

Response to Anonymous Referee #1 on “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends” by A.J. Sutton et al.

We thank all referees for their thoughtful and constructive comments and suggestions on our manuscript “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends.” The revised manuscript will be much improved as a result of the careful critiques. Below we discuss the comments from Referee #1 point by point including original referee comments and our responses bulleted (--) underneath.

Sutton et al. release a comprehensive data product for $p\text{CO}_2$ and pH (among other variables) from 40 surface ocean buoys around the globe. Further, this paper briefly analyzes the time series data to compute Time of Emergence (ToE) of the anthropogenic emissions signal. They propose conservative estimates of ToE, since their relatively short time series do not capture the influence of decadal variability. The data product is extremely accessible and the website is well put together. One can acquire plots of near real-time pH and $p\text{CO}_2$ via the web server as well as select a buoy of interest from a map to retrieve well-labeled and quality-controlled data. I suggest that this manuscript be published in ESSD following minor revisions. I only have a few very minor comments/clarifications.

2 Major Comments

1. I appreciate the attention to detail on limitations to ToE with such short time series (i.e., taking an estimate of decadal variability on the TAO buoys and applying that to all other stations). However, I'd be curious to see what the influence of the differing IAV estimates does to the ToE estimate. I.e., what is the difference in the ToE when using the detrended vs. not detrended estimate of anomalies in Equation 1? I imagine that the 12% change in IAV from this tactic might propagate a decent bit of uncertainty into ToE (that is separate from the decadal variability uncertainty).

-- We find that ToE estimates are on average 55% shorter using detrended monthly anomalies compared to ToE estimated using not detrended monthly anomalies (page 9 line 21). This is different from the detrending applied to the WHOTS example for IAV. IAV is typically calculated on data with the long-term trend removed; however, we did not do this, as the long-term trend is unknown at most sites and the time series are relatively short (<12 years). The 12% change was presented here to highlight the uncertainty in the IAV estimates, which are separate from the ToE calculation.

3 Minor Comments

2. Lines 31–33 (pg. 3): “. . . magnification of the seasonal amplitude of $p\text{CO}_2$ due to warming, . . . resulting in increased detection time.” You could cite Kwiatkowski and Orr (2018) and Landschützer et al. (2018) here, which cover this topic.

-- Good suggestion. Those references have been added.

3. Lines 1–3 (pg. 6): Perhaps expand here on what future efforts will be done to improve IAV estimates. What can be done other than waiting for longer time series to develop?

-- Good point. We have added the following to that section: "Future efforts to improve these IAV estimates can rely on future assessment of longer time series (moored or observations from other platforms) and regional models that better characterize all modes of temporal variability."

4. Lines 10–11 (pg. 9): "Since ToE is dependent on the variability . . . tend to have longer ToE estimates." I would suggest more clear wording for this sentence. In the case of this application, ToE is mainly variability-induced, since all stations share a commonly imposed trend of $2 \mu\text{atm yr}^{-1}$. However, in many cases, long ToE estimates can be also driven by a weak signal, and short ToE estimates by a very strong signal, etc.

-- We agree it was confusing to mention the imposed long term trend here and have modified the sentence to focus on the correlation between variability and ToE: "In this application ToE is dependent on the variability in the data, resulting in the pattern where sites that exhibit larger seasonal to interannual variability (Figs. 1 and 2) tend to have longer ToE estimates (Fig. 5)." We also suspect that our use of the term "emergence" may add confusion. Multi-ensemble modeling assessments of emergence of a forced trend over model variability typically also use the emergence terminology. This manuscript addresses a slightly different approach in assessing the time period of observations required to detect a long-term trend above natural variability. As such, throughout the manuscript we have added more description of this observation-based trend detection time approach of the method.

5. Figures 1 and 2: When using a discrete color bar, it is generally advised that the tick marks align with discrete color boundaries. In their current format, both color bars have tick marks placed arbitrarily within color bounds, which makes these color divisions useless. E.g., in Figure 1, setting 10 color boundaries with colorbrewer would align the ticks/color boundaries in $25 \mu\text{atm}$ increments.

-- Thank you for catching that. Color bar modified to align ticks/color boundaries.

6. Figure 3: I suggest changing the color scheme for (b) and (c) to be mindful of those that are red-green color blind.

-- Again, thank for you catching that. Color scheme modified.

Response to Anonymous Referee #2 on “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends” by A.J. Sutton et al.

We thank all referees for their thoughtful and constructive comments and suggestions on our manuscript “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends.” The revised manuscript will be much improved as a result of the careful critiques. Below we discuss the comments from Referee #2 point by point including original referee comments and our responses bulleted (--) underneath.

Major comment Dr. Sutton and colleagues presented a readily accessible data product of autonomous $p\text{CO}_2$ and pH time series from 40 surface buoys from 2004 in open ocean, coastal and coral reef sites, that exhibit extensive daily and interannual variability. Using a time of trend emergence methodology, they estimated the length of time for an anthropogenic trends in oceanic $p\text{CO}_2$ and pH to emerge from natural variability in the 40 time series. Only at two time series datasets (WHOTS and Stratus), surface oceanic $p\text{CO}_2$ significantly increased. However, pH time series data are too short to estimate long-term anthropogenic trends. In addition, description of pH sensor isn't detailed, compared from $p\text{CO}_2$ sensor [Sutton et al., 2014b]. I cannot confirm postcalibrated and quality-controlled pH data (at NCEI data archive) through comparison with in-situ calibration, discrete samples and so on, because pH sensor performance was often limited by biofouling [Bresnahan Jr et al., 2014]. After revising the manuscript to address this comment and the specific comments below, I would support publication of the author's submission.

-- We agree that thorough sensor evaluation and data quality control is critical to confirming pH data quality. Entire publications are dedicated to this topic, like Bresnahan et al. 2014 cited by the reviewer. Similar to the $p\text{CO}_2$ sensor evaluation of Sutton et al. 2014b, the 2016 paper describes in detail the moored pH sensor evaluation and data quality control, which are primarily through comparison to discrete data and independently calculated pH. That analysis determined these sensors (once calibrated and adjusted in the case of the SeaFET) have a total uncertainty of <0.02 in this particular surface buoy application. We agree with the reviewer that this point needed clarification, and we've added the following statement to that section: “Data quality control of these pH time series, including calibration, comparison with discrete samples, and assessment of drift due to sensor performance and biofouling, are described in detail by Sutton et al. (2016).”

Figure 1 I think that only locations and names of 40 fixed moored time series station map is convenient for readers.

-- Very good point that we failed to link Figure 1 with the detailed site information in Table 1. We've added the following to the Figure 1 caption: “Moored time series locations and names are detailed in Table 1.” Also of note, while Figure 1 focuses on illustrating surface seawater $p\text{CO}_2$ mean, seasonal amplitude, and IAV, the data product at NCEI (<https://www.nodc.noaa.gov/ocads/oceans/Moorings/ndp097.html>) includes a figure solely focused on buoy location and names for data users ease.

Line 22, Page 7 How long is it necessary for pH time series to determine a robust estimate of IAV?

-- In this manuscript, we are using the $p\text{CO}_2$ estimate of 3 years of continuous measurements (page 19 line 4; page 21 line 7) as the cutoff for presenting IAV, and as of the assessment described in this manuscript, no pH time series meet that length. Included in the IAV methodology section (page 5 line 34 – page 6 line 4) is a discussion of the uncertainty in these IAV estimates.

Response to Anonymous Referee #3 on “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends” by A.J. Sutton et al.

We thank all referees for their thoughtful and constructive comments and suggestions on our manuscript “Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends.” The revised manuscript will be much improved as a result of the careful critiques. Below we discuss the comments from Referee #3 point by point including original referee comments and our responses bulleted (--) underneath.

In this manuscript, the authors present a data package that incorporates measurements from 40 buoys with $p\text{CO}_2$ and, in some cases, also pH sensors. The authors make a good case for why this dataset is of additional value compared to getting data independently from each buoy at NCEI. The authors also provide time of trend emergence estimates where the record is long enough and compare results for open ocean, coastal, and coral reef sites. This makes the paper interesting not just for potential users of the data, but also for researchers that might want to compare their own data trends to data from these buoys.

I appreciated the specific section on data availability and how to use and properly acknowledge the dataset, which apparently is still too complicated for some data users. This manuscript and product are timely and will be very useful for a variety of researchers, so I recommend publication after addressing the following minor issues:

Page 4 lines 10-15: what type of equilibrators is used? Is it a membrane?

-- This is a bubble-type equilibrator. The MAPCO₂ methodology is described in detail in Sutton et al. 2014b. We have added these details to the following sentence in the referenced section: “Seawater $x\text{CO}_2$ equilibration occurs by cycling a closed loop of air through an floating bubble equilibrator at the sea surface for 10 minutes, which is described in detail by Sutton et al. (2014b).”

Page 4, line 20-26: At what temperature is $p\text{H}_T$ reported? Is there enough data at this point to evaluate the most adequate of the two sensors for long term monitoring?

-- We have added to line 24 that $p\text{H}_T$ is reported at in situ SST. Evaluating the two sensors requires both an analysis of existing data as presented here and targeted side-by-side test deployments of both sensors at select mooring time series sites. Because of the latter requirement, we believe this evaluation is outside of the scope of this manuscript.

Page 9, lines 26-28. How likely do you think it is that this warm event will happen again? If you are discussing ToE and this event could happen again in the next 1-2 decades, wouldn't it make sense to keep it in the record for the ToE calculations and comparisons?

-- To our knowledge, there have not been any assessments predicting future likelihood of similar North Pacific warm anomalies; however, we do cite Bond et al. 2015, which proposes the mechanisms that influenced development of the 2014-2015 anomaly. We do indeed include the 2014-2015 data in the ToE calculation for WHOTS. The section referenced by the reviewer is on the separate calculation of trends. We remove the anomalous event because it occurs at the endpoint of the time series, disproportionately

influencing the linear regression as described in the more detailed trend assessment of Sutton et al. 2017 cited in this section.

Page 2 Line 30: change “although” for “however”

-- Done.

Page 4, line 20: add reference to Table 1

-- Good suggestion. Done.

Page 8, lines 22-23: “reflecting the influence of short term of the local active reef community” please rewrite this.

-- Thank you for pointing that out. Rewritten as: “reflecting the influence of short-term (~1-2 days) carbonate chemistry variability of the local active reef community”

Autonomous seawater $p\text{CO}_2$ and pH time series from 40 surface buoys and the emergence of anthropogenic trends

Adrienne J. Sutton¹, Richard A. Feely¹, Stacy Maenner-Jones¹, Sylvia Musielwicz^{1,2}, John Osborne^{1,2}, Colin Dietrich^{1,2}, Natalie Monacchi³, Jessica Cross¹, Randy Bott¹, Alex Kozyr⁴, Andreas J. Andersson⁵, Nicholas R. Bates^{6,7}, Wei-Jun Cai⁸, Meghan F. Cronin¹, Eric H. De Carlo⁹, Burke Hales¹⁰, Stephan D. Howden¹¹, Charity M. Lee¹², Derek P. Manzello¹³, Michael J. McPhaden¹, Melissa Meléndez^{14,15}, John B. Mickett¹⁶, Jan A. Newton¹⁶, Scott E. Noakes¹⁷, Jae Hoon Noh¹⁸, Solveig R. Olafsdottir¹⁹, Joseph E. Salisbury²⁰, Uwe Send⁵, Thomas W. Trull^{21,22,23}, Douglas C. Vandemark²⁰, Robert A. Weller²⁴

¹Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, Washington, USA

²Joint Institute for the Study of the Atmosphere and Ocean, University of Washington, Seattle, Washington, USA

³Ocean Acidification Research Center, University of Alaska Fairbanks, Fairbanks, Alaska, USA

⁴National Centers for Environmental Information, National Oceanic and Atmospheric Administration, Silver Spring, Maryland, USA

⁵Scripps Institution of Oceanography, University of California, San Diego, California, USA

⁶Bermuda Institute of Ocean Sciences, St. Georges, Bermuda

⁷Department of Ocean and Earth Science, University of Southampton, Southampton, UK

⁸University of Delaware, School of Marine Science and Policy, Newark, Delaware, USA

⁹University of Hawai'i at Mānoa, School of Ocean and Earth Science and Technology, Honolulu, Hawaii, USA

¹⁰College of Earth, Ocean and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA

¹¹Department of Marine Science, University of Southern Mississippi, Stennis Space Center, Mississippi, USA

¹²Ocean Policy Institute, Korea Institute of Ocean Science and Technology, Busan, Korea

¹³Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, Miami, Florida, USA

¹⁴Department of Earth Sciences and Ocean Processes Analysis Laboratory, University of New Hampshire, Durham, New Hampshire, USA

¹⁵Caribbean Coastal Ocean Observing System, University of Puerto Rico, Mayagüez, Puerto Rico

¹⁶Applied Physics Laboratory, University of Washington, Seattle, Washington, USA

¹⁷Center for Applied Isotope Studies, University of Georgia, Athens, Georgia, USA

¹⁸Marine Ecosystem Research Center, Korea Institute of Ocean Science and Technology, Busan, Korea

¹⁹Marine and Freshwater Research Institute, Reykjavik, Iceland

²⁰Ocean Process Analysis Laboratory, University of New Hampshire, Durham, New Hampshire, USA

²¹Climate Science Centre, Oceans and Atmosphere, Commonwealth Scientific and Industrial Research Organisation, Hobart, Australia

²²Antarctic Climate and Ecosystems Cooperative Research Centre, Hobart, Australia

²³Institute of Marine and Antarctic Studies, University of Tasmania, Hobart, Australia

²⁴Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA

Correspondence to: Adrienne J. Sutton (adrienne.sutton@noaa.gov)

Abstract. Ship-based time series, some now approaching over three decades long, are critical climate records that have dramatically improved our ability to characterize natural and anthropogenic drivers of ocean carbon dioxide (CO_2) uptake and biogeochemical processes. Advancements in autonomous marine carbon sensors and technologies over the last two decades have led to the expansion of observations at fixed time series sites, thereby improving the capability of characterizing sub-seasonal variability in the ocean. Here, we present a data product of 40 individual autonomous moored surface ocean $p\text{CO}_2$ (partial pressure of CO_2) time series established between 2004 and 2013, of which 17 also include autonomous pH measurements. These time series characterize a wide range of surface ocean carbonate conditions in different oceanic (17 sites), coastal (13 sites), and coral reef (10 sites) regimes. A time of trend emergence (ToE) methodology applied to the time series that exhibit well-constrained daily to interannual variability and an estimate of decadal variability indicates that the length of sustained observations necessary to detect statistically significant anthropogenic trends varies by marine environment. The ToE estimates for seawater $p\text{CO}_2$ and pH range

from 8 to 15 years at the open ocean sites, 16 to 41 years at the coastal sites, and 9 to 22 years at the coral reef sites. Only two open ocean $p\text{CO}_2$ time series, Woods Hole Oceanographic Institution Hawaii Ocean Time-series Station (WHOTS) in the subtropical North Pacific and Stratus in the South Pacific gyre, have been deployed longer than the estimated trend detection time and, for these, deseasoned monthly means show estimated anthropogenic trends of $1.9 \pm 0.3 \mu\text{atm yr}^{-1}$ and $1.6 \pm 0.3 \mu\text{atm yr}^{-1}$, respectively. In the future, it is possible that updates to this product will allow for estimating anthropogenic trends at more sites; however, the product currently provides a valuable tool in an accessible format for evaluating climatology and natural variability of surface ocean carbonate chemistry in a variety of regions. Data are available at <https://doi.org/10.7289/V5DB8043> and <https://www.nodc.noaa.gov/ocads/oceans/Moorings/ndp097.html>.

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1 Introduction

Biogeochemical cycling leads to remarkable temporal and spatial variability of carbon in the mixed layer of the global ocean and particularly in coastal seas. The ocean carbon cycle, specifically surface ocean CO_2 -carbonate chemistry, is primarily influenced by local physical conditions and biological processes, basin-wide circulation patterns, and fluxes between the ocean and land/atmosphere. Since the industrial period, increasing atmospheric CO_2 has been an additional forcing on ocean biogeochemistry, with the ocean absorbing roughly 30% of anthropogenic CO_2 (Khatiwala et al., 2013; Le Quéré et al., 2018). The resulting decrease of seawater pH and carbonate ion concentration, referred to as ocean acidification, has the potential to impact marine life such as calcifying organisms (Bednaršek et al., 2017b; Chan and Connolly, 2013; Davis et al., 2017; Fabricius et al., 2011; Gattuso et al., 2015). Shellfish, shallow-water tropical corals, and calcareous plankton are a few examples of economically and ecologically important marine calcifiers potentially affected by ocean acidification.

Open ocean observations have shown that the inorganic carbon chemistry of the surface ocean is changing globally at a mean rate consistent with atmospheric CO_2 increases of approximately $2.0 \mu\text{atm yr}^{-1}$ (Bates et al., 2014; Takahashi et al., 2009; Wanninkhof et al., 2013). However, natural and anthropogenic processes can magnify temporal and spatial variability in some regions, especially coastal systems through eutrophication, freshwater input, exchange with tidal wetlands and the sea floor, seasonal biological productivity, and coastal upwelling (Bauer et al., 2013). This enhanced variability can complicate and at times obscure detection and attribution of longer-scale ocean carbon changes. There are also processes that can act in the opposite direction; for example, riverine and estuarine sources of alkalinity increase buffering capacity of coastal waters and reduce the variability of other carbon parameters.

Efforts to observe and predict the impact of ocean acidification on marine ecosystems must be integrated with an understanding of both the natural and anthropogenic processes that control the ocean carbonate system. Marine organisms experience highly heterogeneous seawater carbonate chemistry conditions, and it is unclear what exact conditions in the natural environment will lead to physiological responses (Hofmann et al., 2010). However, responses associated with exposure to corrosive carbonate conditions such as low values of aragonite saturation state ($\Omega_{\text{aragonite}}$) have been observed (e.g., Barton et al., 2012, 2015; Bednaršek et al., 2014, 2016, 2017a; Reum et al., 2015). Observations show that present-day surface seawater pH and $\Omega_{\text{aragonite}}$ conditions throughout most of the open ocean exceed the natural range of preindustrial variability and in some coastal ecosystems, known biological thresholds for shellfish larvae are exceeded during certain times of the seasonal cycle (Sutton et al., 2016). Are these present-day conditions significantly impacting marine life in the natural environment? How will intensity, frequency, and duration of corrosive carbonate conditions change as surface seawater pH and $\Omega_{\text{aragonite}}$ continue to decline and influence other processes of the biogeochemical cycle in the coastal zone? Paired chemical and biological observations at timescales relevant to biological

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processes, such as food availability, seasonal spawning, larval growth, and recruitment, can be one tool for identifying and tracking the response of marine life to ocean acidification.

Long-term, sustained time-series observations resolving diurnal to seasonal conditions encompass many timescales relevant to biological processes and can help to characterize both natural variability and anthropogenic change in ocean carbon. Fixed time-series observations fill a unique niche in ocean observing as they can serve as sites of multidisciplinary observations and process studies, high-quality reference stations for validating and assessing satellite measurements and earth system models, and test beds for developing and evaluating new ocean sensing technology. If of sufficient length and measurement quality to detect the anthropogenic signal above the noise (i.e., in this case the natural variability of the ocean carbon system), these observations can also serve as critical climate records.

Here, we introduce time-series data from 40 moored stations in open ocean, coastal, and coral reef environments. These time series include 3-hourly autonomous measurements of surface seawater temperature (SST), salinity (SSS), mole fraction of atmospheric CO₂ (xCO₂), partial pressure of atmospheric and seawater CO₂ (pCO₂), and seawater pH. This data product was developed to provide easy access to uninterrupted time series of high-quality pCO₂ and pH data for those who do not require the detailed deployment-level information archived at the National Centers for Environmental Information (NCEI; https://www.nodc.noaa.gov/ocads/oceans/time_series_moorings.html).

We also present an overview of the seasonal variability to long-term trends revealed in the pCO₂ and pH observations, as well as an estimate of the length of time series required to detect an anthropogenic signal at each location. We use a statistical method described by Tiao et al. (1990) and further applied to environmental data by Weatherhead et al. (1998) to estimate the number of years of observations needed to detect a statistically significant trend over variability, which we refer to here as time of emergence (ToE). An input required in this statistical model is an estimate of the trend. We adopt a trend in seawater pCO₂ of 2 μatm yr⁻¹, which assumes surface seawater changes track the current rate of globally-averaged atmospheric CO₂ increase. This assumption allows for comparing the trend-to-variance pattern across the network of 40 time series locations. The ToE methodology does not allow for identifying actual long-term trends that may be different from 2 μatm yr⁻¹ due to other long-term changes in, for example, biological production/respiration or coastal carbon sources/sinks. Nor does it address at what point in time a system may cross the envelope of pre-industrial variability or biological thresholds (e.g., Pacella et al., 2018; Sutton et al., 2016). It indicates the time at which the imposed signal of 2 μatm yr⁻¹ emerges from the variance, and not necessarily when the actual anthropogenic signal may emerge or when organisms may be impacted.

Another caveat of this methodology is that the results apply to present-day conditions, and these estimates will change as the time series lengthen due to continued anthropogenic forcing. For example, even if using seasonally detrended monthly anomalies (i.e., when the mean seasonality of ocean carbonate chemistry is accounted for), magnification of the seasonal amplitude of pCO₂ due to warming, reduction in buffering capacity, and/or other carbon cycle feedbacks could add variance to the monthly anomalies, resulting in increased detection time (Kwiatkowski and Orr, 2018; Landschützer et al., 2018). Changes in circulation, stratification, and meltwater inputs in the Arctic cryosphere due to anthropogenic warming could also influence these estimates over time. For regions where the drivers of anthropogenic forcing and natural variability are well constrained, the methodology could be modified to provide more accurate estimates of trend detection time. However, ToE estimates presented here use monthly anomalies of present-day observations and a fixed anthropogenic pCO₂ trend of 2 μatm yr⁻¹ to compare the trend-to-variance patterns across the network of 40 moored time series. These estimates provide a starting point for trend calculations using this data product.

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2 Methods

2.1 Site and sensor description

The 40 fixed time series stations are located in the Pacific (29), Atlantic (9), Indian (1), and Southern (1) ocean basins in open ocean (17), coastal (13), and coral reef (10) ecosystems (Table 1; Fig. 1). All surface ocean $p\text{CO}_2$ and pH time series were established between 2004 and 2013. Thirty-three of these stations are active, while three have been moved to nearby locations better representing regional biogeochemical processes and four have been discontinued due to lack of sustained funding. The range of support and partnerships for maintaining these moored time series is extensive; see Acknowledgements for details. Many of these 40 moored time series stations also make physical oceanographic and marine boundary layer meteorological measurements, thus enabling multi-disciplinary studies involving carbon cycle dynamics.

A Moored Autonomous $p\text{CO}_2$ (MAPCO₂) system measuring marine boundary layer air at 0.5–1 m height and seawater at <0.5 m depth is deployed at each fixed time series site (Sutton et al., 2014b). The MAPCO₂ systems measure $x\text{CO}_2$ in equilibrium with surface seawater by a nondispersive infrared gas analyzer (LI-COR: model LI-820) calibrated prior to each measurement with a reference gas traceable to World Meteorological Organization standards. Seawater $x\text{CO}_2$ equilibration occurs by cycling a closed loop of air through an [floating bubble](#) equilibrator at the sea surface for 10 minutes, [which is described in detail by Sutton et al. \(2014b\)](#). Each time series site has either a Sea-Bird Electronics (SBE) 16plus V2 Sea-CAT or a SBE 37 MicroCAT deployed at approximately 0.5 m measuring sea surface temperature (SST) and salinity (SSS). These measurements are used to calculate $p\text{CO}_2$ and the fugacity of CO_2 ($f\text{CO}_2$) consistent with standard operating procedures (Dickson et al., 2007; Weiss, 1974). Total estimated uncertainties of the resulting $p\text{CO}_2$ measurements are <2 μatm for seawater $p\text{CO}_2$ and <1 μatm for air $p\text{CO}_2$. For a detailed description of the MAPCO₂ methodology, calculations, data reduction, and data quality control, see Sutton et al. (2014b).

In addition to $p\text{CO}_2$, SST, and SSS, 17 of the time series also include seawater pH measurements at 0.5 m depth ([Table 1](#)). These measurements are made by either the spectrophotometric-based Sunburst SAMI pH sensors (Seidel et al., 2008) or ion sensitive field effect transistor-based SeaFET pH sensors (Bresnahan et al., 2014; Martz et al., 2010). Field-based sensor validation suggests these sensors (once calibrated and adjusted in the case of the SeaFET) have a total uncertainty of <0.02 in this surface buoy application (Sutton et al., 2016). [Data quality control of these pH time series, including calibration, comparison with discrete samples, and assessment of drift due to sensor performance and biofouling, are described in detail by Sutton et al. \(2016\)](#). All seawater pH data are expressed in the total scale [and reported at in situ SST](#). At 3-hourly sampling intervals, this configuration of MAPCO₂ and associated sensors is typically deployed for one year before recovery, maintenance, and redeployment of the buoy and sensors.

2.2 Data product description

All post-calibrated and quality-controlled data are archived at NCEI: https://www.nodc.noaa.gov/ocads/oceans/time_series_moorings.html. For each site, an annual deployment has data and quality control descriptors at the data archive, including: (1) 3-hourly MAPCO₂ and associated data, including measured parameters such as $x\text{CO}_2$, humidity, and atmospheric pressure so data users can recalculate $p\text{CO}_2$ if desired; (2) a data quality flag (QF) log that identifies and describes likely bad (QF = 3) or bad (QF = 4) CO_2 and pH data included in the data set; and (3) a metadata file with deployment-level information such as reference gas value and MAPCO₂ air value comparisons to the GLOBALVIEW-CO₂ Marine Boundary Layer (MBL) product (GLOBALVIEW-CO₂, 2013). The reader is referred to Sutton et al. (2014b) for a detailed description of this deployment-level archived information. In addition to data archival at NCEI, these deployment-level mooring data sets are also included in the annual Surface Ocean CO₂ Atlas data product (Bakker et al., 2016). Future data management

plans include integrating the $p\text{CO}_2$ and pH data into OceanSITES, which would provide a single access point to open ocean biogeochemical, physical oceanographic, and marine boundary layer meteorological measurements in a common, self-documented format.

The data product presented here is a compiled and simplified time series developed from these deployment-level archived files.

- 5 Each fixed moored location has one file with a header including the following basic metadata: (1) data source and contact information; (2) data use request; (3) data product citation; (4) time series name, time range, and coordinates; (5) description of variables; (6) methodology references; and (7) links to deployment-level archived data and metadata at NCEI. Following the header, each fixed moored time series file includes the entire time series of SST, SSS, seawater $p\text{CO}_2$, air $p\text{CO}_2$, air $x\text{CO}_2$, and pH with an associated timestamp.
- 10 The time series data product only includes data from the original deployment-level data files assigned QF = 2 (good data). Any missing values or values assigned QF of 3 or 4 in the original deployment-level data are replaced with “NaN” in the time series product. Of the data assigned QF of 2, 3, or 4, the good data (QF = 2) retained in this data product comprise 96% of all seawater $x\text{CO}_2$ measurements and 88% of all seawater pH measurements. Missing or bad SST or SSS data further reduce the quantity of seawater $p\text{CO}_2$ values to 85% compared to the archived deployment-level data. Data users interested in all available $x\text{CO}_2$ and pH
- 15 data should continue to retrieve deployment-level data from the NCEI archive.

Two time-series locations are exceptions to the above detail. Because 3-hourly SST and SSS are not available for the Twanoh and Dabob sites, the data archived at NCEI for those two sites includes $x\text{CO}_2$ (dry) air and seawater values but not calculated $p\text{CO}_2$. In order to calculate $p\text{CO}_2$ for those sites, the data user can incorporate atmospheric pressure, SST, and SSS from other sources. Atmospheric pressure at 3-hourly intervals can be found in the deployment-level archived data files at NCEI. Other data sources,

20 including 2-hourly SST and SSS data at both Twanoh and Dabob, can also be located through the data portal of the Northwest Association of Networked Ocean Observing Systems: <http://nvs.nanoos.org/>. Since interpolating 2-hourly data with the 3-hourly MAPCO₂ data requires making assumptions about temporal variability that may differ according to the research interests of the data user, data from these two locations are only available in the deployment-level data files archived at NCEI.

- This data product has been developed to provide easier access to quality-assured seawater $p\text{CO}_2$ and pH data and broaden the user
- 25 base of these data. This data product is ideal for modelers interested in using fixed time series data to validate earth system model output or other data users accustomed to working with ship-based time series data. It also makes the time series more accessible to students, researchers from other disciplines, and marine resource managers who may not have a seawater CO₂-carbonate chemistry background or the resources necessary to process and interpret the more detailed deployment-level data.

2.3 Statistical analyses

- 30 Descriptive statistics from these time series products are presented here to compare variability in seawater $p\text{CO}_2$ and pH across the 40 locations. Seasonal amplitude is the difference in the mean of all observations during winter and summer. For Northern Hemisphere sites, winter is defined as December, January, and February, and summer is June, July, and August (vice versa for Southern Hemisphere sites).

The climatological mean is derived by averaging means for each of the 12 months over the composite, multiyear time series.

- 35 Interannual variability (IAV) is presented as the standard deviation of individual yearly means throughout the time series. In the case of missing observations, climatological monthly means are substituted to calculate yearly means for IAV. This approach seeks to minimize the impact of data gaps on the IAV estimates. Because long-term trends in $p\text{CO}_2$ and pH are not well constrained at

all locations, data are not detrended before calculating IAV. At Woods Hole Oceanographic Institution Hawaii Ocean Time-series Station (WHOTS), for example, removing a trend of $2 \mu\text{atm yr}^{-1}$ changes the IAV estimate by 12%. Therefore, IAV likely has high uncertainty due to lack of detrending, data gaps, and the relatively short time series lengths (≤ 12 years). Future efforts to improve these IAV estimates can rely on future assessment of longer time series (moored or observations from other platforms) and regional models that better characterize all modes of temporal variability.

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The seasonal cycle is removed from the data using the approaches described in detail in Bates (2001) and Takahashi et al. (2009). This method results in a time series of seasonally detrended monthly anomalies, which are monthly residuals after removing the climatological monthly means.

When applied to environmental data, ToE is a statistical method that estimates the number of years necessary in a time series to detect an anthropogenic signal over the natural variability. This method has been used to determine ToE from, for example, chlorophyll satellite records (Henson et al., 2010) and ocean biogeochemical models (Lovenduski et al., 2015). ToE_{ts} (in years) of each time series is derived using the method of Weatherhead et al. (1998):

$$ToE_{ts} = \left(\frac{3.3\sigma_N}{|\omega_0|} \sqrt{\frac{1+\phi}{1-\phi}} \right)^{2/3} \quad (1)$$

where σ_N and ϕ are the standard deviation and autocorrelation (at lag 1) of monthly anomalies, respectively, and ω_0 is the anthropogenic signal of $2 \mu\text{atm } p\text{CO}_2$ or 0.002 pH per year, assuming surface seawater in equilibrium with the global mean rate of atmospheric CO_2 increase. This method results in a 90% probability (dictated by the factor of 3.3 in Eq. 1) of trend detection by the estimated ToE_{ts} at the 95% confidence interval. Uncertainty in ToE_{ts} , u_{ToE} , is calculated by:

$$u_{ToE} = ToE_{ts} \times e^B \quad (2)$$

where B is the uncertainty factor calculated using the method of Weatherhead et al. (1998). Uncertainty is based on the number of months (m) in the time series and autocorrelation of monthly anomalies (ϕ):

$$B = \frac{4}{3\sqrt{m}} \sqrt{\frac{1+\phi}{1-\phi}} \quad (3)$$

With time series lengths of ≤ 12 years, most of the moored time series characterize diurnal to interannual variability of surface ocean $p\text{CO}_2$; however, low-frequency decadal variability may not yet be fully captured. Decadal variability of surface ocean carbon is poorly quantified by observations in general (Keller et al., 2012; McKinley et al., 2011; Schuster and Watson, 2007; Séférian et al., 2013). In the absence of constraint of decadal variability at each of these locations, we consider an example in the tropical Pacific to estimate the impact of decadal variability on ToE_{ts} . For this example, we assume the decadal-scale forcing (i.e., primarily the Pacific Decadal Oscillation; Newman et al., 2016) leads to a 27% change in CO_2 flux in the tropical Pacific (Feely et al. 2006). We take a conservative approach and assume this forcing is driven primarily by decadal changes in surface seawater $p\text{CO}_2$ of as much as 15% and determine the impact that added decadal variability has to the ToE estimates at the 7 sites on the Tropical Atmosphere Ocean (TAO) array (McPhaden et al, 1998). This is done by repeating the existing $p\text{CO}_2$ time series until time series length is 50 years and applying a 15% offset in the data on 10-year intervals at random. This simulated 50-year time series is then used to recalculate ToE. The simulation with added low-frequency decadal signals increases ToE by an average of 40%, with significant variance across the TAO sites. Decadal forcing has less impact at the eastern Pacific TAO sites where subseasonal to interannual variability controlled by equatorial upwelling, tropical instability waves, and biological productivity is dominant, and more impact in the central and western Pacific where these higher-frequency modes of variability are less pronounced.

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Decadal forcing may be particularly strong in the tropical Pacific due to the influence of the Pacific Decadal Oscillation on equatorial upwelling of CO₂-rich water (Feely et al., 2006; Sutton et al., 2014a) compared to other subtropical sites (Keller et al., 2012; Landschützer et al., 2016; Lovenduski et al., 2015; Schuster and Watson, 2007). However, we apply this 40% increase in ToE_{ts} to all 40 time series in order to provide a conservative estimate of when an anthropogenic signal can be detected using these moored time series data. The reported ToE for each moored time series is the result from Eq. (1) multiplied by 1.4:

$$ToE = ToE_{ts} \times 1.4 \quad (4)$$

For the data sets with time series length greater than these ToE estimates, monthly anomalies are linearly regressed against time to determine the long-term rate of change. Linear regression statistics, including uncertainty in rate and r², are calculated using standard methods described in Glover et al. (2011).

10 3 Results and Discussion

3.1 Climatology and natural variability

Across the 40 moored stations, climatological means of surface ocean pCO₂ range from 255 to 490 μatm (Fig. 1). Seasonal amplitude of seawater pCO₂ vary from 8 to 337 μatm. With more recent establishment of seawater pH observations, only 10 of the 17 sites with pH sensors have seasonally-distributed pH data necessary to determine climatological mean and seasonal amplitude.

15 At these 10 locations, climatological mean and seasonal amplitude of seawater pH vary from 8.00 to 8.21 and 0.01 to 0.14, respectively (Fig. 2). All the sites with seasonal amplitude reported in Figs. 1 and 2 have observations distributed across all seasons (Fig. 3). Seasonal amplitude of surface seawater pCO₂ is largest at the coastal sites (60 to 337 μatm) compared to the open ocean (8 to 71 μatm) and coral reef sites (11 to 178 μatm). While seasonal pH variation is only constrained at 10 of the 40 sites, these patterns hold for pH as well with ranges of 0.08 to 0.14, 0.01 to 0.07, and 0.02 to 0.07 at the coastal, open ocean, and coral sites, respectively.

20 IAV of seawater pCO₂, which is the standard deviation of yearly means, range from 2 to 29 μatm. The largest IAV is found at the coastal and coral sites with values at Coastal MS, Twanoh, and CRIMP2 of 29, 27, and 25 μatm, respectively. With a large IAV of 25 μatm, CRIMP2 tends to be an anomaly among coral sites, with most tropical coral locations exhibiting IAV similar to open ocean sites of ≤5 μatm (Fig. 1). Surface seawater pH time series are not yet long enough to determine a robust estimate of IAV.

25 These descriptive statistics show higher seawater pCO₂ values throughout the year in the tropical Pacific where equatorial upwelling of CO₂-rich water dominates. Seasonal forcing of pCO₂ values in this region is low, but IAV, driven by the El Niño Southern Oscillation (Feely et al., 2006), is the highest of open ocean time series stations (Fig. 1). The coastal time series stations suggest annual CO₂ uptake with climatological means of seawater pCO₂ less than atmospheric CO₂ levels. Seasonal changes of SST and biological productivity drive the large seasonal amplitudes in pCO₂ and pH at the U.S. coastal locations (Fassbender et al., 2018; Reimer et al., 2017; Sutton et al., 2016; Xue et al., 2016). The coastal stations Twanoh and Coastal MS exhibit the highest IAV of seawater pCO₂ (reported as seawater xCO₂ for Twanoh) due to large variability from year to year in circulation, freshwater input, and biological productivity (Fig. 1). Most coral reef time series stations suggest net annual calcification with positive ΔpCO₂ (seawater – air) values. Net calcification has been confirmed by independent assessments at some of these coral reef time series stations (Bates et al., 2010; Courtney et al., 2016; Drupp et al., 2011; Shamberger et al., 2011).

35 Clusters of fixed time series stations in Washington and California State waters, the Hawaiian Island of Oahu, and Bermuda provide examples of how different processes drive ocean carbon chemistry. Seasonal amplitude and IAV are almost twice as large at the

time series stations within the freshwater-influenced Puget Sound (Dabob and Twanoh) compared to the stations on the outer coast of Washington (Chá bã and Cape Elizabeth; Fig. 1b). Dabob is closer to ocean source waters and is deeper compared to Twanoh, which experiences greater water residence time and more persistent stratification, and therefore, increased influence of biological production and respiration on seawater $x\text{CO}_2$ (Fassbender et al., 2018; Lindquist et al., 2017). These processes can cause subsurface hypoxia and low pH (<7.4) and aragonite saturation (<0.6) conditions in this region of Puget Sound (Feely et al., 2010), which likely contribute to the elevated surface seawater $x\text{CO}_2$ levels observed at Dabob and Twanoh. The paired CCE1 and CCE2 moorings in coastal California provide the contrast of open ocean and upwelling regimes, respectively. Climatological mean and seasonal amplitude of $p\text{CO}_2$ are higher at CCE2 where summer upwelling supplies CO_2 -rich water to the surface. IAV is similar at both sites, suggesting interannual drivers of $p\text{CO}_2$, such as the El Niño Southern Oscillation (Nam et al., 2011), likely have an influence throughout the southern California Current Ecosystem.

In both Hawaii and Bermuda, coral reef time series stations are paired with offshore, open ocean $p\text{CO}_2$ observatories, although the offshore Bermuda Testbed Mooring (BTM) station was discontinued before the Bermuda reef sites were established. In both cases, the offshore stations of WHOTS and BTM both exhibit climatological mean seawater $p\text{CO}_2$ slightly below atmospheric values (Fig. 1c), with previous studies indicating these locations are net annual CO_2 sinks (Bates et al., 2014; Dore et al., 2003, 2009; Sutton et al., 2017). The fringing or outer reef sites in Oahu (Kilo Nalu, Ala Wai, Kaneohe) tend to exhibit seawater $p\text{CO}_2$ values closer to these open ocean background levels. The lagoonal Oahu reefs (CRIMP1 and CRIMP2) reflect increased water retention time paired with coral reef photosynthesis/respiration and calcification/dissolution, which elevate both annual mean and daily to interannual variability in seawater $p\text{CO}_2$ values (Fig. 1c; Courtney et al., 2017; Drupp et al., 2011, 2013). One exception is the nearly as large IAV at the fringing reef Ala Wai site, which is impacted by a nearby urban canal/estuary with high nutrient and organic matter input during storm events (Drupp et al., 2013). Positive $\Delta p\text{CO}_2$ values at the lagoonal reef sites also suggest that these sites are a net source of CO_2 to the atmosphere in contrast to the annual net CO_2 uptake at the nearby open ocean sites (Fig. 1c).

In contrast, the outer reef site in Bermuda (Hog Reef) has a higher seasonal amplitude and mean $p\text{CO}_2$ than the inner reef (Crescent Reef) despite having a shorter water residence time (Fig. 1). This is due to the greater biomass at Hog Reef, reflecting the influence of short-term (~ 1 -2 days) [carbonate chemistry variability](#) of the local active reef community, whereas Crescent Reef reflects the integrated signal of multiple habitats and days (~ 6 days; Takeshita et al., 2018). Another caveat is the coral reef time series in this data product have an inherent spatial bias as 80% of the coral reef moorings are located $> 20^\circ$ latitude. The patterns for cooler, high-latitude reefs (e.g., Oahu and Bermuda) may differ from lower latitude reef sites (e.g., La Parguera and Chuuk), which would generally have less pronounced seasonality.

3.2 Marine boundary layer atmospheric CO_2

Atmospheric CO_2 observations at the 40 time series sites all show a positive long-term trend (Fig. 4a). The mean trend at the open ocean sites are not significantly different from the global average rate of change of 2 ppm yr^{-1} (Sutton et al., 2014b). Fig. 4a shows all 40 time series of atmospheric $x\text{CO}_2$ with a rate of change of approximately $20 \mu\text{mol mol}^{-1}$ (or ppm) over a decade; that is, from $380 \mu\text{mol mol}^{-1}$ in January 2006 to $400 \mu\text{mol mol}^{-1}$ in January 2016.

Although the global observing network of atmospheric CO_2 that tracks anthropogenic CO_2 increase requires higher measurement quality ($\leq 0.1 \text{ ppm}$) compared to the measurement quality of the MAP CO_2 system ($\leq 1 \text{ ppm}$), the MAP CO_2 air data may be valuable for regional air CO_2 studies in coastal regions where land-based activities cause larger hourly to interannual variability in atmospheric CO_2 (Bender et al., 2002). In general, the coastal stations exhibit higher annual mean and seasonal amplitude compared

to GLOBALVIEW-CO₂ MBL values, which is a product based on interpolating high-quality atmospheric measurements around the globe to latitudinal distributions of biweekly CO₂ (Fig. 4b,c). Open ocean and coral reef sites do not show this overall pattern compared to GLOBALVIEW-CO₂ MBL values, although there is variability across the sites with some time series exhibiting higher means and seasonal amplitudes compared to the data product and vice versa (Fig. 4b,c).

3.3 Detection of anthropogenic trends in surface seawater pCO₂ and pH

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Estimated length of time for an anthropogenic trend in seawater pCO₂ to emerge from natural variability in the 40 time series varies from 8 to 41 years (Fig. 5). This range is 8 to 15 years at the open ocean sites, 16 to 41 years at the coastal sites, and 9 to 22 years at the coral reef sites. For the pH data sets with long enough time series to calculate ToE (i.e., the circles in Fig. 2), there is no significant difference between ToE of pCO₂ and pH (ToE calculated using hydrogen ion concentration, [H⁺], not -log[H⁺]), therefore, it is likely that ToE presented in Fig. 5 signifies both surface seawater pCO₂ and pH. However, as the pH time series lengthen and variability is better constrained, future work should focus on a more thorough assessment of ToE of seawater pH.

In this application ToE is dependent on the variability in the data, resulting in the pattern where sites that exhibit larger seasonal to interannual variability (Figs. 1 and 2) tend to have longer ToE estimates (Fig. 5). The fringing and outer reef sites of south shore Oahu (Kilo Nalu and Ala Wai) and Kaneohe Bay, respectively, have shorter ToE compared to the lagoonal sites (CRIMP1 and CRIMP2) with larger seasonal to interannual variability. Similarly, the freshwater-influenced, highly-productive Puget Sound sites (Dabob and Twanoh) have the longest ToE of all 40 sites and are approximately twice as long as the nearby time series on the outer coast of Washington (Chá bá and Cape Elizabeth). In the southern California Current, the ToE of the upwelling-influenced CCE2 is 50% longer than the offshore CCE1 site.

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These data also suggest that removing seasonal variability from the times series is essential to reducing ToE and determining accurate long-term trends. The ToE estimates presented in Fig. 5 are based on seasonally detrended monthly anomalies, which are the residuals of the climatological monthly means. These ToE estimates are on average 55% shorter than ToE estimated using raw time series data. This reduction in ToE due to seasonally detrending has a larger impact at higher latitudes where the seasonal amplitude of surface seawater pCO₂ is larger compared to tropical sites. Using anomalies of climatological monthly means also minimizes the impact of start and end month of the time series on the resulting trend estimation.

Of the 40 seawater pCO₂ time series, ToE estimates suggest only the WHOTS and Stratus time series are currently long enough to detect an anthropogenic trend. KEO, Papa, Kilo Nalu, and some TAO time series are approaching ToE, but at this time final data are not yet available through 2017. Data available at the time of publication suggest the anthropogenic trend in surface seawater pCO₂ at WHOTS from 2004 to 2014 is 1.9±0.3 μatm yr⁻¹ (Fig. 6). In this trend analysis we do not include data from the 2014-2015 anomalous event that warmed North Pacific Ocean surface water (Bond et al., 2015) and elevated seawater pCO₂ values (Feely et al., 2017). This WHOTS trend is not significantly different from the seawater pCO₂ trend observed from 1988 to 2013 at the collocated ship-based Station ALOHA of 2.0±0.1 μatm yr⁻¹ (Sutton et al., 2017). Both WHOTS and Station ALOHA trends are not significantly different from the trend expected if surface seawater is in equilibrium with the global average atmospheric CO₂ increase.

The long-term trend at Stratus from 2006 to 2015 is 1.6±0.3 μatm yr⁻¹ (Fig. 6). This trend is slightly lower than expected if seawater pCO₂ change is in equilibrium with the atmosphere. Considering the uncertainty in the ToE_{is} estimate (Table 2) and the added uncertainty around unconstrained decadal variability at each of these locations, continued observations will be necessary at this site to confirm whether this lower rate of change persists. In addition to uptake of atmospheric CO₂, the seawater pCO₂ trend may be impacted by surface meteorological or upper ocean changes in this region. Significant trends in wind speed, wind stress, and

the air–sea exchange of heat, freshwater, and momentum were observed from meteorological and surface ocean measurements on Stratus from 2000 to 2009 (Weller, 2015). These trends are related to intensification of Pacific trade winds over the last two decades across the entire basin (England et al., 2014) and are likely to impact surface ocean $p\text{CO}_2$ and CO_2 flux in other regions of the Pacific. Sustained, continuous time series such as Stratus can contribute to constraining the physical and biogeochemical processes controlling long-term change.

4 Data Availability

Locations of deployment-level archived data at NCEI and the time series data product for each mooring site are listed in Table 2. The Digital Object Identifier (DOI) for this data product is:10.7289/V5DB8043. Data users looking for easier access to quality-assured seawater $p\text{CO}_2$ and pH data designated good (QF = 2; see Sect. 2.2) should consider using this time series data product. The time series data files will be updated each time new deployment-level data are submitted to the NCEI archive. Data users interested in all available MAPCO₂ and pH data should retrieve deployment-level data at NCEI (links also provided in Table 2).

These data are made freely available to the public and the scientific community in the belief that their wide dissemination will lead to greater understanding and new scientific insights. Users of these time series data products should reference this paper and acknowledge the major funding organizations of this work: NOAA’s Ocean Observing and Monitoring Division and Ocean Acidification Program.

5 Conclusions

This product provides a unique data set for a range of users including providing a more accessible format for non-carbon chemists interested in surface ocean $p\text{CO}_2$ and pH time series data. These 40 time series locations represent a range of ocean, coastal, and coral reef regimes that exhibit a broad spectrum of daily to interannual variability. These time series can be used as a tool for estimating climatologies, assessing natural variability, and constraining models to improve predictions of trends in these regions. However, at this time, only two time series data sets (WHOTS and Stratus) are long enough to estimate long-term anthropogenic trends. ToE estimates show at all but these two sites, an anthropogenic signal cannot be discerned at a statistically significant level from the natural variability of surface seawater $p\text{CO}_2$ and pH. If and when that date of trend detection is attained, it is essential to seasonally detrend data prior to any trend analyses. Even though the ToE provided are conservative estimates, data users should still use caution in interpreting that an anthropogenic trend is distinct from decadal-scale ocean forcing that is not well characterized. Future work should be directed at improving upon these ToE estimates in regions where other data, proxies, or knowledge about decadal forcing are more complete.

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Table 1: Region, coordinates, surface ocean carbon parameters measured, year carbon time series established, and current status of the 40 fixed moored time series stations. All time series also include atmospheric CO₂, SST, and SSS.

<u>Abbreviation</u>	<u>Descriptive name</u>	<u>Region</u>	<u>Latitude</u>	<u>Longitude</u>	<u>Carbon parameters</u>	<u>Start year</u>	<u>Status</u>
CCE1	California Current Ecosystem 1	Northeast Pacific Ocean	33.48	-122.51	pCO ₂ , pH	2008	active
Papa	Ocean Station Papa	Northeast Pacific Ocean	50.13	-144.84	pCO ₂ , pH	2007	active
KEO	Kuroshio Extension Observatory	Northwest Pacific Ocean	32.28	144.58	pCO ₂ , pH	2007	active
JKEO	Japanese Kuroshio Extension Observatory	Northwest Pacific Ocean	37.93	146.52	pCO ₂	2007	discontinued in 2007
WHOTS	Woods Hole Oceanographic Institution Hawaii Ocean Time-series Station	Central Pacific Ocean	22.67	-157.98	pCO ₂ , pH	2004 ^a	active
TAO110W	National Data Buoy Center (NDBC) Tropical Atmosphere Ocean 0°, 110°W	Equatorial Pacific Ocean	0.00	-110.00	pCO ₂	2009	active
TAO125W	NDBC Tropical Atmosphere Ocean 0°, 125°W	Equatorial Pacific Ocean	0.00	-125.00	pCO ₂	2004	active
TAO140W	NDBC Tropical Atmosphere Ocean 0°, 140°W	Equatorial Pacific Ocean	0.00	-140.00	pCO ₂	2004	active
TAO155W	NDBC Tropical Atmosphere Ocean 0°, 155°W	Equatorial Pacific Ocean	0.00	-155.00	pCO ₂	2010	active
TAO170W	NDBC Tropical Atmosphere Ocean 0°, 170°W	Equatorial Pacific Ocean	0.00	-170.00	pCO ₂	2005	active
TAO165E	NDBC Tropical Atmosphere Ocean 0°, 165°E	Equatorial Pacific Ocean	0.00	165.00	pCO ₂	2010	active
TAO8S165E	NDBC Tropical Atmosphere Ocean 8°S, 165°E	Equatorial Pacific Ocean	-8.00	165.00	pCO ₂	2009	active
Stratus	Stratus	Southeast Pacific Ocean	-19.70	-85.60	pCO ₂ , pH	2006	active
BTM	Bermuda Testbed Mooring	North Atlantic Ocean	31.50	-64.20	pCO ₂	2005	discontinued in 2007
Iceland	North Atlantic Ocean Acidification Mooring	North Atlantic Ocean	68.00	-12.67	pCO ₂ , pH	2013	active
BOBOA	Bay of Bengal Ocean Acidification Observatory	Indian Ocean	15.00	90.00	pCO ₂ , pH	2013	active
SOFS	Southern Ocean Flux Station	Southern Ocean	-46.80	142.00	pCO ₂	2011	active
GAKOA	Gulf of Alaska Ocean Acidification Mooring	Alaskan Coast	59.910	-149.350	pCO ₂ , pH ^b	2011	active
Kodiak	Kodiak Alaska Ocean Acidification Mooring	Alaskan Coast	57.700	-152.310	pCO ₂ , pH ^b	2013	discontinued in 2016
SEAK	Southeast Alaska Ocean Acidification Mooring	Alaskan Coast	56.260	-134.670	pCO ₂ , pH ^b	2013	discontinued in 2016
M2	Southeastern Bering Sea Mooring Site 2	Bering Sea Coastal Shelf	56.510	-164.040	pCO ₂ , pH ^b	2013	active
Cape Elizabeth	NDBC Buoy 46041 in Olympic Coast National Marine Sanctuary (NMS)	U.S. West Coast	47.353	-124.731	pCO ₂	2006	active
Chá bá	Chá bá Buoy in the Northwest Enhanced Moored Observatory and Olympic Coast NMS	U.S. West Coast	47.936	-125.958	pCO ₂ , pH	2010	active
CCE2	California Current Ecosystem 2	U.S. West Coast	34.324	-120.814	pCO ₂ , pH	2010	active
Dabob	Oceanic Remote Chemical Analyzer (ORCA) buoy at Dabob in Hood Canal	U.S. West Coast	47.803	-122.803	xCO ₂ ^c	2011	active
NH-10	Newport Hydrographic Line Station 10 Ocean Acidification Mooring	U.S. West Coast	44.904	-124.778	pCO ₂ , pH	2014	moved to new location in 2017 ^d
Twanoh	ORCA buoy at Twanoh in Hood Canal	U.S. West Coast	47.375	-123.008	xCO ₂ ^c	2009	active
Ala Wai	Ala Wai Water Quality Buoy at South Shore Oahu	Pacific Island Coral Reef	21.280	-157.850	pCO ₂	2008	active
Chuuk	Chuuk Lagoon Ocean Acidification Mooring	Pacific Island Coral Reef	7.460	151.900	pCO ₂ , pH	2011	active
CRIMP1	Coral Reef Instrumented Monitoring Platform 1	Pacific Island Coral Reef	21.428	-157.788	pCO ₂	2005	moved to CRIMP2 in 2008
CRIMP2	Coral Reef Instrumented Monitoring Platform 2	Pacific Island Coral Reef	21.458	-157.798	pCO ₂	2008	active
Kaneohe	Kaneohe Bay Ocean Acidification Offshore Observatory	Pacific Island Coral Reef	21.480	-157.780	pCO ₂ , pH	2011	active
Kilo Nalu	Kilo Nalu Water Quality Buoy at South Shore Oahu	Pacific Island Coral Reef	21.288	-157.865	pCO ₂	2008	active
Gray's Reef	NDBC Buoy 41008 in Gray's Reef National Marine Sanctuary	U.S. East Coast	31.400	-80.870	pCO ₂ , pH	2006	active
Gulf of Maine	Coastal Western Gulf of Maine Mooring	U.S. East Coast	43.023	-70.542	pCO ₂ , pH	2006	active

Crescent Reef	Crescent Reef Bermuda Buoy	Atlantic Coral Reef	32.400	-64.790	$p\text{CO}_2$	2010	active
Hog Reef	Hog Reef Bermuda Buoy	Atlantic Coral Reef	32.460	-64.830	$p\text{CO}_2$	2010	active
Coastal MS	Central Gulf of Mexico Ocean Observing System Station 01	Gulf of Mexico Coast	30.000	-88.600	$p\text{CO}_2$, pH	2009	moved to new location in 2017 ^c
Cheeca Rocks	Cheeca Rocks Ocean Acidification Mooring in Florida Keys National Marine Sanctuary	Caribbean Coral Reef	24.910	-80.624	$p\text{CO}_2$, pH	2011	active
La Parguera	La Parguera Ocean Acidification Mooring	Caribbean Coral Reef	17.954	-67.051	$p\text{CO}_2$, pH	2009	active

Notes: ^a Data from December 2004 to July 2007 in the WHOTS time series are from the Multi-disciplinary Ocean Sensors for Environmental Analyses and Networks (MOSEAN) station at 22.80°N, 158.10°W (20 km from the WHOTS location). Previous studies have shown the MOSEAN and WHOTS locations have similar surface seawater $p\text{CO}_2$ conditions (Sutton et al., 2014b, 2017) and are therefore combined in this data product as one time series location. ^b

5 Measurements of pH to be included in future updates of the time series data product. ^c SST and SSS data are collected on the Dabob and Twanoh buoys at 2-hourly intervals. Because combining these data with the 3-hourly MAPCO₂ data requires making assumptions about temporal variability that reflect the research interests of the data user, only the direct measurements of CO₂ (i.e., the mole fraction of CO₂ in equilibrium with surface seawater: $x\text{CO}_2$) are available in the NCEI archived data sets. ^d The NH-10 buoy and carbon sensors were moved approximately 75 nm south to Cape Arago, Oregon, following establishment of an Ocean Observatories Initiative buoy at NH-10 with redundant $p\text{CO}_2$ and pH sensors: <https://www.pmel.noaa.gov/co2/story/CB-06>. ^e The Coastal MS buoy and carbon sensors were moved approximately 115 nm southwest to coastal Louisiana waters: <https://www.pmel.noaa.gov/co2/story/Coastal+LA>.

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Table 2: Data access to deployment-level archived data files at NCEI and the time series data product for each moored buoy location. The earliest date of seawater $p\text{CO}_2$ trend **detection** is based on time series product data and calculated by adding the ToE estimate (Eqs. 1-4) to the time series start year (Table 1). The uncertainty presented here is the result of Eqs. (2-3), which is based on ToE_{ts} and does not include any additional uncertainty due to the decadal estimate from Eq. (4). NA denotes sites with less than 3 years of observations where interannual variability is likely not represented in a time series, and therefore, ToE is not calculated.

Buoy name	NCEI archived data files (https://www.nodc.noaa.gov/...)	Time series data product (https://www.pmel.noaa.gov/co2/...)	Earliest date of seawater $p\text{CO}_2$ trend detection
CCE1	ocads/data/0144245.xml	timeseries/CCE1.txt	2020 ± 2
Papa	ocads/data/0100074.xml	timeseries/PAPA.txt	2017 ± 2
KEO	ocads/data/0100071.xml	timeseries/KEO.txt	2018 ± 2
JKEO	ocads/data/0100070.xml	timeseries/JKEO.txt	NA ^a
WHOTS	ocads/data/0100073.xml ^b ocads/data/0100080.xml	timeseries/WHOTS.txt	2013 ± 1
TAO110W	ocads/data/0112885.xml	timeseries/TAO110W.txt	2024 ± 4
TAO125W	ocads/data/0100076.xml	timeseries/TAO125W.txt	2017 ± 4
TAO140W	ocads/data/0100077.xml	timeseries/TAO140W.txt	2018 ± 2
TAO155W	ocads/data/0100084.xml	timeseries/TAO155W.txt	NA
TAO170W	ocads/data/0100078.xml	timeseries/TAO170W.txt	2016 ± 4
TAO165E	ocads/data/0113238.xml	timeseries/TAO165E.txt	NA
TAO8S165E	ocads/data/0117073.xml	timeseries/TAO8S165E.txt	2021 ± 2
Stratus	ocads/data/0100075.xml	timeseries/STRATUS.txt	2015 ± 1
BTM	ocads/data/0100065.xml	timeseries/BTM.txt	NA ^a
Iceland	ocads/data/0157396.xml	timeseries/ICELAND.txt	NA
BOBOA	ocads/data/0162473.xml	timeseries/BOBOA.txt	NA
SOFS	ocads/data/0118546.xml	timeseries/SOFS.txt	NA
GAKOA	ocads/data/0116714.xml	timeseries/GAKOA.txt	2027 ± 3
Kodiak	ocads/data/0157347.xml	timeseries/KODIAK.txt	2028 ± 3 ^a
SEAK	ocads/data/0157601.xml	timeseries/SEAK.txt	NA ^a
M2	ocads/data/0157599.xml	timeseries/M2.txt	NA
Cape Elizabeth	ocads/data/0115322.xml	timeseries/CAPEELIZABETH.txt	2030 ± 4
Chá bã	ocads/data/0100072.xml	timeseries/CHABA.txt	2033 ± 4
CCE2	ocads/data/0084099.xml	timeseries/CCE2.txt	2028 ± 3
Dabob	ocads/data/0116715.xml	use NCEI files	2050 ± 6
NH-10	ocads/data/0157247.xml	timeseries/NH10.txt	NA ^a
Twanoh	ocads/data/0157600.xml	use NCEI files	2050 ± 6
Ala Wai	ocads/data/0157360.xml	timeseries/ALAWAI.txt	2024 ± 3
Chuuk	ocads/data/0157443.xml	timeseries/CHUUK.txt	2021 ± 2

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CRIMP1	ocads/data/0100069.xml	timeseries/CRIMP1.txt	2022 ± 4 ^a
CRIMP2	ocads/data/0157415.xml	timeseries/CRIMP2.txt	2030 ± 3
Kaneohe	ocads/data/0157297.xml	timeseries/KANEOHE.txt	<i>N/A</i>
Kilo Nalu	ocads/data/0157251.xml	timeseries/KILONALU.txt	2017 ± 2
Gray's Reef	ocads/data/0109904.xml	timeseries/GRAYSREEF.txt	2027 ± 3
Gulf of Maine	ocads/data/0115402.xml	timeseries/GULFOFMAINE.txt	2023 ± 3
Crescent Reef	ocads/data/0117059.xml	timeseries/CRESCENTREEF.txt	2020 ± 2
Hog Reef	ocads/data/0117060.xml	timeseries/HOGREEF.txt	2023 ± 3
Coastal MS	ocads/data/0100068.xml	timeseries/COASTALMS.txt	2046 ± 7
Cheeca Rocks	ocads/data/0157417.xml	timeseries/CHEECAROCKS.txt	2020 ± 2
La Parguera	ocads/data/0117354.xml	timeseries/LAPARGUERA.txt	2019 ± 2

Notes: a Discontinued sites where a long-term trend cannot be quantified solely from this time series data product. b Links to NCEI archived deployment-level data files are provided for both MOSEAN and WHOTS; however, these time series are combined in the time series data product.

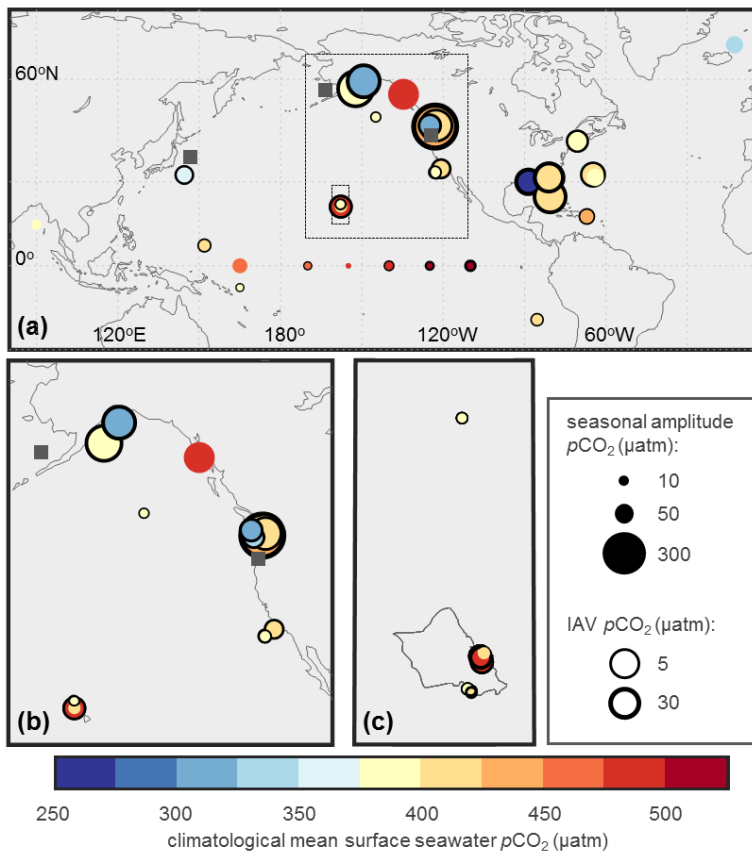


Figure 1: Location of (a) 40 moored $p\text{CO}_2$ time series with insets enlarged for the (b) U.S. West Coast and (c) Hawaiian Island of Oahu. Circle color represents climatological mean seawater $p\text{CO}_2$ (μatm), size of circle represents seasonal amplitude, and thickness of circle outline represents interannual variability (IAV). Gray squares show the locations of JKEO, M2, and NH-10 where insufficient winter observations prevent the calculation of climatological mean or seasonal amplitude. IAV is not shown for sites with less than 3 years of observations (Kaneohe, Iceland, BOBOA, SEAK, M2, SOFS, BTM, TAO165E, TAO155W, NH-10, and JKEO). Dabob and Twanoh data shown here are $x\text{CO}_2$ ($\mu\text{mol mol}^{-1}$). [Moored time series locations and names are detailed in Table 1.](#)

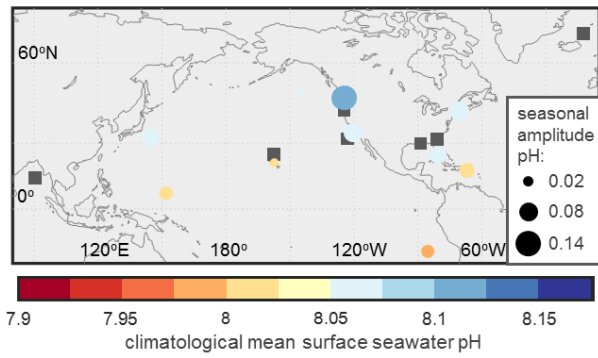


Figure 2: Location of 17 moored pH time series. Circle color represents climatological mean seawater pH and size of circle represents seasonal amplitude. Gray squares show the locations of moored pH time series where lack of seasonal distribution of measurements prevent the calculation of climatological mean or seasonal amplitude. No pH time series are of sufficient length to estimate IAV as presented for seawater $p\text{CO}_2$ in Figure 1.

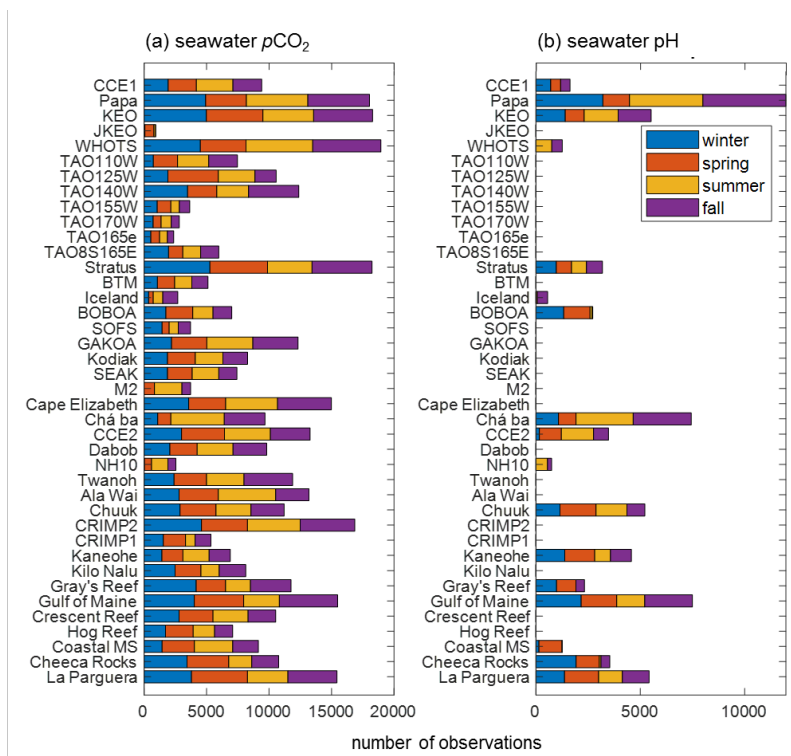


Figure 3: Number of surface seawater (a) pCO₂ and (b) pH observations by season in each of the 40 moored time series. For Northern Hemisphere sites, winter is defined as December, January, February; spring is March, April, May; summer is June, July, August; and fall is September, October, November (seasons reversed for Southern Hemisphere sites). Number of observations for Dabob and Twanoh shown here are seawater xCO₂.

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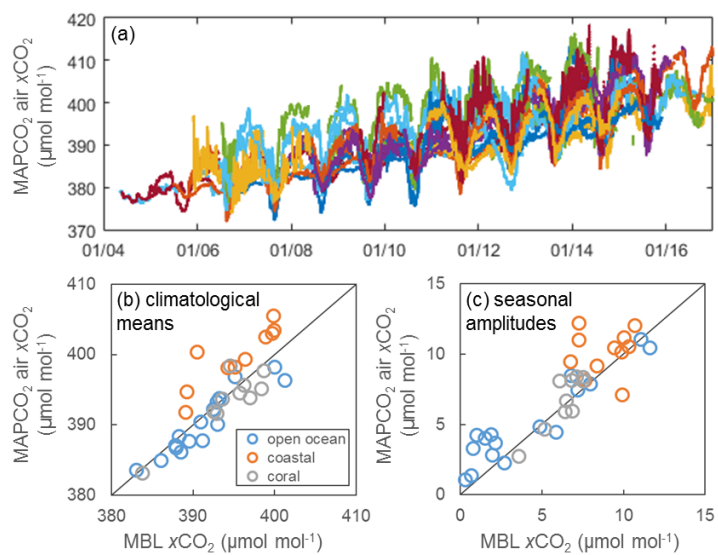


Figure 4: (a) Weekly averaged air $x\text{CO}_2$ observations from the 40 time series. Different colors represent different time series. Dates are MM/YY. (b) Climatological means and (c) seasonal amplitudes of air $x\text{CO}_2$ from the MAPCO₂ measurements compared to the GLOBALVIEW-CO₂ MBL data product (GLOBALVIEW-CO₂, 2013) for open ocean (blue), coastal (green), and coral reef (red) time series locations.

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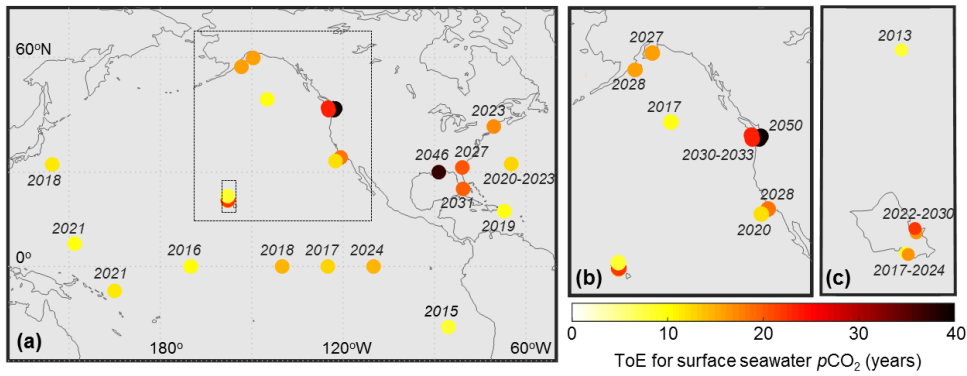


Figure 5: (a) Time of trend emergence (ToE) estimates, i.e., number of years of observations necessary to detect an anthropogenic trend, with insets enlarged for the (b) U.S. West Coast and (c) Hawaiian Island of Oahu. ToE is not shown for sites with less than 3 years of observations (Kaneohe, Iceland, BOBOA, M2, SEAK, SOFS, BTM, TAO165E, TAO155W, NH-10, and JKEO). Years shown are the earliest dates of seawater pCO₂ trend detection for each time series, which is the ToE estimate plus the time series start year (Table 1). These years of trend detection and associated uncertainty are also shown in Table 2. For the pH data sets with long enough time series to calculate ToE (i.e., the circles in Fig. 2), there is no significant difference between ToE of pCO₂ and pH.

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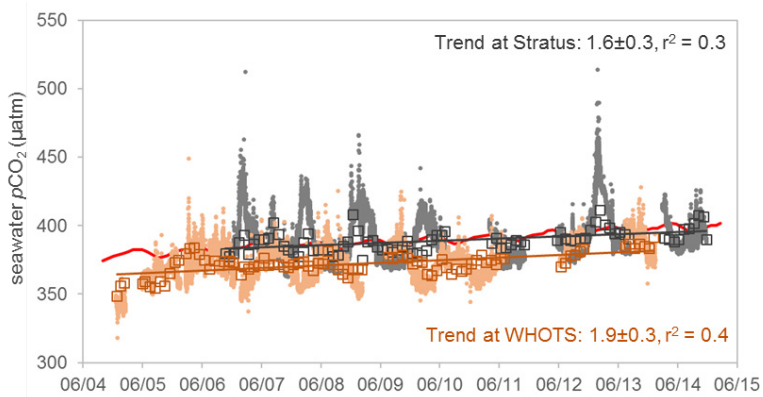


Figure 6: Surface seawater pCO₂ (µatm) 3-hourly observations (dots), deseasoned monthly anomalies (squares), and trends (lines) for the Stratus (gray) and WHOTS (orange) time series. The time series in red is monthly averaged atmospheric xCO₂ (µmol mol⁻¹) from Mauna Loa, Hawaii (NOAA ESRL Global Monitoring Division, 2016). Dates are MM/YY.