data are calibrated by synchronization with the interpolated calibration slope and intercept values. The slopes and intercepts are calculated from the mean standard values in the last 30 seconds of the interval during a stable signal as illustrate in Figure 17 and then interpolated over the time interval between calibrations. Figure 22 shows examples of calibrated PCO₂ and TCO₂ time series data. These data were collect from 5/19-5/23/2012 at Netarts Bay, Oregon. Oscillations are consistent with diurnal frequency and are driven by biological production in the bay. The significant decrease in TCO₂ and salinity during May 21, 2012 are explained by intrusion of the Columbia River plume into the bay during periods of downwelling-favorable winds (see Figure 28). The maximum rates of change seen in the carbonate conditions during the time series were 123 $\mu\text{M hr}^{-1}$ for TCO₂ and 103 $\mu\text{atm hr}^{-1}$ for PCO₂, corresponding to changes of 2.4°C hr⁻¹ in temperature and 2.6 psu hr⁻¹ in salinity. This illustrates the instrument's ability to capture the high variability seen in the bay.

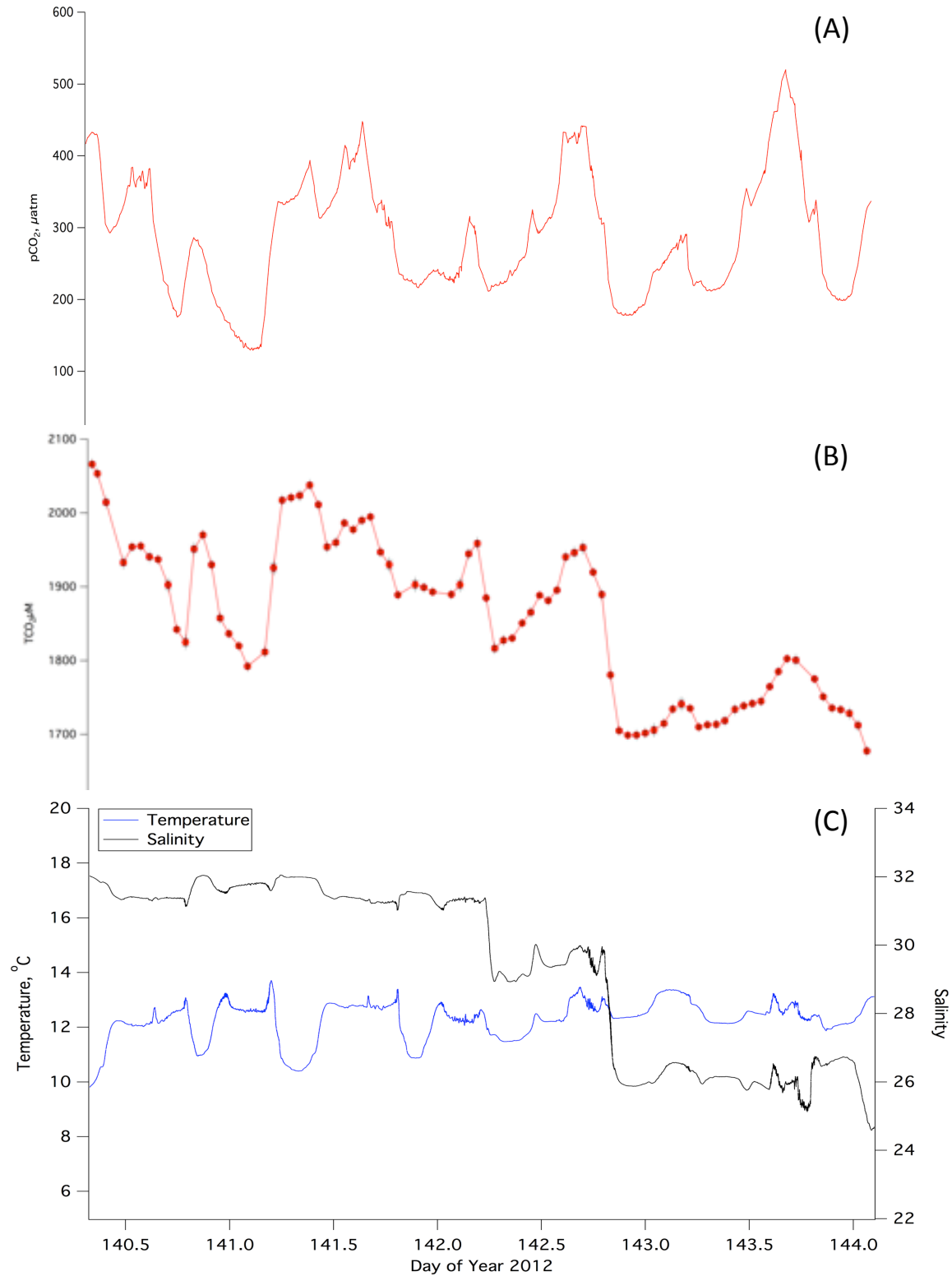


Figure 22. Time series data of continuously sampled seawater from Netarts Bay, Oregon was analyzed from 5/19-5/23/12. (A) Temperature-corrected, calibrated $p\text{CO}_2$. (B) Calibrated TCO_2 with 1 standard deviation error bars. (C) Temperature and salinity data taken at the time of $p\text{CO}_2$ and TCO_2 measurements.

3.6 Interpolation Model

In order to construct a time series of the other carbonate parameters, PCO_2 and TCO_2 data must be consolidated and interpolated through time in a way that is consistent with natural variability. To accomplish this we created an interpolation model that was discussed in section 2.7.2. After PCO_2 and TCO_2 data are synchronized alkalinity is calculated. The relation between alkalinity and salinity is tightly correlated and is not subject to decoupling the way TCO_2 and salinity may be due to photosynthesis and respiration. Given the strong correlation between alkalinity and salinity, a single linear regression approach may have been considered sufficient. However, evaluating a single linear regression of the alkalinity and salinity data (shown in Figure 23) from time series data presented above, the mean percent error of predicted alkalinity was 1.499%.

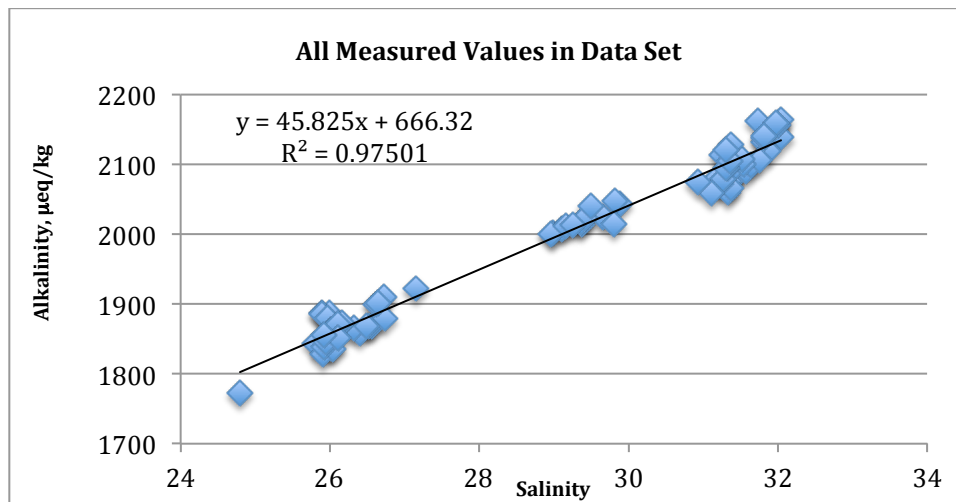


Figure 23. Linear model of alkalinity-salinity relationship based on a single regression of all values in the time series data for PCO_2 and TCO_2 measurements of seawater from Netarts Bay, Oregon was analyzed from 5/19-5/23/12.

The highly dynamic setting of Netarts Bay requires a more complex approach to capture the variability in the alkalinity-salinity relationship over short timescales. We have developed an approach that models alkalinity with significantly less error. As noted before and illustrated in Figure 24, the model steps through the data at 30-minute increments looking for alkalinity and salinity data in a 6-hour window.

Linear regressions are recursively performed on the alkalinity and salinity data arrays throughout the time series. This accurately captures the alkalinity-salinity relationship and allows for variability through time.

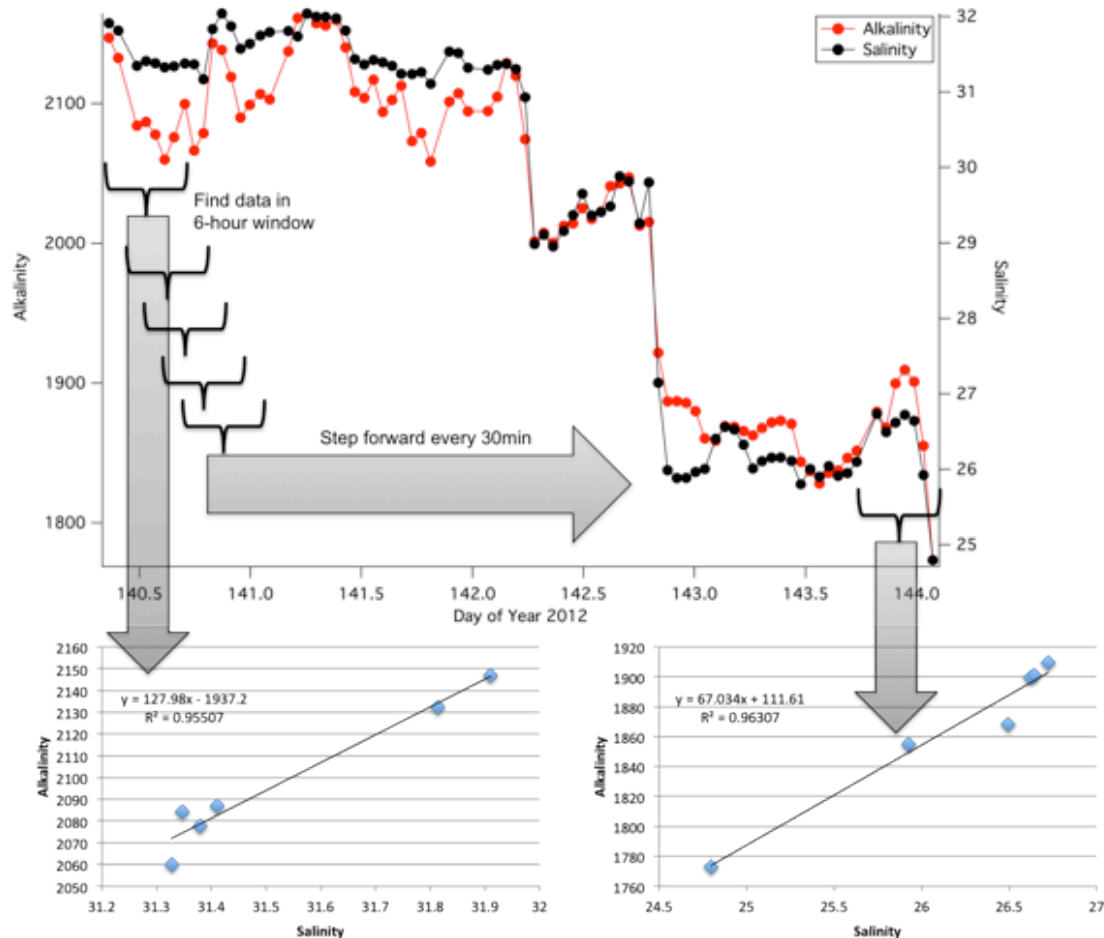


Figure 24. Scheme for determining alkalinity-salinity relationship through time series data by recursively fitting a linear regression to windows of data. This allows the natural variability in the relationship to be easily modeled.

We investigated the predictive power of a single linear regression using data in a 6-hour window. Figure 25 shows that the percent error increases as a function of time beyond the 6-hour window. This illustrates the 6-hour interval is appropriate to capture variability conditions and minimize error in calculating alkalinity from salinity. The percent error is less than 1% within this interval, whereas if the linear fit is applied to conditions out to a 24-hour window the percent error approaches 4%.

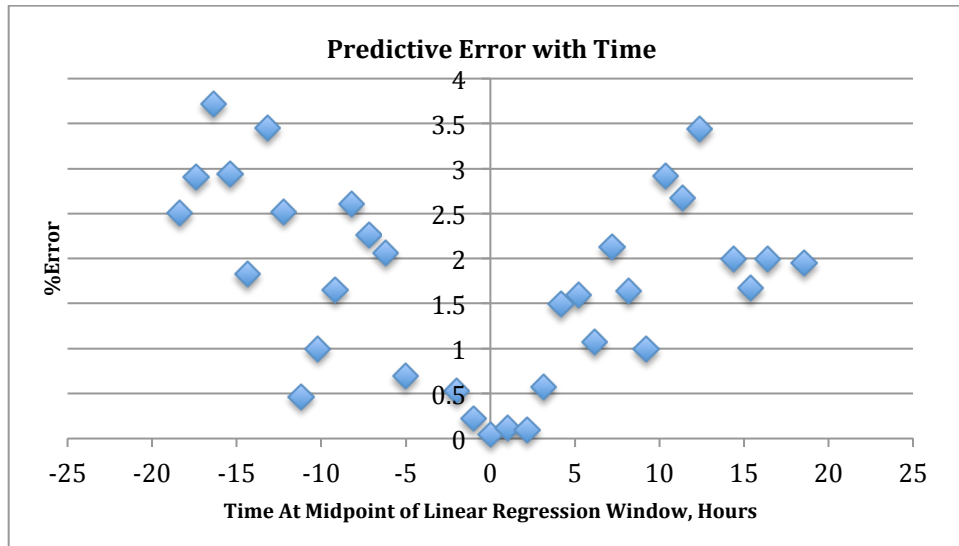


Figure 25. Plot of the percent error of the alkalinity predictability using a single linear regression of data in a 6-hour window as a function of time. Error becomes significantly worse beyond the 6-hour window.

The goodness of fit for the single regression and recursive regression models are shown in Figures 26 and 27. These plots show the predicted alkalinity versus alkalinity calculated from measured parameters, TCO_2 and PCO_2 . The goodness of fit for our recursive regression model is significantly improved over the single regression model. Further, the mean percent error of predicted alkalinity is three times less using the recursive approach.

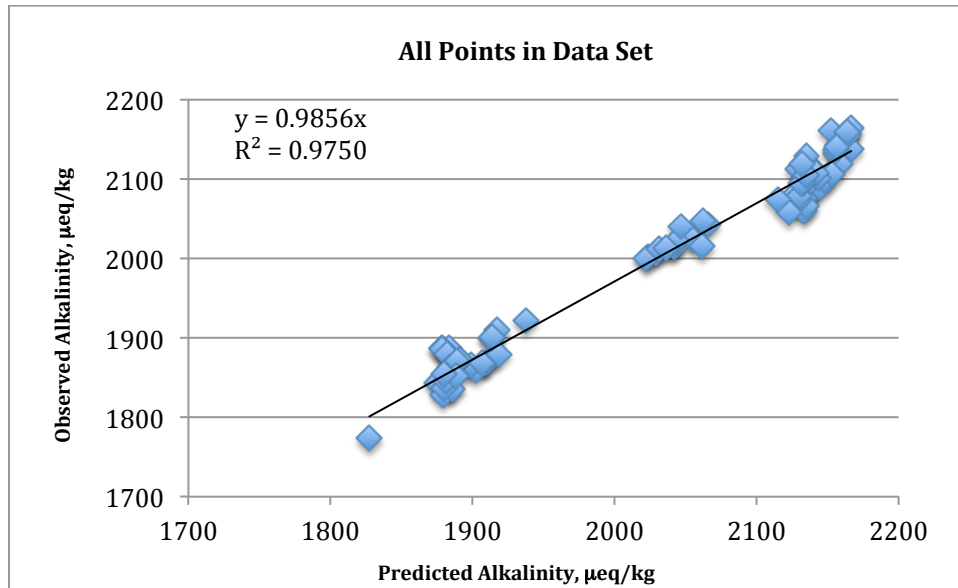


Figure 26. Plot of fitted alkalinity using a single linear regression approach versus alkalinity calculated from measured PCO_2 and TCO_2 . The mean percent error using the single regression model is 1.499%.

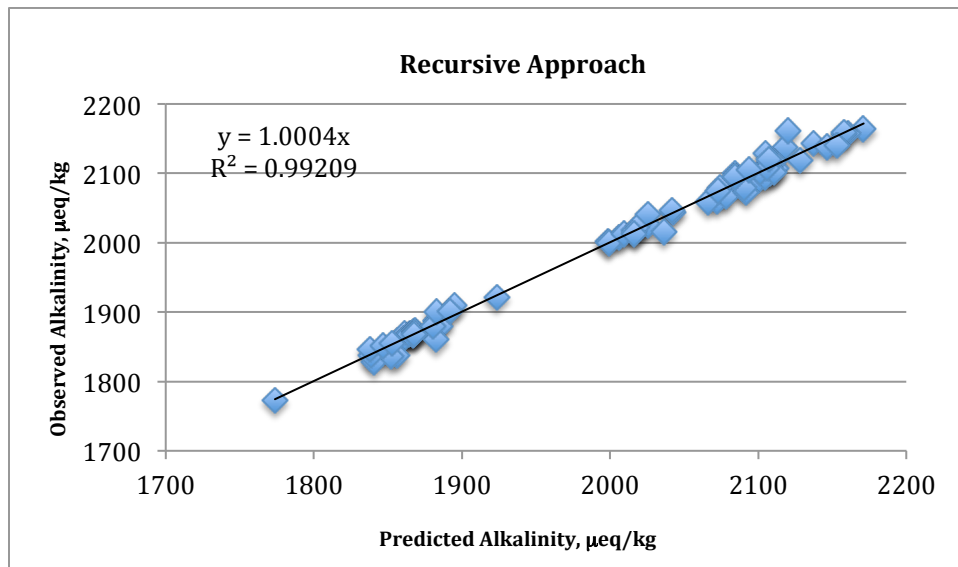


Figure 27. Plot of fitted alkalinity using the recursive approach versus alkalinity calculated from measured PCO_2 and TCO_2 . The mean percent error using the recursive regression model is 0.457%.

This model is then applied to PCO_2 mode interval and the alkalinity is calculated from salinity. The modeled alkalinity and measured PCO_2 are then used to calculate the carbonate parameters resulting in a high-resolution time series of carbonate system data. The carbonate system values that were calculated directly

from the synchronized measured PCO_2 and TCO_2 data in the steps above provide a further check on the goodness of fit for this interpolation model. Figure 28 shows the saturation state time series. The dashed lines represent the data interpolated through the PCO_2 interval while the markers represent the calculations from the synchronized $\text{PCO}_2/\text{TCO}_2$ measurements. The mean deviation of the predicted values from the measured observation is within 1.6% for both aragonite and calcite saturation states.

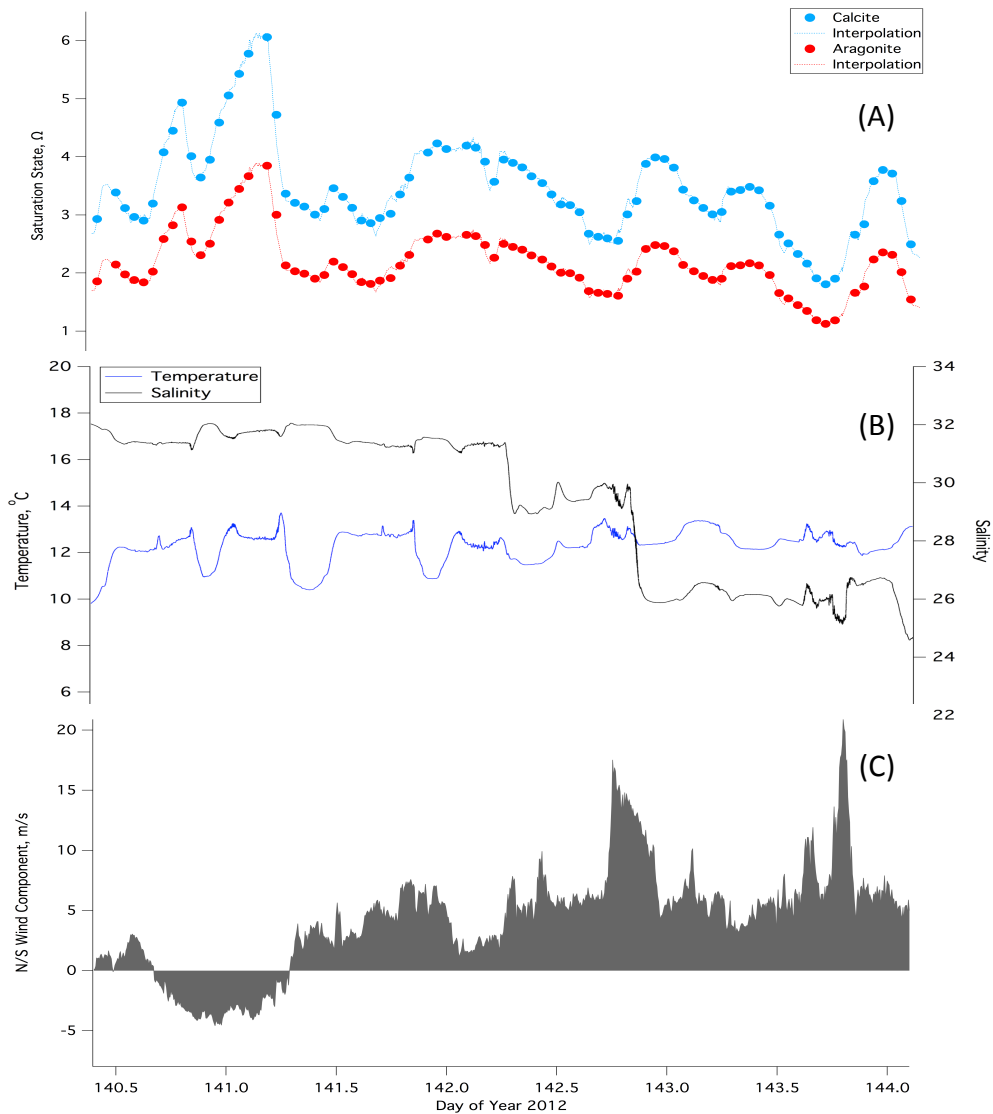


Figure 28. Time series data of (A) the saturation state of calcite and aragonite carbonate minerals from data collected in Netarts Bay from 5/19-5/23/12. The dashed lines represent interpolated data and are within 1.6% agreement with the data represented by markers that was calculated from measurements constraining the carbonate system. (B) Temperature and salinity data taken at the time of PCO_2 and TCO_2 measurements. (C) North-south wind forcing data taken from NOAA Buoy 9437540 at Garibaldi, OR approximately 10 miles north of field site.

The interpolation model appears to be quite successful at capturing natural variability in the seawater seen in the bay. Table 5 shows the standard errors of the predicted values of interpolated carbonate parameters.

N = 84	ALK	DIC	pH _{sws}	Omega-C	Omega-A
Standard Error of Estimate	10.7000	9.5470	0.0074	0.0539	0.0343
Percent Deviation	0.5328	0.5277	0.0912	1.5670	1.5814
R²	0.9913	0.9912	0.9953	0.9954	0.9955

Table 5. Standard error of estimates using the interpolation model developed to create time series of carbonate system parameters. This model captures the natural variability to within 1% of the measurements.

The inherent error of alkalinity calculated from PCO_2 and TCO_2 measurements is +/- $3.0\mu\text{mol/kg}$ [18]. This error must be taken into account when evaluating the accuracy of the composite time series data. This increases the mean deviation in interpolated alkalinity values to 0.677%. With up to $13.0\mu\text{mol/kg}$ uncertainty in interpolated alkalinity and a maximum error of 3.5% in pCO_2 , the error of interpolated saturation state of calcium carbonate is less than 3.6%.

4. Conclusion

I have built a system that automatically makes high-frequency measurements of PCO_2 and TCO_2 for constraint of the carbonate system and real-time calculation and display of the saturation state of calcium carbonate in a dynamically-changing flowing stream of natural seawater. The system makes continuous measurements at programmable intervals using a flow-through design with the capability of running discrete samples. The system uses a non-dispersive infrared detector to measure CO_2 content of either an equilibrated headspace for PCO_2 measurements or evolved gas from an acidified sample stream for TCO_2 measurements.

At this point in development the precision of instrument is within 0.5%. The internal accuracy of the system with respect to TCO_2 measurements is 0.8%. TCO_2 measurements were within 1% agreement with established measurements at the Hales lab at Oregon State University, while PCO_2 measurements were within 3% agreement. However, absolute accuracy has yet to be established. The discrete sample mode of operation performs well with discrete PCO_2 measurements being

within 0.5% of the shower-type flow-through equilibrator while discrete TCO_2 samples were within 0.3% of the flow through apparatus.

The numerical methods used to construct time series of carbonate data from combined $\text{PCO}_2/\text{TCO}_2$ operations accurately interpolates through PCO_2 mode using synchronized PCO_2 and TCO_2 measurements to model variability in the alkalinity-salinity relationship. Alkalinity is interpolated to within 0.5% leading to aragonite calculations that are within 3.6% given uncertainty in the measurements and calculations.

There was significant deviation in real-time calculation of saturation states due to miscalculations and/or synchronization problems in the software program. However, since the instrument is capable of reproducing measurements and has shown to be stable for multiple days of continuous operation, I feel this will be a simple programming issue to resolve.

I have shown a successful proof-of-concept with acceptable stability, precision and internal consistency; although validation of accuracy must be pursued. With that, this instrument remains a cost-effective, small-footprint system for high-resolution measurements to constrain the carbonate chemistry. This provides a powerful tool for studying ocean acidification and variability and mechanisms of carbon cycling, particularly in highly dynamic coastal settings.

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APPENDICIES

Appendix A. Recipe for liquid carbonate standards. Crystalline bicarbonate and carbonate was dissolved into artificial seawater.

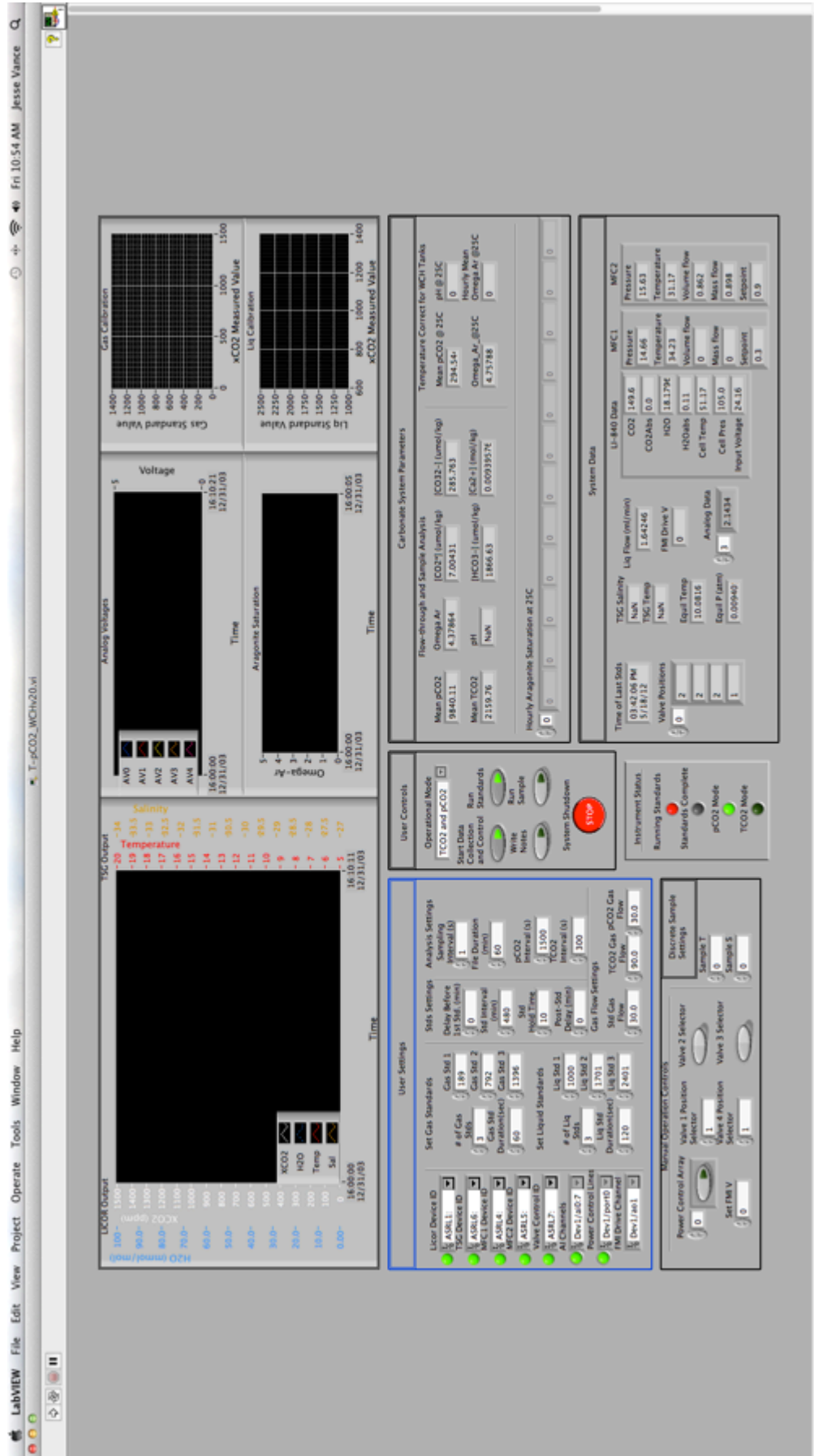
NaHCO ₃	1.0 mM	1.7 mM	2.4 mM	Na ₂ CO ₃	1.0 mM	1.7 mM	2.4 mM
Target mass (g)	0.14266	0.242521	0.342383	Target mass (g)	0.031871	0.05418	0.07649
Actual mass	0.1426	0.2426	0.3425	Actual mass	0.0319	0.0543	0.0765
Buoyancy corr. [▼]	1.00106	1.00106	1.00106	Buoyancy corr.	1.00106	1.00106	1.00106
Corr. Mass	0.142751	0.242857	0.342863	Corr. Mass	0.031934	0.054358	0.076581
Mol wt. (g/mole)	84.01	84.01	84.01	Mol wt. (g/mole)	105.99	105.99	105.99
Moles	0.001699	0.002891	0.004081	Moles	0.000301	0.000513	0.000723
Flask Vol (L)	2.00094	2.00094	2.00094	Flask Vol	2.00094	2.00094	2.00094
mM	0.849209	1.444727	2.03965		0.150575	0.256307	0.361096
Total CO₃ (mM)	1.000	1.701	2.401				

Appendix B. Comparison of real-time and post-processed calibration parameters from linear regressions of gas and liquid standards data.

Table E.1. The detector calibrations show the slopes and intercepts from linear regressions between gas standards and detector responses at various time points. The TCO₂ calibrations show the slopes and intercepts from linear regressions between liquid standards and detector response at synchronized time points. The real-time and post-processing calculations are compared for each calibration. Both the detector and TCO₂ calibrations exhibit an offset between the real-time and post-processing methods.

Detector Calibration						
DOY	Post Gas Slope	Real Time Gas Slope	% Difference	Post Gas Intercept	Real Time Gas Intercept	% Difference
140.32900	1.021	1.021	0.027	24.361	23.860	2.076
141.02000	1.016	1.017	0.121	22.754	21.859	4.009
141.70300	1.016	1.017	0.134	22.454	21.662	3.593
142.72790	1.015	1.017	0.162	22.382	21.582	3.638
143.75410	1.014	1.016	0.137	22.241	21.546	3.177
		Average	0.116		Average	3.299
TCO ₂ Calibration						
DOY	Post TCO ₂ Slope	Real Time TCO ₂ Slope	% Difference	Post TCO ₂ Intercept	Real Time TCO ₂ Intercept	% Difference
140.33260	1.885	1.872	0.681	-35.222	-104.558	99.208
141.02360	1.858	1.852	0.316	-36.664	-97.958	91.061
141.70660	1.871	1.863	0.417	-41.456	-102.578	84.871
142.73160	1.863	1.860	0.173	-36.522	-100.902	93.695
143.07340	1.868	1.859	0.474	-27.790	-83.065	99.726
143.75770	1.857	1.853	0.237	-33.196	-92.066	93.994
		Average	0.383		Average	93.759

Appendix C. Screen shot of software user interface. Graphical displays of the $x\text{CO}_2$, H_2O , temp and salinity are graphically displayed in the upper left quadrant. Analog voltage inputs and the saturation state are given in the graphically shown in the middle. The upper right quadrant displays the detector and TCO_2 calibrations. User settings are programmed in the blue box on the left. Beneath that are the manual controls used during discrete sample mode. In the center are the user controls and instrument status indicators. On the right are the measured and calculated carbonate system parameters. Beneath that are the system data.



Appendix D. Example of linear fits of alkalinity versus salinity. Data is chosen from inside 6-hour windows. The midpoint time is stepped forward in 30-min intervals.

```

6 Header lines
CO2 data from files in
/SharedResources/Data/WCH/WCH_may23/WCH_may23_CO2_CarbVars
Linear fits created with program WCH_Alk-Sfit, written by Jesse Vance
Processed by JMV
Slopes and intercepts for Alk vs Salinity linear regressions

```

Intval#	Ave_DOY	Intercept	Slope	Redchisq	No_data
1	140.472961	-3690.4334	183.865295	24.689627	6
2	140.493774	-1600.4238	117.386482	3.354579	5
3	140.514618	-1906.3516	126.993713	7.192436	5
4	140.535431	-1906.3516	126.993713	7.192436	5
5	140.556274	-4710.3999	216.429703	6.65667	5
6	140.577087	-4710.3999	216.429703	6.65667	5
7	140.597931	-6963.2002	288.360687	9.223169	6
8	140.618744	-6963.2002	288.360687	9.223169	6
9	140.639587	-8192	327.411194	9.90315	6
10	140.6604	-8192	327.411194	9.90315	6
11	140.681244	1638.40002	13.982456	12.323068	6
12	140.702057	1638.40002	13.982456	12.323068	6
13	140.7229	-1538.8497	115.475082	14.511154	6
14	140.743713	-1538.8497	115.475082	14.511154	6
15	140.764557	-694.03497	88.652382	12.968541	6
16	140.78537	-694.03497	88.652382	12.968541	6
17	140.806213	-411.51401	79.69426	13.138586	6
18	140.827026	-411.51401	79.69426	13.138586	6
19	140.84787	-631.37824	86.510063	12.955894	6
20	140.868683	-631.37824	86.510063	12.955894	6
21	140.889526	-311.51492	76.46357	11.11509	6
22	140.910339	-311.51492	76.46357	11.11509	6
23	140.931183	-1383.7838	110.11412	9.761927	6
24	140.951996	-1383.7838	110.11412	9.761927	6
25	140.972839	-1045.0411	99.268265	3.733458	6
26	140.993652	-1045.0411	99.268265	3.733458	6
27	141.014496	-529.06671	82.985878	3.46376	5
28	141.035309	-529.06671	82.985878	3.46376	5
29	141.056152	64.503937	64.227058	2.929837	4
30	141.076965	-2142.1609	134.000519	10.495995	5
31	141.097809	-2581.041	147.813568	11.684401	4
32	141.118622	-1881.946	126.113007	22.901024	5
33	141.139465	9284.26758	-225.26987	22.781355	4
34	141.160278	-1635.0967	118.451225	22.490549	5
35	141.181122	-590.58606	85.796257	22.562267	4
36	141.201935	-738.39453	90.451256	20.206272	5

Appendix E. Example of alkalinity calculated from salinity through PCO₂ interval.

7 Header lines

Times series data to be used for calculation of carbonate variables

Calculated using WCH_Calc_Alk, written by Jesse Vance

Processed by jv

Alkalinity calculated from salinity data from files in

/SharedResources/Data/WCH/WCH_may23/WCH_may23_CO2_pCO2data

DOY	Source_T	Analysis_T	Salinity	Depth	pCO2	ALK	Slope	Intercept
140.534088	12.04	12.15	31.41	0	354.8561	2082.521	126.9937	-1906.3516
140.534531	12.04	12.16	31.41	0	354.9215	2082.521	126.9937	-1906.3516
140.535126	12.04	12.16	31.41	0	355.2153	2082.521	126.9937	-1906.3516
140.535461	12.05	12.17	31.41	0	355.568	2082.7911	131.7009	-2053.9331
140.535995	12.05	12.17	31.41	0	356.2373	2083.0613	136.408	-2201.5146
140.536667	12.05	12.17	31.41	0	356.8382	2083.3321	141.1152	-2349.0959
140.537018	12.05	12.18	31.41	0	357.3703	2083.6023	145.8223	-2496.6775
140.537582	12.05	12.17	31.41	0	358.1199	2083.8724	150.5295	-2644.259
140.538025	12.05	12.15	31.41	0	358.7734	2084.1426	155.2366	-2791.8406
140.538681	12.04	12.17	31.41	0	358.7793	2084.4134	159.9438	-2939.4219
140.54245	12.06	12.18	31.4	0	358.7107	2083.0371	164.651	-3087.0034
140.542801	12.06	12.17	31.4	0	358.7568	2083.2601	169.3581	-3234.585
140.543152	12.06	12.18	31.4	0	358.1841	2083.4832	174.0653	-3382.1665
140.543564	12.06	12.19	31.4	0	357.839	2083.7067	178.7724	-3529.748
140.544144	12.06	12.19	31.4	0	357.4626	2083.9298	183.4796	-3677.3296
140.544495	12.06	12.19	31.4	0	357.4879	2084.1531	188.1868	-3824.9109
140.544952	12.07	12.19	31.4	0	357.7908	2084.3762	192.8939	-3972.4924
140.54538	12.07	12.2	31.4	0	357.6678	2084.6	197.6011	-4120.0737
140.545822	12.07	12.21	31.4	0	358.1934	2084.8231	202.3082	-4267.6553
140.552658	12.07	12.19	31.39	0	377.2584	2082.976	207.0154	-4415.2368
140.553207	12.06	12.18	31.39	0	381.0224	2083.152	211.7225	-4562.8184
140.553665	12.06	12.19	31.39	0	383.5496	2083.3285	216.4297	-4710.3999
140.559875	12.06	12.2	31.39	0	384.2091	2083.3285	216.4297	-4710.3999
140.56041	12.06	12.19	31.39	0	382.5255	2083.3285	216.4297	-4710.3999
140.560776	12.06	12.18	31.39	0	381.2933	2083.3285	216.4297	-4710.3999
140.561127	12.06	12.19	31.39	0	379.8202	2083.3285	216.4297	-4710.3999
140.561478	12.06	12.2	31.39	0	378.535	2083.3285	216.4297	-4710.3999
140.561829	12.06	12.17	31.39	0	377.9881	2083.3285	216.4297	-4710.3999
140.562485	12.06	12.18	31.39	0	375.4364	2083.3285	216.4297	-4710.3999
140.563141	12.06	12.18	31.39	0	373.6383	2083.3285	216.4297	-4710.3999
140.563568	12.06	12.17	31.39	0	372.5103	2083.3285	216.4297	-4710.3999
140.564148	12.06	12.19	31.39	0	369.8759	2083.3285	216.4297	-4710.3999
140.564743	12.06	12.2	31.39	0	367.7621	2083.3285	216.4297	-4710.3999
140.565094	12.06	12.19	31.39	0	366.8692	2083.3285	216.4297	-4710.3999
140.565414	12.06	12.2	31.39	0	365.5422	2083.3285	216.4297	-4710.3999
140.573776	12.05	12.18	31.38	0	356.4267	2081.1642	216.4297	-4710.3999
140.574326	12.05	12.16	31.38	0	356.568	2081.1642	216.4297	-4710.3999
140.574799	12.05	12.18	31.38	0	356.5106	2081.1642	216.4297	-4710.3999
140.575226	12.05	12.16	31.38	0	357.264	2081.1642	216.4297	-4710.3999
140.57579	12.06	12.19	31.38	0	357.9027	2081.1642	216.4297	-4710.3999
140.576248	12.06	12.2	31.38	0	358.8871	2081.1642	216.4297	-4710.3999
140.576828	12.06	12.19	31.38	0	360.3475	2081.1642	216.4297	-4710.3999
140.577301	12.06	12.19	31.38	0	361.3675	2081.7135	225.4211	-4992
140.577728	12.07	12.2	31.38	0	362.3698	2082.2624	234.4124	-5273.6001
140.57811	12.06	12.19	31.38	0	363.6101	2082.8118	243.4038	-5555.2002
140.578552	12.07	12.17	31.38	0	365.4792	2083.3617	252.3952	-5836.7998
140.594559	12.07	12.2	31.36	0	372.6522	2078.6828	261.3866	-6118.3999
140.595078	12.07	12.2	31.37	0	369.8344	2081.7557	270.3779	-6400
140.595673	12.08	12.23	31.36	0	367.5647	2079.4219	279.3693	-6681.6001

Appendix F. Example of carbonate parameters calculated from PCO₂ and interpolated alkalinity.

7 Header lines
Carbonate parameters calculated from pCO₂ and Alkalinity data from:
/SharedResources/Data/WCH/WCH_May23/WCH_May23_CO2_pCO2_Alk
Calculated using WCH_CO2_Calc2, written by Jesse Vance
Processed by JMV

DOY	Source_T	Analysis_T	Salinity	Depth	ALK	DIC	pCO2	CO2	HCO3	CO3	pHsws	Omega-C	Omega-A
140.334763	9.87	9.96	32	0	2193.2561	2041.1697	416.6726	18.682	1910.141	112.3467	8.018	2.75	1.739
140.335175	9.87	9.97	32	0	2193.2561	2041.6953	418.1374	18.7477	1910.9049	112.0427	8.017	2.743	1.734
140.343246	9.93	10.04	31.98	0	2189.5789	2040.6345	425.4128	19.0382	1911.1735	110.4228	8.01	2.703	1.709
140.343719	9.93	10.04	31.98	0	2189.5789	2040.7159	425.6573	19.0491	1911.2936	110.3733	8.009	2.702	1.708
140.344193	9.93	10.05	31.98	0	2189.5789	2040.6764	425.5348	19.0436	1911.2346	110.3982	8.009	2.703	1.709
140.344788	9.94	10.04	31.98	0	2189.5789	2040.7094	425.8131	19.0497	1911.2766	110.383	8.009	2.702	1.709
140.345428	9.95	10.05	31.97	0	2187.74	2039.1172	425.8899	19.0479	1909.8436	110.2256	8.009	2.699	1.706
140.346008	9.95	10.06	31.97	0	2187.74	2039.1721	426.0411	19.0547	1909.9219	110.1955	8.009	2.698	1.706
140.346603	9.96	10.07	31.97	0	2187.74	2039.1458	426.1634	19.0539	1909.8813	110.2104	8.009	2.698	1.706
140.347137	9.97	10.09	31.97	0	2187.74	2039.1521	426.3598	19.0563	1909.8845	110.2113	8.008	2.698	1.706
140.347519	9.97	10.09	31.97	0	2187.74	2039.1672	426.3923	19.0578	1909.9043	110.2052	8.008	2.698	1.706
140.34819	9.98	10.09	31.96	0	2185.9016	2037.6447	426.6749	19.0652	1908.5723	110.0072	8.008	2.694	1.703
140.348755	9.98	10.11	31.96	0	2185.9016	2037.6997	426.8205	19.0717	1908.6494	109.9786	8.008	2.693	1.703
140.349319	9.99	10.11	31.96	0	2185.9016	2037.7828	427.2453	19.0844	1908.7651	109.9333	8.007	2.692	1.702
140.349854	9.99	10.09	31.96	0	2185.9016	2037.9556	427.7532	19.107	1909.0167	109.8317	8.007	2.689	1.7
140.350525	10.01	10.14	31.96	0	2185.9016	2037.7451	427.5037	19.0833	1908.6979	109.964	8.007	2.693	1.702
140.351105	10.01	10.12	31.95	0	2184.0627	2036.3124	428.2988	19.1199	1907.5826	109.6098	8.006	2.684	1.697
140.351669	10.02	10.13	31.95	0	2184.0627	2036.2972	428.4365	19.1197	1907.556	109.6215	8.006	2.684	1.697
140.352356	10.03	10.13	31.95	0	2184.0627	2036.3739	428.8285	19.1308	1907.6584	109.5845	8.006	2.683	1.697
140.352921	10.04	10.15	31.95	0	2184.0627	2036.319	428.863	19.1261	1907.5762	109.6167	8.006	2.684	1.697
140.353577	10.04	10.13	31.95	0	2184.0627	2036.5111	429.4212	19.151	1907.854	109.5061	8.005	2.681	1.695
140.354095	10.05	10.15	31.94	0	2182.2241	2034.8993	429.4502	19.147	1906.3912	109.3611	8.005	2.678	1.693
140.354462	10.06	10.16	31.94	0	2182.2241	2034.8746	429.5583	19.1455	1906.3507	109.3785	8.005	2.678	1.694
140.355026	10.06	10.17	31.94	0	2182.2241	2034.8499	429.4792	19.142	1906.3136	109.3943	8.005	2.679	1.694
140.355576	10.07	10.19	31.94	0	2182.2241	2034.8076	429.5374	19.1382	1906.2458	109.4236	8.005	2.68	1.694
140.356262	10.08	10.18	31.93	0	2180.3855	2033.427	430.2425	19.1644	1905.1189	109.1437	8.004	2.673	1.69
140.364578	10.21	10.32	31.9	0	2174.8696	2028.7446	433.0268	19.2091	1900.9758	108.5597	8.001	2.659	1.682
140.36525	10.23	10.33	31.9	0	2174.8696	2028.6455	433.1097	19.2001	1900.8225	108.6229	8.001	2.661	1.683
140.365707	10.24	10.34	31.89	0	2173.031	2026.9307	432.8248	19.1823	1899.2107	108.5377	8	2.659	1.681
140.36618	10.25	10.36	31.89	0	2173.031	2026.7578	432.5104	19.1619	1898.9565	108.6393	8.001	2.661	1.683
140.366547	10.25	10.35	31.89	0	2173.031	2026.8121	432.6678	19.1689	1899.0344	108.6087	8.001	2.661	1.683
140.367203	10.27	10.37	31.89	0	2173.031	2026.7152	432.7492	19.16	1898.8831	108.6721	8.001	2.662	1.684
140.367783	10.29	10.42	31.88	0	2171.1924	2024.8158	432.099	19.1192	1896.9955	108.701	8.001	2.663	1.684
140.368134	10.3	10.43	31.88	0	2171.1924	2024.7395	432.0487	19.1111	1896.8799	108.7486	8.001	2.664	1.685
140.368805	10.31	10.4	31.88	0	2171.1924	2024.9062	432.718	19.1345	1897.1152	108.6566	8	2.662	1.684
140.369247	10.32	10.43	31.88	0	2171.1924	2024.6809	432.2425	19.1072	1896.7838	108.7899	8.001	2.665	1.686
140.36972	10.33	10.45	31.87	0	2169.3535	2022.8737	432.1435	19.0975	1895.1221	108.654	8.001	2.662	1.684
140.370316	10.34	10.45	31.87	0	2169.3535	2022.7671	432.0037	19.085	1894.9613	108.7207	8.001	2.664	1.685
140.370911	10.36	10.47	31.87	0	2169.3535	2022.6688	432.0791	19.0758	1894.8071	108.7859	8.001	2.665	1.686
140.371338	10.37	10.47	31.87	0	2169.3535	2022.6621	432.2529	19.0773	1894.7949	108.7899	8	2.665	1.686
140.371811	10.38	10.49	31.86	0	2167.5149	2020.92	431.8949	19.0563	1893.1449	108.7188	8.001	2.664	1.685
140.372269	10.39	10.5	31.86	0	2167.5149	2020.7655	431.6399	19.0387	1892.9192	108.8076	8.001	2.666	1.686
140.37291	10.41	10.51	31.86	0	2167.5149	2020.6604	431.6963	19.0287	1892.7549	108.8768	8.001	2.668	1.687
140.373489	10.43	10.53	31.86	0	2167.5149	2020.4475	431.4288	19.0044	1892.4347	109.0084	8.001	2.671	1.69
140.373784	10.44	10.52	31.85	0	2165.6763	2018.9285	431.7103	19.0117	1891.1031	108.8136	8	2.666	1.687
140.374313	10.44	10.55	31.85	0	2165.6763	2018.7297	431.1206	18.9857	1890.8148	108.9292	8.001	2.669	1.689
140.374741	10.45	10.55	31.85	0	2165.6763	2018.6617	431.1036	18.9787	1890.7118	108.9713	8.001	2.67	1.689
140.375107	10.46	10.59	31.85	0	2165.6763	2018.3684	430.4322	18.9429	1890.2819	109.1436	8.002	2.674	1.692
140.375687	10.47	10.57	31.85	0	2165.6763	2018.4139	430.7489	18.9506	1890.3433	109.1201	8.001	2.674	1.692
140.376282	10.48	10.58	31.84	0	2163.8376	2016.6058	430.6305	18.9402	1888.6781	108.9876	8.001	2.671	1.69
140.376648	10.49	10.6	31.84	0	2163.8376	2016.4794	430.4563	18.9264	1888.4933	109.0597	8.001	2.673	1.691
140.376984	10.49	10.62	31.84	0	2163.8376	2016.2822	429.8804	18.901	1888.2084	109.1729	8.002	2.675	1.692
140.377533	10.51	10.63	31.84	0	2163.8376	2016.0856	429.661	18.879	1887.911	109.2955	8.002	2.678	1.694
140.385452	10.54	10.68	31.84	0	2163.8376	2016.0952	430.24	18.8859	1887.9077	109.3016	8.002	2.679	1.695
140.386093	10.54	10.65	31.84	0	2163.8376	2016.2789	430.778	18.9095	1888.1737	109.1958	8.001	2.676	1.693
140.386551	10.54	10.65	31.84	0	2163.8376	2016.2014	430.549	18.8994	1888.0612	109.2409	8.001	2.677	1.694
140.387146	10.54	10.66	31.84	0	2163.8376	2016	429.9611	18.8736	1887.7698	109.3565	8.002	2.68	1.695
140.387512	10.54	10.66	31.84	0	2163.8376	2015.9607	429.8551	18.869	1887.7146	109.3771	8.002	2.68	1.696
140.388062	10.55	10.64	31.84	0	2163.8376	2015.9747	430.0719	18.8723	1887.7284	109.374	8.002	2.68	1.696
140.388641	10.55	10.65	31.84	0	2163.8376	2015.7681	429.4677	18.8458	1887.4291	109.4932	8.002	2.683	1.698
140.389099	10.55	10.67	31.84	0	2163.8376	2015.6195	429.405	18.8273	1887.2159	109.5763	8.003	2.685	1.699
140.389511	10.55	10.67	31.84	0	2163.8376	2015.4821	428.6369	18.8094	1887.0154	109.6573	8.003	2.687	1.7
140.390015	10.56	10.66	31.84	0	2163.8376	2015.3715	428.4959	18.797	1886.8488	109.7257	8.003	2.689	1.701
140.390686	10.57	10.68	31.85	0	2165.6763	2016.8408	427.9933	18.7677	1888.0098	110.0633	8.004	2.697	1.706
140.391266	10.58	10.7	31.85	0	2165.6763	2016.4137	426.9341	18.7151	1887.3845	110.314	8.005	2.703	1.71
140.391647	10.58	10.69	31.84	0	2163.8376	2014.4969	426.3227	18.6894	1885.5702	110.2373	8.005	2.702	1.709
140.392273	10.6	10.71	31.84	0	2163.8376	2014.0798	425.4807	18.6403	1884.953	110.4866	8.006	2.708	1.713
140.392746	10.61	10.73	31.84	0	2163.8376	2013.7177	424.6366	18.5972	1884.4254	110.6951	8.007	2.713	1.716
140.393158	10.62	10.72	31.84	0	2163.8376	2013.5427	424.3138	18.577	1884.166	110.7998	8.007	2.715	1.718
140.393723	10.63	10.75	31.84	0	2163.8376	2013.0094	422.961	18.5116	1883.3843	111.1136	8.008	2.723	1.723
140.39415	10.64	10.76	31.84	0	2163.8376	2012.7712	422.4652	18.4839	1883.0328	111.2545	8.009	2.726	1.725
140.394714	10.66	10.77	31.84	0	2163.8376	2012.4937	422.0389	18.4532	1882.6189	111.4217	8.009	2.73	1.728

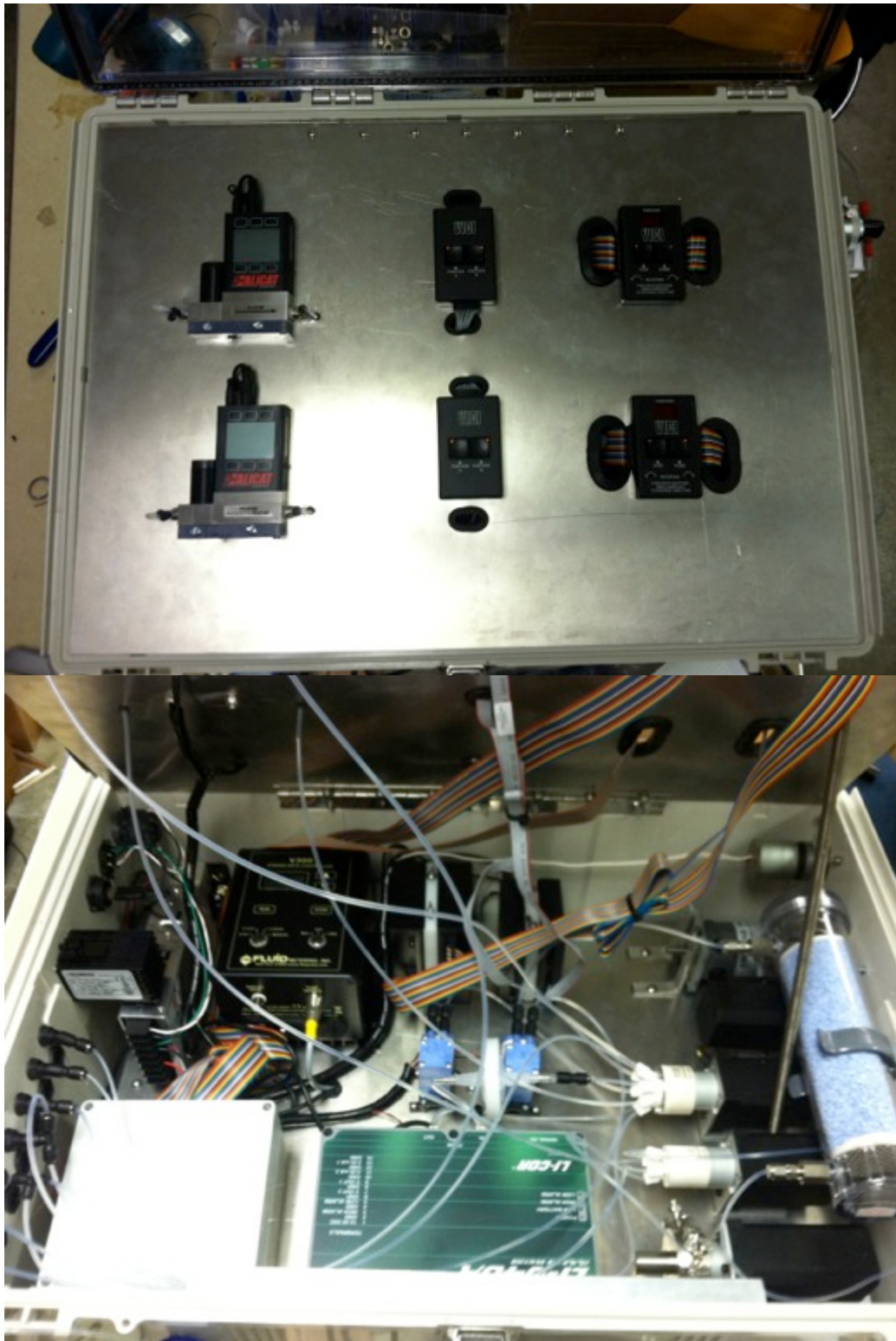
Appendix G. Comparison of carbonate parameters calculated from PCO₂ and TCO₂ measurements (observed) to those calculated from the interpolated alkalinity and PCO₂ (modeled). Seawater from Netarts Bay, OR was analyzed from 5/19/12 – 05/23/12.

Table AA.1. Day of year of measurements and calculated alkalinity, DIC, [CO₂], [HCO₃⁻], [CO₃²⁻], pH, Ω_{Ca}, Ω_{Ar}. Observed parameters are calculated from measurements, Modeled parameters are calculated from the interpolated alkalinity and measured pCO₂

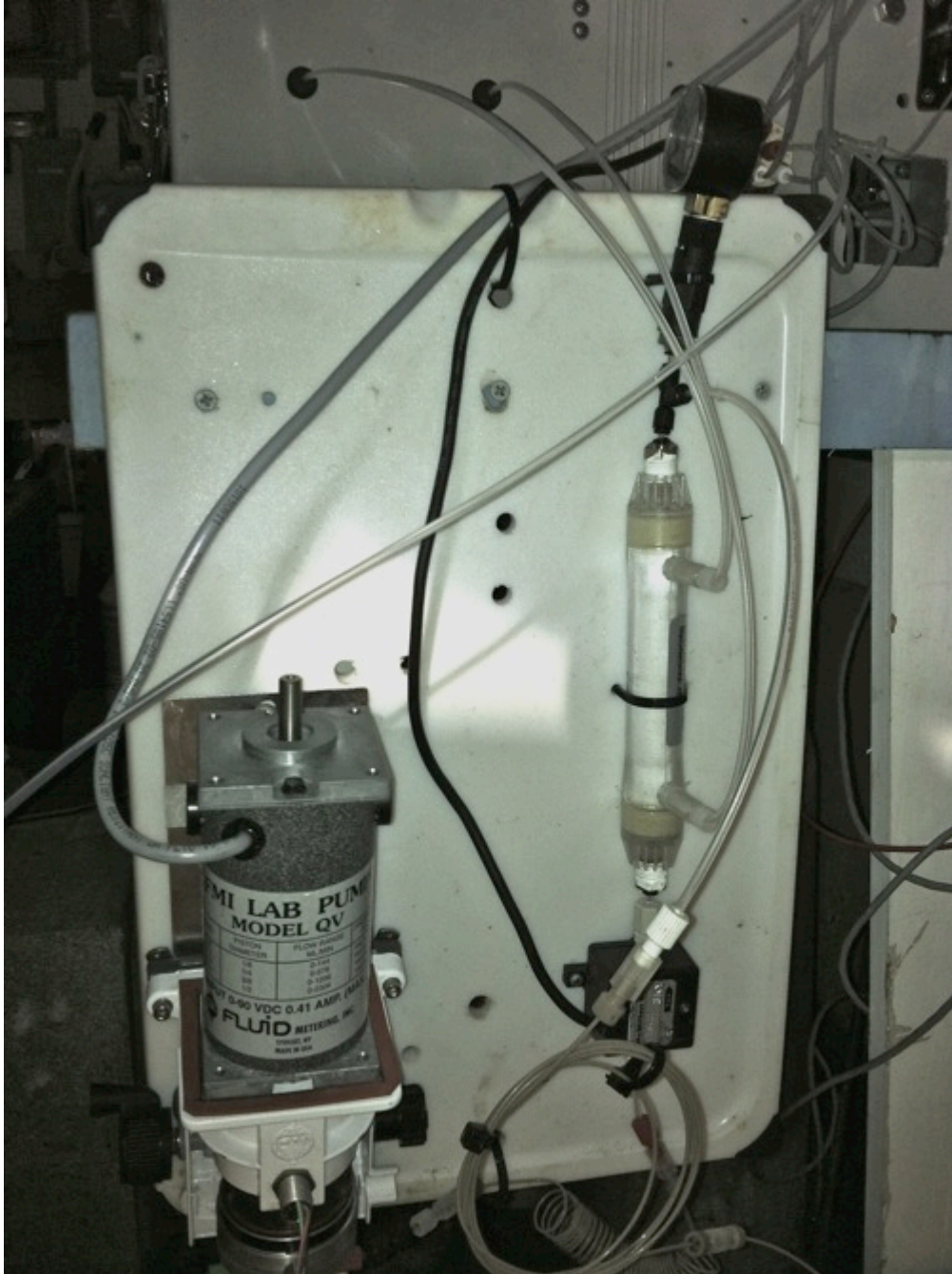
DOY	ALK Observed	ALK Modeled	DIC Observed	DIC Modeled	CO2 Observed	CO2 Modeled	HCO3 Observed	HCO3 Modeled
140.400452	2132.54	2160.1602	1966.1469	2001.1875	16.3705	17.5608	1830.2521	1867.73
140.485718	2084.1919	2075.2095	1886.3174	1877.8694	12.8806	12.8101	1735.7633	1727.9094
140.526245	2086.8115	2082.521	1907.0341	1902.0449	14.4592	14.3417	1765.7344	1760.5956
140.569595	2077.8145	2082.2466	1908.1428	1910.2267	15.3045	15.126	1772.1954	1772.9788
140.612091	2059.9482	2074.0239	1893.9883	1905.7926	15.4415	15.4016	1760.542	1770.7112
140.650818	2075.8442	2075.6152	1890.5305	1894.7195	13.813	14.2789	1746.7781	1753.082
140.698181	2099.6125	2078.4346	1856.7944	1840.3448	10.0636	10.1444	1680.8973	1668.0557
140.738663	2066.4324	2083.6685	1797.8823	1808.9795	8.4755	8.3413	1608.5513	1615.3379
140.781494	2078.8337	2076.0957	1781.0099	1776.4631	7.341	7.2561	1573.3167	1568.1387
140.823364	2143.0061	2117.4287	1904.365	1880.3105	10.7122	10.57	1729.9821	1707.5613
140.869537	2138.3564	2140.3652	1922.9868	1924.9531	12.1992	12.2133	1761.9656	1763.8517
140.907349	2119.0898	2128.3779	1883.5411	1892.6096	10.7159	10.7903	1711.7058	1720.3873
140.948502	2089.9468	2094.6528	1812.9967	1816.7283	8.3594	8.3505	1617.8221	1620.8468
140.994827	2099.0085	2093.3354	1792.3577	1787.4225	7.2351	7.2245	1579.2112	1575.0242
141.039185	2106.8752	2104.8545	1776.2739	1774.4908	6.4587	6.454	1548.6525	1547.177
141.085602	2102.9661	2115.022	1749.2036	1760.2872	5.753	5.7917	1508.0164	1517.62
141.169128	2137.3872	2132.7915	1768.0358	1764.3757	5.539	5.5338	1515.4149	1512.4235
141.204712	2161.1948	2128.2603	1879.4587	1850.9763	8.7959	8.857	1678.2339	1653.5173
141.247742	2164.406	2158.1426	1968.9257	1961.7299	14.0163	13.9	1817.4207	1809.6788
141.294708	2157.3806	2158.0986	1972.3978	1972.4873	14.7726	14.7243	1826.6162	1826.3657
141.336761	2155.7432	2158.1978	1975.0284	1976.5933	15.1497	15.0845	1831.5188	1832.5406
141.383072	2159.728	2156.6479	1988.8674	1985.7795	16.2325	16.1805	1849.9202	1846.9893
141.420227	2140.1436	2146.3938	1962.9227	1973.4188	15.4445	15.9489	1821.0276	1833.5254
141.468657	2108.4321	2112.1716	1907.0311	1909.4734	12.9958	12.9326	1753.317	1754.9099
141.510635	2104.0583	2101.0981	1912.8212	1909.5029	13.742	13.678	1764.4646	1761.1412
141.550476	2116.9731	2107.4641	1938.7151	1929.3418	15.0856	14.9808	1796.6422	1787.6886
141.592773	2093.9939	2106.2026	1929.9108	1939.4801	16.2202	16.1006	1795.5848	1803.3547
141.63623	2102.6213	2101.0532	1942.2446	1939.4094	16.7369	16.5634	1809.355	1805.9897
141.673401	2112.6624	2089.0649	1946.873	1934.3365	16.2173	17.1911	1810.9281	1804.5845
141.719727	2072.9851	2084.0806	1900.1743	1894.9684	14.9823	13.6409	1762.5701	1748.6013
141.768463	2078.8621	2088.1182	1883.6763	1892.4324	13.0944	13.1598	1734.3361	1742.4294
141.807953	2058.4583	2075.1826	1843.5656	1865.8169	11.4083	11.9791	1684.3893	1708.9692
141.894043	2101.4236	2107.0312	1857.3469	1861.8289	9.8703	9.8573	1681.5079	1685.1282
141.935822	2107.2908	2104.8589	1853.4865	1851.5905	9.4509	9.4478	1671.7157	1670.2177
141.977554	2094.3848	2095.8945	1847.5278	1848.5159	9.7698	9.7495	1669.6198	1670.3044
142.065125	2094.5063	2096.6855	1844.2601	1844.5941	9.5842	9.5072	1664.2767	1663.5421
142.110382	2104.8252	2111.8755	1857.0076	1861.2733	9.8076	9.7192	1678.1029	1680.4409
142.146057	2128.8997	2114.5752	1897.9266	1885.9265	11.0233	11.0425	1727.5514	1717.376
142.186768	2119.8826	2107.1807	1911.6835	1902.5875	12.4993	12.624	1754.0497	1747.3989
142.23056	2074.4353	2100.1772	1839.6108	1857.7366	10.1282	10.0026	1669.0961	1681.925
142.277817	2001.4325	2000.0195	1772.9155	1771.1768	9.3278	9.3048	1607.2184	1605.4609
142.319702	2007.517	2007.4041	1783.5981	1783.032	9.6557	9.629	1602.5419	1619.7791
142.361664	2000.2371	2000.906	1786.2456	1785.6511	10.1499	10.077	1628.9729	1627.6599
142.410278	2012.4928	2008.3239	1806.2358	1802.2296	10.8403	10.7986	1652.8531	1649.0952
142.451553	2014.1716	2014.5139	1820.4996	1819.4612	11.8481	11.7325	1673.8344	1672.0317
142.488861	2025.1788	2031.3392	1842.995	1845.4095	13.0062	12.8159	1701.9238	1702.2266
142.535889	2017.4197	2020.1326	1836.1125	1837.9812	12.9048	12.8539	1695.7972	1697.0454
142.577789	2022.7307	2021.8115	1849.8209	1848.4387	13.725	13.6606	1713.5653	1711.9779
142.613953	2040.8489	2026.6106	1893.8513	1880.3517	16.7023	16.6222	1769.4741	1756.8198
142.661911	2042.8165	2047.5144	1899.4155	1903.1226	17.4483	17.3739	1776.2804	1779.3684
142.70343	2047.2172	2037.3385	1906.1646	1895.9846	17.7387	17.5723	1783.8831	1773.9606
142.744705	2012.6619	2021.0759	1873.6355	1877.4321	17.223	16.8891	1753.8317	1755.1165
142.78627	2015.2797	2024.4373	1844.2069	1848.097	14.0242	13.5884	1708.9652	1709.7258
142.830139	1921.8224	1949.1925	1737.6614	1761.0115	11.0356	11.2358	1598.1233	1618.3473
142.873367	1886.8981	1889.5792	1664.0406	1665.5413	8.05	8.0196	1502.9136	1503.6987
142.919342	1887.1561	1883.074	1657.9121	1653.9211	7.7121	7.6886	1492.8141	1489.1658
142.961334	1885.7839	1878.3716	1658.1898	1651.3682	7.7892	7.7572	1494.1283	1488.0288
143.00322	1879.9448	1880.0281	1660.9379	1660.5717	8.2008	8.1729	1502.2739	1501.6536
143.042999	1860.4453	1877.0951	1664.7906	1678.2363	9.4066	9.3668	1519.9863	1531.0505
143.093445	1858.7714	1867.667	1673.467	1680.2207	10.2126	10.1444	1534.8833	1540.0193
143.135651	1869.2905	1865.381	1692.5477	1688.6908	10.9883	10.9484	1558.2474	1554.5865
143.177521	1868.8831	1866.8518	1699.4199	1696.6377	11.5249	11.448	1568.9097	1565.8749
143.219574	1865.7524	1865.8333	1693.4969	1693.9185	11.1714	11.221	1561.7645	1562.2517
143.260376	1862.6251	1866.4572	1668.7661	1671.217	9.4989	9.4683	1525.0967	1526.7366
143.301682	1867.9717	1867.9324	1671.849	1671.0295	9.3904	9.3414	1527.0558	1525.817
143.341492	1871.849	1869.0221	1672.3312	1669.239	9.2226	9.1783	1525.5199	1522.3887
143.384644	1873.092	1872.4878	1677.1604	1676.2305	9.4668	9.4229	1532.4355	1531.1899
143.432281	1870.8867	1866.2565	1692.136	1687.6077	10.5945	10.5483	1556.8064	1552.5088
143.472397	1843.6735	1834.9728	1696.9541	1686.0466	12.9533	12.6882	1579.095	1567.4408
143.512115	1837.1545	1838.8158	1699.9178	1707.5376	13.9108	14.5975	1586.9675	1597.3301
143.555237	1828.0577	1839.3971	1702.9204	1712.324	15.1432	15.0804	1595.9644	1604.0793
143.598816	1835.8923	1838.9188	1722.2941	1723.9233	16.8953	16.7003	1620.0883	1620.9524
143.641418	1837.4846	1843.1135	1742.1707	1745.7341	19.7064	19.5126	1647.1871	1649.6677
143.680908	1846.4719	1836.5537	1759.1976	1751.8105	21.3839	21.6959	1666.5664	1660.5082
143.727295	1851.6222	1848.7202	1757.3394	1753.2158	20.2382	20.0005	1662.0239	1657.5637
143.816376	1879.4524	1883.6897	1732.4648	1736.5146	13.6447	13.6562	1613.4695	1617.2871
143.854904	1868.1586	1877.4324	1708.8774	1712.4861	12.1997	11.9361	1584.3093	1584.405
143.899841	1899.7498	1888.0598	1693.8635	1683.7778	9.1925	9.1729	1542.7924	1534.1501
143.946014	1909.6222	1896.0354	1691.7225	1679.8987	8.6364	8.6083	1533.4797	1523.2399
143.98793	1900.958	1897.3951	1686.9653	1683.5935	8.7601	8.7348	1531.2252	1528.0869
144.024963	1855.1683	1861.135	1671.1608	1675.1404	10.0483	10.0019	1533.3849	1536.0637
144.065796	1773.2922	1786.3289	1637.2328	1647.76	12.929	12.8952	1526.6984	1535.5225

CO3 Observed	CO3 Modeled	pHsws Observed	pHsws Modeled	Q _{CO2} Observed	Q _{CO2} Modeled	Q _{CH4} Observed	Q _{CH4} Modeled
119.5243	115.8968	8.043	8.024	2.93	2.84	1.856	1.799
137.6734	137.1497	8.115	8.116	3.386	3.373	2.146	2.138
126.8404	127.1075	8.073	8.076	3.118	3.125	1.976	1.98
120.6429	122.1219	8.051	8.056	2.966	3.003	1.88	1.902
118.0048	119.68	8.044	8.047	2.902	2.944	1.839	1.865
129.9394	127.3586	8.088	8.074	3.196	3.132	2.025	1.986
165.8335	162.1449	8.206	8.2	4.078	3.988	2.586	2.528
180.8556	185.3004	8.259	8.269	4.449	4.557	2.822	2.891
200.3523	201.0684	8.309	8.313	4.935	4.95	3.131	3.141
163.6708	162.1792	8.201	8.2	4.012	3.979	2.542	2.52
148.8221	148.8881	8.155	8.156	3.644	3.645	2.308	2.309
161.1194	161.4321	8.192	8.193	3.95	3.956	2.504	2.508
186.8152	187.5309	8.264	8.267	4.591	4.608	2.915	2.925
205.9114	205.1737	8.315	8.314	5.058	5.041	3.213	3.201
221.1628	220.8599	8.359	8.359	5.428	5.42	3.447	3.442
235.4343	236.8755	8.398	8.398	5.776	5.812	3.668	3.691
247.0819	246.4187	8.417	8.416	6.062	6.046	3.849	3.84
192.429	188.6019	8.254	8.248	4.725	4.633	3.004	2.945
137.4888	138.151	8.111	8.111	3.366	3.383	2.132	2.143
131.009	131.3975	8.094	8.095	3.208	3.217	2.03	2.036
128.36	128.968	8.085	8.087	3.143	3.158	1.989	1.998
122.7148	122.6099	8.056	8.057	3.005	3.003	1.903	1.901
126.4505	123.9444	8.06	8.052	3.101	3.038	1.966	1.926
140.7182	141.6307	8.108	8.111	3.46	3.483	2.196	2.211
134.6146	134.6838	8.087	8.089	3.312	3.313	2.102	2.103
126.9874	126.6723	8.056	8.056	3.123	3.115	1.981	1.977
118.1057	120.0247	8.023	8.028	2.905	2.952	1.843	1.873
116.1527	116.8564	8.013	8.017	2.858	2.875	1.813	1.824
119.7277	112.561	8.028	8	2.947	2.771	1.869	1.758
122.622	132.7262	8.052	8.089	3.019	3.267	1.914	2.072
136.2459	136.843	8.102	8.102	3.354	3.368	2.127	2.137
147.7679	144.8684	8.146	8.134	3.642	3.568	2.311	2.263
165.9687	166.8434	8.231	8.233	4.075	4.097	2.577	2.591
172.3198	171.925	8.242	8.243	4.232	4.222	2.679	2.673
168.1383	168.4619	8.217	8.219	4.136	4.144	2.622	2.627
170.3992	171.5448	8.224	8.227	4.193	4.22	2.658	2.675
169.097	171.1132	8.219	8.223	4.158	4.208	2.636	2.668
159.3519	157.5081	8.181	8.178	3.918	3.873	2.484	2.456
145.1344	142.5647	8.131	8.125	3.571	3.507	2.264	2.223
160.3865	165.8089	8.207	8.212	3.953	4.084	2.502	2.587
156.3694	156.4108	8.238	8.239	3.896	3.898	2.449	2.45
153.4006	153.6241	8.229	8.229	3.819	3.825	2.401	2.404
147.1228	147.9142	8.21	8.212	3.666	3.686	2.303	2.316
142.5423	142.3358	8.185	8.186	3.548	3.543	2.231	2.228
134.8171	135.6969	8.147	8.151	3.353	3.376	2.112	2.125
128.0649	130.3671	8.109	8.114	3.181	3.236	2.006	2.042
127.4106	128.0818	8.113	8.115	3.169	3.186	1.997	2.007
122.5307	122.8002	8.09	8.092	3.047	3.054	1.92	1.924
107.6749	106.9095	8.017	8.018	2.677	2.658	1.688	1.676
105.6868	106.3803	7.989	7.993	2.623	2.641	1.659	1.669
104.5427	104.4518	7.986	7.987	2.596	2.594	1.641	1.64
102.5809	105.4264	7.999	8.007	2.554	2.623	1.61	1.655
121.2175	124.7828	8.07	8.088	3.01	3.102	1.902	1.958
128.5024	131.4284	8.164	8.16	3.237	3.302	2.024	2.069
153.077	153.8228	8.282	8.283	3.88	3.898	2.414	2.425
157.3858	157.0667	8.298	8.298	3.991	3.984	2.482	2.477
156.2724	155.5822	8.293	8.293	3.963	3.946	2.465	2.454
150.4631	150.7451	8.272	8.273	3.815	3.822	2.374	2.378
135.3979	137.8189	8.211	8.217	3.435	3.497	2.14	2.178
128.3712	130.0571	8.175	8.179	3.251	3.293	2.03	2.056
123.3121	123.1559	8.148	8.149	3.12	3.116	1.949	1.947
118.9854	119.3148	8.132	8.134	3.01	3.018	1.881	1.885
120.561	120.4458	8.149	8.148	3.052	3.049	1.903	1.902
134.1705	135.0123	8.213	8.215	3.402	3.423	2.118	2.131
135.4029	135.8712	8.222	8.224	3.429	3.441	2.134	2.141
137.5888	137.6722	8.23	8.232	3.483	3.485	2.168	2.169
135.2581	135.6175	8.221	8.222	3.424	3.433	2.131	2.136
124.7351	124.5506	8.179	8.18	3.159	3.154	1.965	1.962
104.9059	105.9175	8.096	8.104	2.662	2.687	1.655	1.671
99.0396	95.6101	8.066	8.048	2.511	2.424	1.563	1.509
91.8129	93.1642	8.032	8.036	2.328	2.363	1.448	1.47
85.3106	86.2707	7.988	7.994	2.163	2.188	1.347	1.362
75.2772	76.5539	7.93	7.933	1.909	1.941	1.188	1.208
71.2473	69.6064	7.898	7.891	1.807	1.766	1.125	1.099
75.0773	75.6517	7.919	7.922	1.903	1.918	1.186	1.195
105.3506	105.5712	8.078	8.08	2.66	2.666	1.66	1.663
112.3684	116.145	8.126	8.136	2.839	2.935	1.768	1.829
141.8787	140.4547	8.235	8.234	3.582	3.546	2.233	2.211
149.6063	148.0504	8.258	8.257	3.775	3.737	2.355	2.331
146.9799	146.7718	8.251	8.252	3.711	3.706	2.314	2.311
127.7276	129.0746	8.193	8.196	3.239	3.27	2.015	2.036
97.6054	99.3423	8.082	8.086	2.493	2.534	1.545	1.571

Appendix H. Image of instrument construction and layout.



Appendix I. Image of wetted components of TCO₂ system. FMI QV pump, mixing coil, flow meter, membrane contactor and pressure gauge are mounted on PVC plastic for stability and orientation.



Appendix J. Image of shower-type equilibrator of PC₂ measurements.



Appendix K. Image of filter and transverse flow orientation used to sample intake water for TCO₂ analysis.

